



Comparative study for the removal and destruction of pentachlorophenol using activated magnesium treatment systems



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HIGHLIGHTS

- Majority of PCP degradation occurred within four minutes with ball-milled ZVMg/C.
- PCP degradation and phenol formation followed first order kinetics for all systems.
- Order of increasing kinetics for PCP degradation was ZVMg < ZVMg/C < ZVMg/Pd.

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ABSTRACT

Chlorophenols are highly toxic, environmentally-persistent compounds which have been classified as probable human carcinogens by the United States Environmental Protection Agency. Due to the high toxicity of these compounds, it is necessary to treat water and soils with concentrations of chlorophenols above the detection limit set by regulatory agencies. The aim of this work is to demonstrate the capabilities of using ball-milled magnesium for the dechlorination of PCP. Comparison of dechlorination processes were performed in an attempt to determine the most effective system for degradation of PCP to phenol. Three systems with powerful capabilities of treatment were studied: ball-milled zero-valent magnesium (ZVMg), ball-milled zero-valent magnesium carbon (ZVMg/C), and ball-milled zero-valent magnesium with palladium (ZVMg/Pd). In addition to measuring PCP disappearance, all byproducts were identified and quantified for each degradation system. The results of these studies indicate that all three of the systems degrade PCP within 30 min. The most rapid and complete PCP dechlorination is achieved using ball-milled Mg/Pd and a matrix consisting of at least 0.02 g Mg/0/mL ethanol, and 10 μ L acetic acid/mL ethanol, in which case 20 ng/ μ L of PCP was dechlorinated to chlorophenols in approximately 15 min with complete dechlorination achieved in six days. Carbon mass balances of 90.16% for Mg, 94.76% (Mg/C) and 97.05% (Mg/Pd) verify dechlorination was responsible for declining concentrations of PCP. The reactions of PCP degradation and phenol formation were found to follow pseudo-first order kinetics for all systems. Further work will consist of optimization and development of field-scale applications.

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1. Introduction

Chlorinated phenols (CPs) are produced in large quantities; annual global production is estimated to be around 150,000 tons. CPs have a variety of different applications, mainly in wood preservation. Improper management of industrial wastes, accidental spills, leakages, runoff, domestic sewage and liberal use of pesticides in crops have resulted in the prevalence of CPs in natural waters and soil (the maximum contaminant level (MCL) for total

CPs is 0.01 mg/L) (Cass et al., 2000). The persistence and toxicity of CPs have incited a public awareness, caused them to be on the list of the eleven priority phenol derivatives of the United States Environmental Protection Agency (Solanki and Murthy, 2011) and prompted a desire to remediate polluted sites in order to prevent further risks to ecosystems (Cass et al., 2000; Trapido et al., 1997). In recent developments, work has been done on the biodegradation of 4-chlorophenol by the bacterium *Pseudomonas putida* (Li and Loh, 2007), the biodegradability of 2,4-dichlorophenol in an upflow anaerobic sludge bed bioreactor (Chen et al., 2005) and a hybrid-loop bio-reactor scheme to treat wastewater containing 2,4,6-trichlorophenol (Eker and Kargi, 2007). However, such treatment technologies are insufficient (Torres et al., 2010), mainly because

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highly chlorinated CPs (PCP being the most toxic, since the toxicity of CPs increases with the number of chloro groups substituted on the ring (Kim and Carraway, 2003)), are xenobiotic and usually toxic to microorganisms, and also due to the inability of the bacteria to function under standard conditions (Kim and Carraway, 2003).

In the last 20 years, the use of zero-valent metals (ZVM), such as iron, zinc and magnesium, has shown great promise for in situ remediation of chlorinated aromatic hydrocarbons such as PCP (Chen et al., 2007; Grittini, 1997; Kim and Carraway, 2000, 2003). Although rapid PCP dechlorination was observed in a study conducted by Ravary and Lipczynska-Kochany using zero valent iron (ZVI), the results may be at least partially due to loss of the analyte from adsorption (Kim and Carraway, 2003). In a series of batch experiments performed by Kim and Carraway, reductive dechlorination of penta-, tetra-, and trichlorophenol by zero-valent zinc (ZVZ) begot less-chlorinated reduction products of their respective phenols. Further studies have confirmed ZVZ to be better suited than ZVI for PCP removal due to its greater reduction potential (Kim and Carraway, 2003). Despite the much higher reactivity of ZVZ than ZVI towards CPs, limited work has been made of ZVZ on account of the discharge of toxic Zn species released from zinc particles. These species may present a risk to the environment (Kim and Carraway, 2003).

Although reductive dechlorination can be possible with single metallic reaction systems, bimetallic systems can be much more efficient even at normal temperature and pressure. In work done by Grittini (1997) such degradation byproducts as phenol, 2,4,6-triCP and 2,3,4,5-tetraCP were observed using a Pd-Fe bimetallic system. Trends have been observed in the success of bimetallic systems which rely on the great negative reduction potential of zero-valent magnesium (ZVMg) to give off hydrogen for reductive dechlorination (Coutts et al., 2011). One advantage of using magnesium over iron is its reactivity under aerobic conditions. Due to the formation of oxide layers on the surface of iron, studies must be performed in an anaerobic environment (De Vor et al., 2009). Magnesium, however, can be used freely under normal atmospheric conditions (De Vor et al., 2008). Furthermore, the great negative reduction potential of magnesium ($\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}^0$, $E^0 = -2.37$ V) offers more free-energy to drive the reaction, than iron ($\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}^0$, $E^0 = -0.44$ V) or zinc ($\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}^0$, $E^0 = -0.76$ V) (De Vor et al., 2009).

Due to the advantages of magnesium as an electron-donating zero-valent metal, it has been employed in polychlorinated biphenyl (PCB) degradation studies. Kinetic studies on the degradation of PCB-151 performed by Maloney et al. (2011), determined the ideal reaction conditions with magnesium powder and alcohol solvents using a variety of carboxylic acids. The results showed an approximate degradation rate of $1.25 \text{ ng } \mu\text{L}^{-1} \text{ min}^{-1}$ (Maloney et al., 2011). In another study done by Doyle et al. (1998), complete dechlorination of a PCB mixture (Aroclor 1221) to biphenyl was achieved utilizing a Mg/Pd bimetal system. Additionally, other halogenated analytes, such as DDT and a variety of CPs, naphthalenes and polychlorinated dibenzo-p-dioxin (PCDD), have also seen successful degradation using Mg/Pd in different solvents (Engelmann et al., 2001; Hadnagy et al., 2007; Patel, and Suresh, 2007). Recent work (Coutts et al., 2011; De Vor et al., 2008; De Vor et al., 2009), proved a bimetallic system of ball-milled magnesium and palladium (1% on graphite) to be effective in degrading PCBs. Ball-milling offers a preparation method for catalyzed bimetallic systems to be able to function in aqueous solvent systems with minimal oxidation. Previous preparation methods have involved in situ synthesis of the bimetallic system through a spontaneous oxidation process between Pd^{4+} and zero-valent metal, followed by immediate application (Morales et al., 2002; Patel, and Suresh, 2007). However, these procedures must be

performed at the time of treatment, and do not allow for convenient long-term storage of the reactants. Additionally, oxidation on the surface of the un-altered metal leads to rapid formation of insoluble oxides which decrease reactivity. Research done by Huot et al. (2001) and Soave et al. (2001) have shown that the ball-milling process enhances the reactivity of zero-valent magnesium metal by cracking the superficial hydroxide/oxide layer, which changes the microstructure creating more surface defects. Fig. S1 in the Supplementary Material illustrates a drastic decrease in the concentration of PCB 151 over time by degradation with ball-milled ZVMg, compared to the changes observed with unmilled ZVMg (Maloney et al., 2011). The proven efficacy of ball-milling as a metal particle preparation has offered promising leads in the advancement of degradation technology.

The objective of this research is to compare the dechlorination processes of ZVMg systems to establish a technology for use as an in situ application for the remediation of PCP. This research focuses on three systems with great capabilities of treatment: ball-milled magnesium powder, ball-milled magnesium carbon, and ball-milled ZVMg with a catalyst, in this case palladium, creating a bimetallic system capable of dechlorinating PCP very rapidly to less toxic CPs.

2. Methods

2.1. Materials and chemicals

Neat PCP standards were obtained from Accustandard and standard solutions were prepared by diluting the neat standards to their desired concentration with absolute ethanol from Pharmco-AAPER. Inc. Absolute ethanol, Optima[®] grade hexane, toluene, potassium carbonate and acetic anhydride were obtained from Fisher Scientific (Ottawa, ON, Canada). Glacial acetic acid (≥ 99.8) was acquired from Acros Organics through Fisher Scientific. Micro-scale unmilled magnesium ($\sim 4 \mu\text{m}$) was obtained from Heart Metals, Inc (Tamaqua, PA, United States). Palladium on graphite (5 wt%) and sodium sulfate were obtained from Sigma-Aldrich Chemicals. Helium gas, for gas chromatography-mass spectrometry (GC/MS) analysis, was purchased from Air Gas (Atlanta, GA, United States). All chemicals were high purity ($\geq 98\%$) and ACS reagent, analytical grade. All chemicals were used in the form in which they were received unless otherwise noted. A precision microscale analytical balance (Model AE 260-S from Mettler-Toledo AG, Greifensee, Switzerland) was used to measure the different Mg loadings.

2.2. Ball-milling procedure

Magnesium activity is increased through ball-milling, a process in which the passivated hydroxide/oxide surface layer is cracked, thereby creating more surface defects which change the microstructure (Maloney et al., 2011). In this study, magnesium powder, magnesium carbon (Mg/C), and ZVMg with palladium on carbon, were ball-milled under optimized conditions. The ballmilling was performed using a Red Devil 5400 series paint shaker, fitted with custom plates to hold milling canisters, which provided 670 rpm for ball milling of the metal (Coutts et al., 2011). The canister and balls are made of stainless steel. Magnesium powder (85 g) was introduced into the canister with 16 steel balls, of 1.5 cm diameter, having a total mass of 261.15 g, corresponding to a ball/powder mass ratio of 3:1. The canister was sealed under a nitrogen atmosphere. The milling duration was 45 min. To obtain ball-milled magnesium/carbon, 76.5 g Mg powder and 8.5 g of graphite (C) were introduced into the canister. The material was then ball-milled for 30 min using the aforementioned paint mixer. Finally, the a ~ 0.1 wt% palladium powder/magnesium mixture was

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