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***IN SITU* REMEDIATION OF POLYCHLORINATED BIPHENYLS USING
PALLADIUM COATED IRON OR MAGNESIUM**

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ABSTRACT

The remediation of polychlorinated biphenyls (PCBs) and other chlorinated synthetic aromatic compounds are of great concern due to their toxicity and persistence in the environment. When released into the environment, PCBs are sorbed to particulate matter that can then disperse over large areas. Although the US Environmental Protection Agency (EPA) has banned the manufacture of PCBs since 1979, they are still present in the environment posing possible adverse health affects to both humans and animals. Thus, it is of utmost importance to develop a method that remediates PCB-contaminated soil, sediments, and water.

The objective of our research was to develop an in-situ PCB remediation technique that is applicable for the treatment of soils and sediments. Previous research conducted at the University of Central Florida (UCF) proved the feasibility of using an emulsified system to dehalogenate a dense non-aqueous phase liquid (DNAPL) source, such as TCE, in the subsurface by means of an *in-situ* injection. The generation of a hydrophobic emulsion system drew the DNAPL TCE, through the oil membrane where it diffused to the iron particle and underwent degradation. TCE continued to enter, diffuse, degrade and exit the droplet maintaining a concentration gradient across the membrane, thus maintaining the driving force of the reaction.

The use of iron as a reductant has proven useful for treating chlorinated aliphatics but not

chlorinated aromatics. Studies have shown that a light palladium coating on the surface of iron or magnesium will dechlorinate these compounds. While the Pd/Fe and Pd/Mg bimetallic particles have been shown to effectively remove dissolved phase PCBs, the use of the Pd/Fe and Pd/Mg particles to treat sorbed phase hydrophobic PCBs is expected to be minimized by the hydrophilic nature of the Pd/Fe and Pd/Mg bimetallic particle. The emulsion technology developed by UCF to remediate TCE DNAPL pools in the subsurface could also be used to remediate PCB-contaminated soil and sediments. The generation of a hydrophobic emulsion system draws the PCBs through the hydrophobic membrane where it can diffuse to the Pd/Fe or Pd/Mg particle and undergo degradation. The PCBs, like the DNAPL TCE will continue to enter, diffuse, degrade, and biphenyl will exit the particle maintaining a concentration gradient across the membrane and thus maintaining a driving force of the reaction.

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1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of synthetic aromatic compounds with the general formula $C_{12}H_{10-x}Cl_x$ that have been widely used because of their excellent dielectric properties and their resistance to heat and chemical degradation (1). PCBs have been introduced into the environment via improper disposal and accidental leaks from transformers, heat exchangers, and hydraulic systems. PCBs in the environment are transported primarily by particulate matter containing the adsorbed compounds and as a consequence are dispersed worldwide. The uptake of PCB-contaminated sediments by biota at the water-sediment interface can introduce PCBs into the food chain and may cause serious health problems in humans. It is of utmost importance, therefore, to seek effective methods to remove PCBs from the environment. This work demonstrates a simple method for the rapid and complete dechlorination of PCBs that are present in contaminated soils. The PCBs that were tested in this project are those that are present in commercially available mixtures Aroclor 1260 and Aroclor 1254.

The methodology that we tested consists of micrometer size iron and magnesium particles that have been surface doped with elemental palladium. These bimetallic micro-particles are then incorporated into an emulsion in which the nano particles are contained within the aqueous zone of a droplet while the outer skin of the droplet is hydrophobic. When the droplet comes into contact with a PCB molecule it passes through the droplet wall and then is adsorbed onto the bimetallic micro particle where it is dechlorinated and reduced to biphenyl and chloride ions. The elemental iron and magnesium serves as the reducing agent and is oxidized to ferrous and ferric ions. The palladium on the surface of the iron and magnesium particle serves as a catalyst for the dechlorination reaction.

The uniqueness of the technique is that it can be applied in situ directly into the PCB zone where remediation can take place with a minimal disruption in surface related activities. This methodology also poses no threat of accelerating the spread of PCB contamination in the vadose or saturated soil zones. The UCF research team, with support from NASA-KSC, has demonstrated that zero-valent nanometer-size and micron iron particles can be stabilized in an emulsion that possesses a hydrophobic interior. These emulsion system has been shown to rapidly dechlorinate trichloroethylene (TCE) to ethene in a soil matrix (2). It has been documented that this emulsion system can be pumped through a soil column and it remains intact when pumping pressures are removed. The emulsion has been shown to capture free-phase TCE and 'pull' it into the droplet where dehalogenation occurs. While this emulsion system has been demonstrated to very actively dehalogenate chlorinated aliphatic hydrocarbons it does not completely dehalogenate PCBs.

However, several studies have documented that palladized iron and magnesium particles will very rapidly completely dehalogenate PCBs (3, 4). Thus, the primary objective of this project was to combine our metallic emulsion system with the palladized iron and magnesium particles for the purpose of developing a methodology for the in situ remediation of soils

contaminated with PCBs.

2. EXPERIMENTAL SECTION

Primary experiments conducted included:

1. Develop analytical techniques for measuring the concentration of PCBs and byproducts within a soil matrix, a water-methanol solution and an emulsion.
2. Prepare palladized microiron and magnesium particles
3. Incorporate palladized iron or magnesium particles into emulsion that is built from corn oil or limonene, a nonionic surfactant (i.e. SPAN 85) and water.
4. Study the PCB degradation rates in vials containing soil-water and palladized iron or magnesium emulsion.

3. RESULTS

Over forty batches of palladized iron were made and the consistency of the palladium coating process remained a problem. Some of the batches were highly active while others were not as reactive or not active at all with respect to PCB degradation. We used two different plating processes. One used potassium hexachloropalladate and the second used a commercially available coating mix that is used for industrial plating processes. Pallamorse™ (Technic, Inc., Cranston, R.I.), a solution containing Pd²⁺, was added to a vial containing acid-washed microscale iron particles and stirred for 2 minutes. The bimetal was then filtered and dried and tested for reactivity with PCBs. The results indicate that not only does Pallamorse coat the iron consistently (based on degradation efficiency) but also PCB dechlorination proceeds at a faster rate. However, a recurring problem with both methods is the sensitivity of the Pd/Fe system to oxygen exposure. Under careful conditions in a nitrogen atmosphere, the Pd/Fe emulsion system will dechlorinate 5% of Aroclor 1260 to biphenyl in 14-days.

The emulsion formulation that has been found to be the most active with the Pd/Fe system used limonene and food-grade surfactant (Span 85) in the hydrophobic exterior of the emulsion. This change was made in an effort to enhance the mass transport of PCBs across the membrane of the emulsion droplet. We found that in terms of reactivity, this formulation provided the most active emulsion, however, previous emulsions had been stable for several months while this formulation began to dissociate into its components after only three weeks. Because this emulsion is not structurally stable for as long as the vegetable oil/surfactant emulsion, more work is necessary to alter the formulation to provide for an emulsion that can remain stable for the time necessary for field injection.

The Pd/Mg system has thus far proven to be a more rigorous system that doesn't show the sensitivity to oxygen that was a problem with the Pd/Fe system. Reactivity is very fast with 20% conversion to biphenyl (using Aroclor 1260) in only 19-hours. Further experiments are underway to verify that the Pd/Mg system will work as effectively in the emulsified system.

Since the terminal product of the dehalogenation of all PCBs is biphenyl, the rate of PCB degradation can be determined by monitoring the rate of biphenyl production. The appearance of biphenyl proves that the PCBs have sorbed into the emulsion droplet where dehalogenation reactions take place.

Several emulsions were tested for their reactivity by extracting the aqueous sample with a

solvent followed by acid clean up. The emulsions that were tested were all stable and flowable. An emulsion formulation made with the addition of limonene to the oil phase (micrographs shown in Figure 1) was able to dehalogenate the PCBs to their final product, biphenyl. These studies indicate that PCBs enter the emulsion droplet and degradation occurs. Any lesser-chlorinated PCB congeners produced during the dehalogenation process remain in the emulsion and are eventually converted to biphenyl.

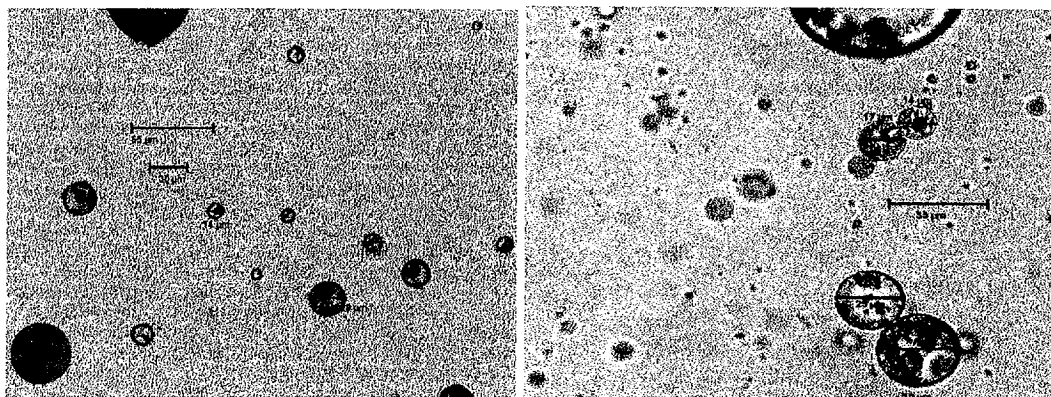


Figure 1. Micrographs of palladized, microscale zero valent iron emulsion (limonene formulation) droplets.

4. CONCLUSIONS

Many experiments were performed in an attempt to find a consistent plating technique that would produce consistent destruction efficiencies with regard to the bimetal alone with PCB mixtures Aroclor 1254 and Aroclor 1260 in an aqueous environment. The problems associated with the technique caused inconsistent rates of degradation to biphenyl. A new plating process using a commercially available liquid plating solution (Pallamerse) containing palladium (II) has been used and the degradation rates are fairly consistent (under nitrogen atmosphere) and faster than found in even the successfully plated iron using the potassium hexachloropalladate.

The use of limonene in the hydrophobic membrane improved the transport of PCBs across the membrane. This emulsion was effective at removing PCBs and degrading them to biphenyl. The stability of this emulsion was not at the same level of earlier emulsions so further work on the formulation is necessary. All emulsions that were prepared showed good physical properties with respect to density and viscosity indicating that the ability to inject the emulsions into soil or sediments can be accomplished.

The use of magnesium instead of iron shows great promise. The fact that this bimetallic system is active even when exposed to oxygen will mean a much easier transition to field scale use. The rates on initial experiments were fast with biphenyl production in as little as 10-minutes. Further experiments with this bimetal in an emulsified system are currently under way.

With the successful formulation of an emulsion and in light of the stability and viscosity of early emulsion formulations, this technology shows promise for widespread use for remediation of contaminated soils, sediments and water.

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