REMEDIAL EXTRACTION AND CATALYTIC HYDRODEHALOGENATION FOR TREATMENT OF SOILS CONTAMINATED BY HALOGENATED HYDROPHOBIC ORGANIC COMPOUNDS

A Dissertation

by

HUN YOUNG WEE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2007

Major Subject: Civil Engineering

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Approved by:

Co-Chairs of Committee,	Jeffrey A Cunningham
	Bill Batchelor
Committee Members,	Robin Autenrieth
	Hongbin Zhan
Head of Department,	David V. Rosowsky

May 2007

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ABSTRACT

Remedial Extraction and Catalytic Hydrodehalogenation for
Treatment of Soils Contaminated by
Halogenated Hydrophobic Organic Compounds.
(May 2007)

Hun Young Wee, B.Eng., Chungbuk National University, Republic of Korea;
M.S., Texas A&M University
Co-Chairs of Advisory Committee: Dr. Jeffrey A. Cunningham
Dr. Bill Batchelor

The overall objective of this research was to develop and assess a new method, named _r_emedial _e_xtraction _a_nd _c_atalytic _h_ydrodehalogenation (REACH), for removing and destroying soil contaminants. In particular, I considered hydrophobic halogenated organic compounds (HHOCs). In this research, I developed a closed-loop treatment process that catalytically destroys the contaminants of concern, and does not generate a secondary waste stream. Mixtures of water and ethanol appear to be good candidates for the extraction of 1,2,4,5-tetrachlorobenzne (TeCB) or pentachlorophenol (PCP) from contaminated soil. Palladium-catalyzed hydrodehalogenation (HDH) was applied for destroying TeCB or PCP in mixtures of water and ethanol in a batch mode.

The experimental results are all consistent with a Langmuir-Hinshelwood model for heterogeneous catalysis. Major findings that can be interpreted within the Langmuir-Hinshelwood framework are as follows: the rate of HDH depends strongly on the solvent composition, increasing as the water fraction of the solvent increases; the kinetics of the

HDH reaction are apparently first-order with respect to the concentration of TeCB in the solvent; and the HDH rate increases as the catalyst concentration in the reactor increases. Also, TeCB is converted rapidly and quantitatively to benzene, with only trace concentrations of 1,2,4-trichlorobenzene appearing as a reactive intermediate. PCP is transformed to phenol by sequential reductive dehalogenation to tetrachlorophenols, then to trichlorophenols, then to phenol. The degradation of PCP does not follow first-order kinetics, probably because of competitive reactions of intermediate products that are generated during PCP degradation. Following the batch studies, the REACH technology was applied in continuous mode under baseline conditions for a span of 7 weeks to treat soils that had been synthetically contaminated by HHOCs in the laboratory. Extraction of TeCB and PCP from soils was almost completed within two days by a 50:50 mixture of water and ethanol. Higher reaction rates were observed for TeCB than for PCP. The activity of the catalyst was slowly lost as contaminant mass was removed from the soil. The deactivated catalyst was successfully regenerated with a dilute sodium hypochlorite solution. The results of this research suggest that REACH could be a viable technology for some contaminated soils.

ACKNOWLEDGMENTS

I would like to express sincere thanks to my advisor, Dr. Jeffrey A. Cunningham, for his direction, encouragement, and support throughout my doctoral program. I dare to say that I learned how to approach and conduct advanced research in the environmental engineering field from this doctoral training under Dr. Cunningham's supervision.

I would also like to thank my co-advisor, Dr. Bill Batchelor, for his valuable advice on my research and important administrative support of my Ph.D. program. I also thank members of my committee, Dr. Robin Autenrieth and Dr. Honbin Zhan, for their advice and assistance with my Ph.D. program and dissertation.

I would like to present special thanks to Dr. Kwangyul Kim and Dr. Hang-Bae Jun, at Chungbuk National University in Republic of Korea for their encouragement and for giving me momentum to pursue master's and doctoral degrees in the United States.

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I would like to thank my parents for their encouragement, patience, and support throughout my life. I have to thank to my lovely wife, Jung-Min Lee, for her love and endless support for my graduate study. I am also grateful to my daughter, In-Seo for her graceful smiles.

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CHAPTER I

INTRODUCTION

1.1. Problem statement

According to the U.S. Environmental Protection Agency (EPA), halogenated hydrophobic organic compounds (HHOCs) are among the most commonly found contaminants at sites on the National Priorities List (US EPA, 2006b). Polychlorinated biphenyls (PCBs), pentachlorophenol (PCP), chlorinated benzenes, chlorinated aliphatic hydrocarbons and their breakdown products (e.g., tetrachloroethene, trichloroethene, and dichloroethene), and some pesticides (e.g., DDT, chlordane) belong to the category of HHOCs. In general, the HHOCs are persistent in the environment and have harmful effects to the public. Therefore, a need exists to clean up these contaminants within a short time period and with low cost.

The purpose of this research was to develop and assess a new method for removing and destroying soil contaminants, in particular HHOCs. Many of the HHOCs tend to reside preferentially in soil as opposed to air or water, because of their hydrophobic chemistry and their relatively low volatility.

Unfortunately, the biodegradation rates of HHOCs in soil are often very slow,

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This dissertation follows the style and format of Water Research.

requiring months or years for adequate remediation (Speitel and Closmannn, 1991). Incineration of those compounds is feasible, but high energy consumption is required to reach the necessary temperatures, and incineration by-products such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) can be generated (Liljelind et al., 2003). Numerous innovative treatment technologies already exist for treating soils contaminated by HHOCs, each method with its own advantages and disadvantages (US EPA, 1996a), but the method to be developed in this research is a significant improvement over existing techniques, as explained below.

Here, I focus particularly on one method for soil clean-up, namely, solvent extraction. Fig. 1.1 is a schematic diagram of a typical solvent extraction operation (US EPA, 2001). One of the principal problems with this technology is that it generates a secondary waste stream of polluted material, which requires further treatment or disposal in a landfill. Either of these methods of dealing with the secondary waste stream can be expensive, and, in the case of landfill disposal, can still pose a risk of environmental exposure to future populations. Therefore, in this research, I have proposed to develop a closed-loop treatment process that catalytically destroys the contaminants of concern, and does not generate a secondary waste stream. I call this process remedial extraction and catalytic hydrodehalogenation, or REACH. This will result in a treatment technology that is both more cost-effective and more environmentally benign than the existing solvent extraction technique. Contaminants will be destroyed, not merely transferred from one phase to another.

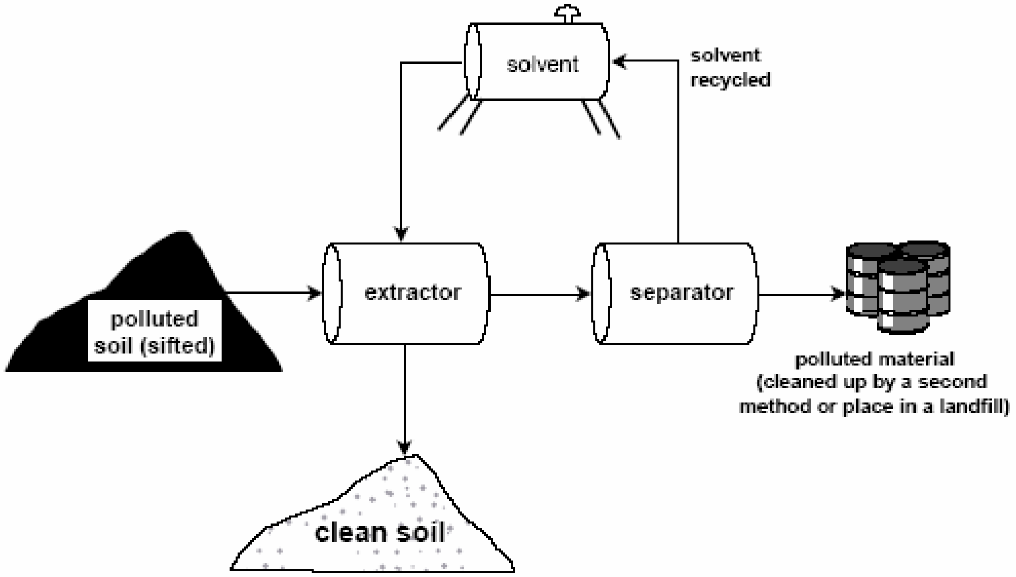

Fig. 1.1 - Schematic diagram for typical operation of solvent extraction for treating contaminated soil (US EPA, 2001).

Fig. 1.2 is a schematic diagram of the REACH technology that I proposed to develop in this research. It is conceptually similar to that shown in Fig. 1.1, but with an important difference. Instead of a separator, from which issues a secondary waste stream, I have proposed to use catalytic treatment to destroy the contaminants of concern.

The research proposed here is innovative because it combines contaminant extraction and contaminant destruction in a closed-loop system, to avoid the generation of a secondary waste stream. Most of the target contaminants are suspected or known to be amenable to destruction via palladium-catalyzed hydrodehalogenation (Hoke et al., 1992; Schuth and Reinhard, 1998; Lowry and Reinhard, 1999; Liu et al., 2001; Morales et al., 2002).

1.2. Background on Pd-catalyzed hydrodehalogenation

In recent years, catalysts have received significant attention as a potential means of treating contaminated groundwater and/or wastewater. In particular, catalysts can be used to accelerate hydrodehalogenation (HDH) reactions, in which the halogen atoms (usually chlorine or bromine) of a contaminant are replaced by hydrogen atoms, resulting in a benign (or, at least, less toxic) product. This typically requires that hydrogen gas, or an alternative reductant, is supplied to the solution in which the HDH reactions occur. Many contaminants or groups of contaminants have been studied for their potential for catalytic treatment, including the following:

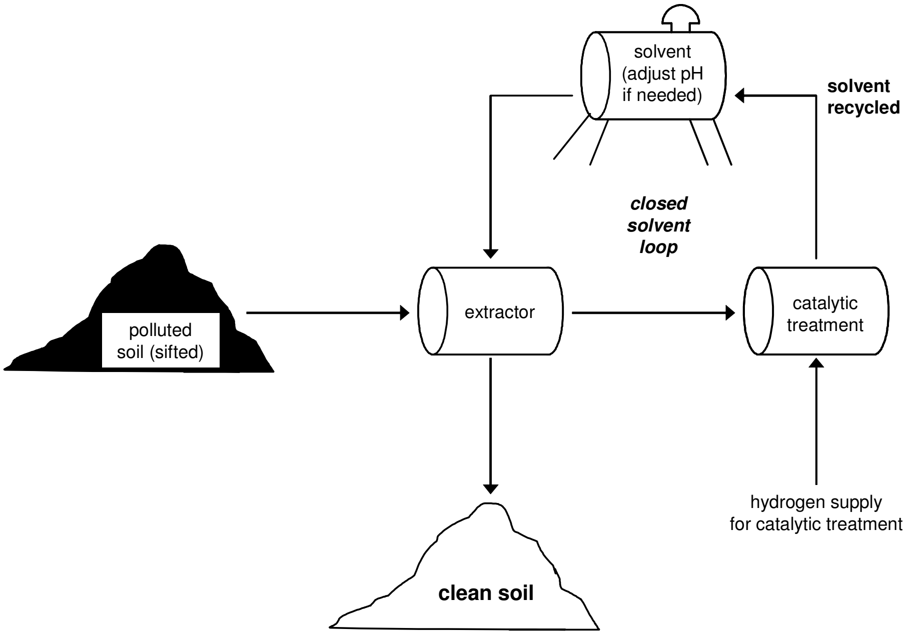

Fig. 1.2 - Schematic diagram for the Remedial Extraction and Catalytic Hydrodehalogenation (REACH) technology. The result is a closed-loop system with no secondary waste stream.

- chlorinated alkanes (Kovenklioglu et al., 1992; McNab and Ruiz, 1998; Lowry and Reinhard, 1999; McNab et al., 2000; Kopinke et al., 2003);
- chlorinated ethenes (Kovenklioglu et al., 1992; Schreier and Reinhard, 1995; McNab and Ruiz, 1998; Perrone et al., 1998; Lowry and Reinhard, 1999; Lowry and Reinhard, 2000; McNab et al., 2000; Lowry and Reinhard, 2001; Korte et al., 2002);
- chlorinated benzene (Coq et al., 1986; Kovenklioglu et al., 1992; Schuth et al., 2000; Fritsch et al., 2002; Murena and Gioia, 2002);
- chlorinated phenols (Hoke et al., 1992; Felis et al., 1999; Yuan and Keane, 2003) ;
- 1,2-dibromo-3-chloropropane (Siantar et al., 1996; Lowry and Reinhard, 1999); and
- polychlorinated biphenyls (PCBs) (Cellier et al., 2003; Ukisu and Miyadera, 2004; Yang et al., 2006).

The HDH reaction typically follows a stoichiometry along the lines of the following (Urbano and Marinas, 2001):

$$\text{R-X}_n + n\text{H}_2 \rightarrow \text{R-H}_n + n\text{H}^+ + n\text{X}^- \qquad (1.1)$$

where X represents a halogen atom, e.g., chlorine or bromine. Note that the products of the reaction include a dehalogenated hydrocarbon (R-H) and an acid (HX); the acid will typically be dissociated in aqueous solution, meaning that a halide ion (X^-) is liberated by the reaction.

Different catalysts are commercially available, but supported palladium (Pd) catalyst was used in this research. Nearly all previous research has confirmed that Pd catalysts exhibit high activity and selectivity for the HDH reaction. Pd catalyst is commercially available as 1%, 2% or 5% Pd by weight, dispersed on a support of porous alumina (Al_2O_3) or activated carbon.

The fundamental idea of this research is to combine solvent extraction, which removes the target contaminants from contaminated soil, with palladium-catalyzed HDH, which destroys the target contaminants. Through this procedure, I eliminate the secondary waste stream of conventional solvent extraction.

1.3. Research objectives

The *overall objective* of this research is to develop and assess the remedial extraction and catalytic hydrodehalogenation (REACH) technology for cleaning soils contaminated by halogenated hydrophobic organic compounds (HHOCs). The *central hypothesis* is that most HHOCs can be extracted from soils with a solvent and destroyed catalytically in the closed-loop system of REACH. The *motivation* of this research is that the development of a new remedial method for destroying soil contaminants with no generation of a secondary waste stream will allow soils to be cleaned more effectively and inexpensively.

The overall objective was to be achieved through the following three *specific objectives*. (1) Quantify the dependence on the key parameters for the extraction of selected HHOCs from soils. (2) Quantify the dependence on the key parameters for the Pd-catalyzed hydrodehalogenation of selected HHOCs. (3) Demonstrate that remedial extraction and catalytic hydrodehalogenation is sustainable for a long period of time in a closed-loop system.

1.4. Dissertation overview

This dissertation is presented in seven Chapters. Chapter I provides the introduction to the dissertation. Chapters II, III, IV, V, and VI comprise the main body of the dissertation and are described in more detail below. Chapter VII presents a summary of the major findings of this research, including recommendations for future work.

Chapter II investigates the extraction of HHOCs from contaminated soils using water-ethanol mixtures in batch mode. Specifically, the effects of solvent composition, extraction time, and solvent volume on the extraction of selected HHOCs are described.

Chapter III presents data on the Pd-catalyzed HDH of 1,2,4,5-tetrachlorobenzene (TeCB) in water-ethanol mixtures. The effects of solvent composition, catalyst concentration, and initial concentration of TeCB are described. In addition, a mathematical model was developed based on the Langmuir-Hishelwood model to express the TeCB degradation kinetics by Pd-catalyzed HDH. I also propose a transformation pathway of TeCB by the Pd-catalyzed hydrodehalogenation.

Chapter IV investigates the Pd-catalyzed HDH of pentachlorophenol (PCP) in water-ethanol mixtures. The effects of solvent composition, catalyst concentration, and H_2 pressure on the Pd-catalyzed HDH reaction rate of PCP were determined. The results of adsorption isotherms are shown to explain the effect of solvent composition on the HDH rate more clearly. A transformation pathway of PCP to phenol is proposed in this Chapter. Also, I propose a hypothesis for why the degradation kinetics of PCP are apparently not first order.

Chapter V provides the data on the performance of REACH for the treatment of soils contaminated by TeCB and PCP. Soils contaminated in a laboratory were subjected to clean-up by REACH. All experiments were conducted for seven weeks in a closed-loop system built in the laboratory. The contaminant extraction rate, contaminant reaction rate, contaminant mass destruction, regeneration of catalyst, and intermediate products are described.

Chapter VI provides the data on the performance of REACH for the treatment of field soils contaminated by PCP. Deactivation of the Pd catalyst is observed and explained. A future area of research is proposed to overcome the problems associated with the application of REACH to the field contaminated soils.

CHAPTER II

EXTRACTION OF HALOGENATED HYDROPHOBIC ORGANIC COMPOUNDS FROM CONTAMINATED SOILS USING WATER-ETHANOL MIXTURES IN BATCH MODE

2.1. Introduction

The purpose of this Chapter is to investigate how well the target HHOCs can be extracted from contaminated soil under different operating conditions when the application of REACH is considered. The operating parameters studied here were solvent composition, ratio of solvent volume to contaminated soil mass, and extraction time. The results obtained here will be useful to construct a bench-scale closed-loop treatment system of the REACH technology, as described in subsequent Chapters of this dissertation.

Although many organic solvents are present for the extraction, water-ethanol mixtures have been successfully applied to remove polycyclic aromatic hydrocarbons (PAHs) (Kilbane, 1998; Khodadoust et al., 2000), pentachlorophenol (PCP) (Khodadoust et al., 1999), and nonaqueous phase liquids (NAPLs) (Imhoff et al., 1995; Rao et al., 1997; Lowe et al., 1999) from contaminated soils. In addition, ethanol is inexpensive and is not environmentally harmful. Mravik et al. (2003) and Ramakrishnan et al. (2005) reported that the ethanol remaining after extraction in soil matrices provided electron donor, eventually enhancing biological reductive degradation when extraction with alcohol was used in situ.

2.2. Materials and methods

2.2.1. Chemicals

Ethanol (99.5%, ACS grade, Aldrich), acetone (≥99%, ReagentPlus grade, Aldrich), hexane (98.5%, HPLC grade, EMD chemicals), toluene (99.9%, HPLC grade, Aldrich), 1,2,4,5-tetrachlorobenzene (98%, Sigma-Aldrich), pentachlorophenol (98%, Sigma-Adrich), and 2,5,-dibromotoluene (98%, Sigma-Aldrich) were employed with no further purification. Mixtures of water and ethanol were prepared using deionized water and 200 proof (99.5%) ethanol.

2.2.2. Soil

Uncontaminated soil was obtained below 10 cm from the top of a field site in College Station, TX. The characteristics of the soil were analyzed by the Soil, Water, and Forage Testing Laboratory at Texas A&M University. The textural class of the soil was a sandy loam with 78% sand, 6% silt, and 16% clay. The fraction of organic matter and pH were 0.30% and 5.1, respectively. These parameters do not appear unusual, so the soil was deemed acceptable for purposes of this study.

The uncontaminated soil was air-dried over night and sieved using a 2.0 mm mesh before subject to contamination with TeCB and PCP. For use throughout the rest of this research, half of the soil was contaminated with TeCB, and half was contaminated with PCP. TeCB and PCP were selected as the two target contaminants for this research. They are common soil contaminants with physical and chemical properties that are representative of HHOCs, as shown in Table 2.1. The target concentrations for the contaminated soil were 100 mg TeCB per kg air-dried soil and 100 mg PCP per kg air-dried soil. These concentrations would not be unusual at a contaminated-soil site.

Soil contamination was performed as follows. First, a stock solution of TeCB was made by dissolving 0.05 g of TeCB into 100 mL of acetone. Then, 500 g of dried soil was placed in a 500-mL amber-glass bottle. The 100 mL of stock solution was added, and the bottle was sealed. The bottle was placed in a tumbler and was mixed for two weeks. Then, the bottle was taken from the tumbler and mixed with hand utensils for 10 minutes. The contaminated soil was then placed on a clean plate and dried in the hood for 24 hours, to allow acetone to volatilize. The contaminated soil was then mixed thoroughly and placed in a clean amber-glass bottle. The entire procedure was repeated for PCP. Based on the addition of 0.05 g of contaminant to 500 g of soil, I anticipated a contaminant concentration of approximately 100 mg/kg if no loss of contaminant occurred.

Following contamination, the soil was aged (stored) in the amber-glass bottles at room temperature for at least 3 months prior to use in further experiments.

Table 2.1 - Physical and chemical properties of TeCB and PCP (IPCS INCHEM, 2007)

Chemical	molecular weight (g/mol)	chemical formula	water solubility (mg/L)	vapor pressure (Pa)	$\mathrm{LogK_{ow}}$
TeCB	215.9	$C_6H_2Cl_4$	2.16 at 25 °C	0.70 at 25 °C	4.90
PCP	266.4	C_6Cl_5OH	10.0 at 20 °C	0.02 at 20 °C	5.01

2.2.3. Determination of concentrations in contaminated soil

In order to determine how the contaminant extraction was affected by solvent composition or by other operating parameters, I first had to know the concentration of TeCB or PCP in the contaminated soil. The target concentration during the contamination step was 100 mg/kg, as described above. However, it is possible that some losses occurred during the contamination, particularly while the soil was dried in the hood, so the actual contaminant concentration in the soil might be less than the target of 100 mg/kg.

Accelerated solvent extraction (ASE) was used for the determination of the contaminant concentration in soil. I used EPA method 3545, pressurized fluid extraction (US EPA, 1996b), employing a Dionex ASE 200 accelerated solvent extraction system. Experimental conditions are given in Table 2.2.

Three samples of the TeCB-contaminated soil were analyzed, as were three samples of the PCP-contaminated soil. The TeCB concentration was determined to be 63±1 mg/kg. The PCP concentration was determined to be 73±10 mg/kg. These values were in reasonable agreement with the target concentration of 100 mg/kg.

The ASE results were validated with a "shaker" method (Wall and Stratton, 1991), which was performed as follows. I placed 10 g of TeCB in a 50-mL centrifuge tube. Then, 10 mL of solvent was added to the tube. The solvent was a mixture of hexane and acetone (hexane:acetone ratio was 4:1, vol:vol, before mixing) for TeCB-contaminated soil or a mixture of toluene and acetone (toluene:acetone ratio was 4:1,

Table 2.2 - Experimental conditions for accelerated solvent extraction (ASE)

Amount of soil extracted	10 g
Extraction solvent	Acetone/toluene (1:1, v/v) for PCP Acetone/hexane (1:1, v/v) for TeCB
Oven temperature	120°C
Pressure of nitrogen gas	1500 psig (10.4 MPa)
Static time	5 min, after 5 min pre-heat equilibrium
Flush volume	50% of the cell volume
Gas purge	60 sec at 150 psig (1.1 MPa)
Static cycle	1

before mixing) for PCP-contaminated soil. The tube was shaken for 1 hr on a mechanical shaker at 200 rpm. Then the tube was centrifuged for 10 min at 10,000×g. The supernatant was poured into a 50-mL volumetric flask. The entire procedure was repeated twice more with the supernatants collected together. The concentration in the solvent was then determined and used to calculate the initial concentration of contaminant in the soil. Three samples of the TeCB-contaminated soil were analyzed with this method, as were three samples of the PCP-contaminated soil. The TeCB concentration was determined to be 64±3 mg/kg, in excellent agreement with the ASE results. The PCP concentration was determined to be 81±7 mg/kg, somewhat higher than predicted by the ASE method. Overall, the two methods agreed well. I conclude that the TeCB concentration in the TeCB-contaminated soil was approximately 64 mg/kg, and the PCP concentration in the PCP-contaminated soil was approximately 80 mg/kg.

Once the concentrations of TeCB and PCP had been determined, I was able to test the efficacy of the water-ethanol mixtures for extraction. I determined the effect of three parameters: solvent composition, volume of solvent used per mass of soil, and extraction time.

2.2.4. Extraction in batch mode

All extraction experiments were conducted in batch mode. Four water-ethanol mixtures, with water:ethanol composition of 100:0, 67:33, 50:50, and 33:67 (vol:vol, before mixing) were used for the extraction of both TeCB- and PCP-contaminated soils. The extraction experiments of TeCB and PCP from the contaminated soils were carried out separately. A desired amount of soil and volume of extractant (water-ethanol mixture) were placed in an amber glass bottle. The glass bottle was shaken on a mechanical shaker at 20 rpm for a desired time interval. At the end of the time interval, an aliquot of solvent was collected. Any soil particles were separated from the solvent using a 0.2-μm membrane filter. The concentration of TeCB or PCP in the solvent was determined by analysis on a gas chromatograph (GC) with electron capture detector (ECD) as described below. Finally, the solution concentration was converted to an equivalent soil concentration that was extracted, i.e., mass of contaminant extracted per mass of soil. All experiments were performed in duplicate.

2.2.5. Analysis

For TeCB analysis, one milliliter of hexane was mixed with an appropriate volume of the filtered water/ethanol solvent in an amber glass vial to be ready for GC analysis. For PCP sample analysis, toluene was used instead of hexane. PCP samples were acidified down to pH 2 with 6 N HCl. Both hexane and toluene contained a known concentration of 2,5-dibromotoluene as an internal standard prior to the liquid-liquid extraction for a GC analysis. Target analytes were extracted into hexane or toluene by shaking the amber glass vials for at least 1 hour. The instrument used for analysis was a Perkin Elmer Clarus 500 GC equipped with ECD. The column used was a DB-5ms capillary column (30 m length × 0.25 mm i.d.) (J&W).

2.3. Results and discussion

2.3.1. *Effect of solvent composition*

In order to investigate the effect of solvent composition, I placed 10 g of contaminated soil in a 250-mL amber-glass bottle with 200 mL of solvent. The water:ethanol compositions I tested were 100:0, 67;33, 50:50, and 33:67 (vol:vol, before mixing).

Fig. 2.1 (A) and (B) show the results for TeCB and PCP, respectively. I found that TeCB could not be effectively extracted by 100% water or by a 67% water solution, even with a contact time of 48 hours. In contrast to TeCB, the PCP could be effectively extracted by a mixture with as little as 33% ethanol. This could be explained by a hydroxyl (-OH) group of PCP. Hydrogen bonding can occur between a solvent (water/ethanol mixture) and PCP (Bettelheim et al., 2001). Consequently, the solubility of PCP in polar solvents can be enhanced.

In general, for the extraction of HHOCs, I would expect the extraction efficiency to increase as the ethanol fraction increases in the solvent. This expected trend was strong for TeCB but only moderate for PCP, probably because PCP is more polar than TeCB and contains the hydroxyl moiety for hydrogen bonding.

2.3.2. *Effect of extraction time*

Fig. 2.1 (A) and (B) indicate the effect of extraction time as well as the effect of solvent composition. As expected, the contaminant mass extracted in solvent increases with

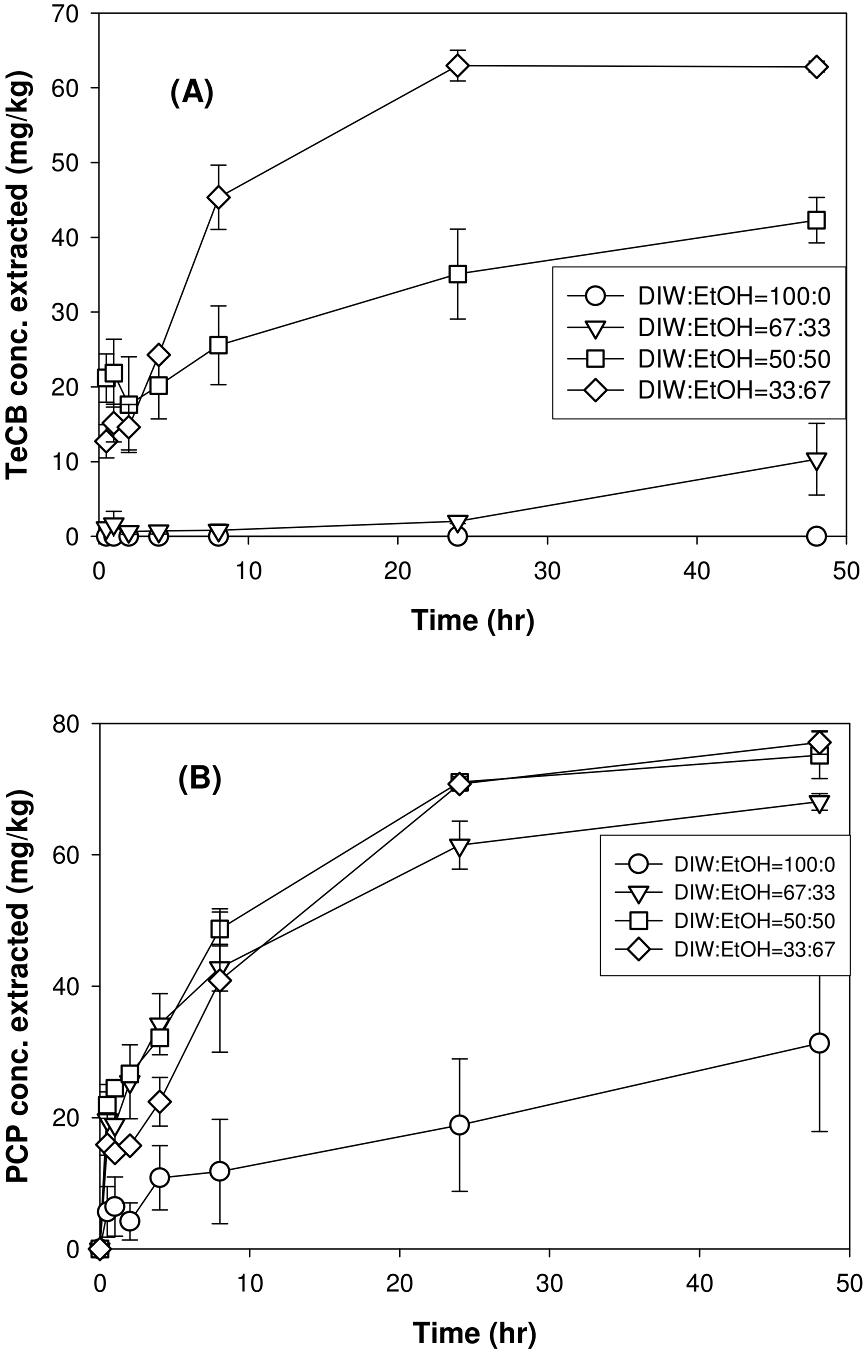

Fig. 2.1 - Effect of solvent composition and extraction time on the extraction of TeCB and PCP from contaminated soil: (A) TeCB contaminated soil; (B) PCP contaminated soil. The ratio of solvent volume to soil mass was 20 L/kg (0.2 L/0.01 kg). DIW refers to deionized water, and EtOH refers to ethanol.

time. Also as expected, for short extraction times, the mass extracted is very sensitive to extraction time. For instance, a contact time of 8 hr provides a significant improvement over a contact time of 1 hr. However, for long extraction times, the system approaches equilibrium, and therefore is not as sensitive to extraction time. Therefore, a contact time of 48 hr provides only slight improvement over a contact time of 24 hr.

2.3.3. Effect of solvent volume

The effect of the solvent volume used in the extraction, or, more specifically, the ratio between the solvent volume and the soil mass was evaluated. In each experiment, I placed 10 g of soil in a 250-mL amber glass bottle, but I varied the volume of solvent added to the bottle. Four different solvent volumes were tested: 50 mL, 100 mL, 150 mL, and 200 mL. These provided four solvent:soil ratios of 5 L/kg, 10 L/kg, 15 L/kg, and 20 L/kg, respectively. In all cases, the bottles were shaken for 24 hours. The extraction time period was determined based on the previous experiment, in which the extraction efficiency was not much different at 24 and 48 hrs.

Fig. 2.2 (A) and (B) show the results for TeCB and PCP, respectively. Surprisingly, I found very little effect of the solvent:soil ratio. For a fixed mass of soil – in this case, 10 g – it is expected that a larger volume of solvent would be able to extract a greater mass of contaminant. However, I found almost no difference between the mass extracted at 5 L/kg and the mass extracted at 20 L/kg. I stress that the results obtained here were found under my experimental conditions and might not apply

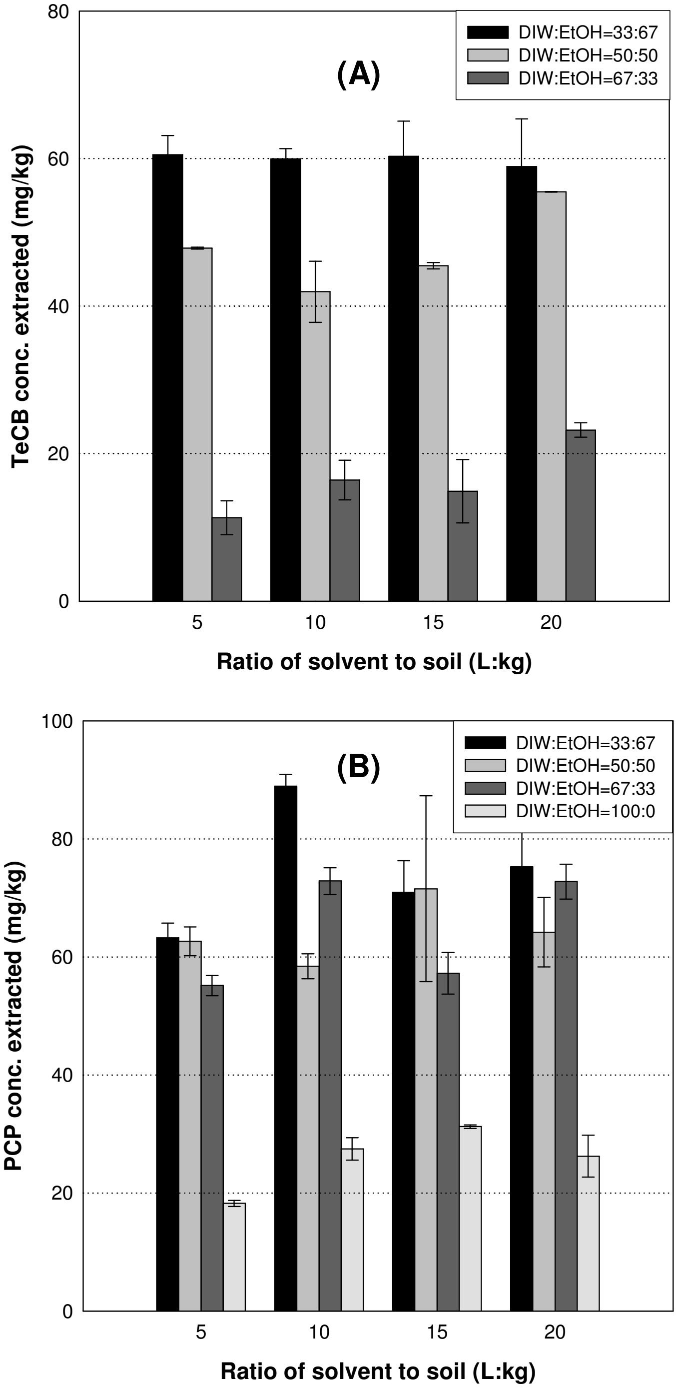

Fig. 2.2 - Effect of solvent volume on the extraction of TeCB and PCP from contaminated soil: (A) TeCB contaminated soil; (B) PCP contaminated soil. Extraction time was 24 hrs for all samples. In the legend, DIW refers to deionized water and EtOH refers to ethanol.

generally. If a higher mass of contaminant were present, the results might be different since each solvent has a certain limitation of solubility for a compound.

As before, I did see an effect of the solvent composition on the extraction efficiency. In fact, the trends were very similar to those described in section 2.3.1., above. For TeCB, the extraction efficiency is low at 67% water but improves with increasing ethanol concentration in the solvent. For PCP, the extraction efficiency is poor for 100% water, but is nearly the same for any ethanol concentration equal to 33% or higher. Thus, Fig. 2.2 (A) and (B) corroborate the trends shown in Fig. 2.1 (A) and (B).

2.4. Conclusions

Extraction of TeCB and PCP from contaminated soil was tested using water-ethanol mixtures in batch mode. It was observed that mixtures of water and ethanol are good candidates to remove TeCB and PCP from contaminated soil by extraction. A composition of at least 50% ethanol (by volume, before mixing) appears necessary to effectively remove TeCB from contaminated soil. PCP could be effectively extracted by mixtures with as little as 33% ethanol. It was observed that the ratio of solvent volume to soil mass has very little effect on the extraction efficiency of both TeCB and PCP under our experimental conditions. For short extraction times, the mass of TeCB or PCP extracted is very sensitive to extraction time. However, for long extraction times, the removal efficiency is not sensitive to extraction time, suggesting an approach to equilibrium.

CHAPTER III

PALLADIUM-CATALYZED HYDRODEHALOGENATION OF 1,2,4,5-TETRACHLOROBENZENE IN WATER-ETHANOL MIXTURES

3.1. Introduction

The long-term goal of this research is to develop the REACH process for full-scale application at contaminated sites. One critical step is to develop a sufficient understanding of the HDH reaction in water/ethanol mixtures. Therefore, the main goals of this Chapter are to demonstrate the feasibility of the technology, to determine the effect of the solvent composition (i.e., the water:ethanol ratio), and to develop a model for the kinetics of the dehalogenation process. These goals have been accomplished through a series of batch kinetic experiments, in which TeCB was spiked into mixtures of water and ethanol, then destroyed via Pd-catalyzed hydrodehalogention (HDH) in a batch reactor. Results of the experiments are interpreted with a Langmuir-Hinshelwood conceptual model for heterogeneous catalysis.

3.2. Materials and methods

3.2.1. Chemicals and catalyst

The chemicals employed in this research are summarized in Table 3.1. Mixtures of water and ethanol were prepared using de-ionized water and 200 proof (99.5%) ethanol. Commerically-available 1% (wt.) Pd-on-Al_2O_3 catalyst was employed, and the palladium content of the catalyst specified by the manufacturer is assumed to be accurate. Detailed physical properties of the catalyst can be found elsewhere (Lowry and Reinhard, 1999). The catalyst was used in the HDH reactions without further treatment. No special effort was given to prevent the catalyst from contacting air. A stock solution of 1,2,4,5-tetrachlorobenzene with concentration 5000 mg/L was prepared by dissolving 0.1 g of TeCB into 20 mL ethanol in a 20-mL clear borosilicate glass vial. The vial containing the stock solution was closed using a PTFE-lined septum and kept in a freezer to minimize volatilization.

3.2.2. Pd-catalyzed HDH reaction studies

In this research, all Pd-catalyzed hydrodehalogenation (HDH) reactions were carried out in a Parr 3911 hydrogenation apparatus (Parr Instrument Company, Moline, IL, USA). The experiments were conducted as follows.

Table 3.1 - Chemicals and catalyst used in experiments

Chemical or catalyst	Specification	Company
1,2,4,5-tetrachlorobenzene (TeCB)	98%	Sigma-Aldrich
Ethanol	99.5%	Sigma-Aldrich
Hexane	HPLC grade, 98.5%	EMD Chemicals
2,5-dibromotoluene	98%	Sigma-Aldrich
Pd-on-Al_2O_3 catalyst	1% Pd by weight	Sigma-Aldrich
De-ionized water	$> 17.5\ M\Omega\cdot cm$	Barnstead

A desired mixture of deionized water (DIW) and ethanol (EtOH) was pre-mixed in a glass beaker and then transferred to a 500-mL reaction bottle. The total volume of solvent (DIW/EtOH mixture) in the reaction bottle was 300 mL for all experiments; for instance, a 50/50 mixture consisted of 150 mL water and 150 mL ethanol mixed and then added to the reaction bottle. After adding the solvent, the desired amount of catalyst and the desired amount of TeCB stock solution were also added to the reaction bottle. The bottle was then placed in the hydrogenation reactor, and air in the headspace was removed by filling the bottle with hydrogen gas up to 0.31 MPa and venting it. Pressurizing and venting were repeated three times. After venting, the reactor headspace was filled with hydrogen gas to 0.21 MPa, and shaking of the reaction bottle was started. The hydrogenation reactor is designed to shake at 200 rpm to ensure complete mixing. After shaking for the desired amount of time, the reactor was stopped, and a sample was collected for analysis.

Four sets of experiments were conducted. Each set of experiments required that different experimental conditions be tested, as summarized in Table 3.2. For each set of conditions, the experimental process was repeated 6 or 7 times to yield kinetic data for 6 or 7 different reaction times.

During the HDH reactions, hydrogen gas was supplied at 0.21 MPa and the reactions were conducted at room temperature (20±3 °C). Each experiment was conducted in duplicate.

Table 3.2 - Experimental conditions for Pd-catalyzed HDH reactions

Initial concentration of TeCB in reactor (mg/L)	C_{cat}^{*} (g/L)	Solvent composition** (DIW(%):EtOH(%))
Determine effect of solvent composition:		
2.0	0.17	67:33
2.0	0.17	50:50
2.0	0.17	33:67
5.0	0.33	67:33
5.0	0.33	50:50
5.0	0.33	33:67
Determine effect of catalyst concentration:		
5.0	0.17	50:50
5.0	0.33	50:50
5.0	0.67	50:50
10.0	0.17	50:50
10.0	0.33	50:50
10.0	0.67	50:50
Determine effect of initial concentration of TeCB:		
5.0	0.33	50:50
10.0	0.33	50:50
Determine transformation products and mass balance:		
5.0	0.33	50:50

Note: * C_{cat} means concentration of catalyst; **DIW and EtOH indicate de-ionized water and EtOH, respectively, v/v ratio.

3.2.3. *Sampling and analysis*

At the end of each HDH run, the shaker was stopped and an appropriate amount of sample was collected using a syringe. Any fine catalyst was separated from the sample using a 0.2-μm membrane filter. An appropriate amount of the filtered sample was placed in an extraction vial with hexane, and the vial was vigorously shaken for 1 hour to transfer TeCB (and any reaction products) to the hexane. Duplicate samples were collected from the reactor and extracted into hexane. The hexane contained a known concentration of 2,5-dibromotoluene as an internal standard. TeCB concentrations in the hexane were determined using gas chromatography (GC) with electron capture detection (ECD). Prior to analysis, the GC was calibrated using standard solutions of TeCB in hexane, prepared by dilutions of the TeCB stock solution. Blank samples were analyzed between each standard to verify that TeCB was eluting properly from the GC and not bleeding from one analysis to the next.

For a set of mass balance studies (described in more detail subsequently), the samples were analyzed by Advanced Technologies & Testing Laboratories (Gainesville, Florida) through the EPA purge-and-trap method 8260 (US EPA, 1996b).

3.2.4. *Control experiments*

For each set of experimental conditions, two kinds of control tests were conducted to verify that any observed disappearance of TeCB was due to catalytic HDH, not any other mechanism (e.g., volatilization or sorption). The first type of control experiments were conducted in exactly the same fashion as described above, with the exception that no catalyst was added to the reaction bottles. This determines the loss of TeCB due to volatilization. The second type of control experiments was performed using nitrogen gas instead of hydrogen gas, with all other experimental conditions the same as described above. This determines the loss of TeCB due to sorption onto the catalyst surface.

For a solvent composition of 67% water, significant volatilization of TeCB was observed: I recovered only 43–47% of the TeCB after venting and 30 minutes of shaking (without catalyst present). For other solvent compositions, no significant loss was observed due to volatilization, with TeCB recoveries from 92 to 103%.

In the sorption control experiments, recoveries of TeCB were 32–64% when a solvent composition of 67% water was used. This is consistent with the results of the volatilization controls, and it is believed that the main mechanism of TeCB loss was due to volatilization, not sorption. In solvent compositions of 50:50 and 33:67 of DIW/EtOH, recoveries of TeCB for sorption controls were in the range 86-89% and 103-107%, respectively. This indicates that sorption onto the catalyst support is only a minor loss mechanism. Therefore, with the exception of TeCB in 67% water, I trust that any observed removal of TeCB is due to catalytic HDH.

3.3. Theoretical and mathematical model

To interpret the results of the Pd-catalyzed HDH experiments, I adopt a Langmuir-Hinshelwood model for the catalytic reaction. According to this framework, the HDH of TeCB occurs via the following steps (Fogler, 1999): (1) mass transfer of the reactants (i.e., TeCB and hydrogen) from the water/ethanol solvent to the catalyst surface; (2) adsorption of the reactants to the catalyst surface; (3) reaction on the surface of the catalyst; (4) desorption of the reaction products from the surface; and (5) mass transfer of the reaction products back into the bulk water/ethanol solvent. This framework enables me to develop a mathematical model to interpret the experimental data, as follows.

First, I assume that the HDH reaction on the catalyst surface follows a simple kinetic expression:

$$r = k_2 \, C_{\mathrm{TeCB}}^{\mathrm{cat}} \, C_{\mathrm{H2}}^{\mathrm{cat}} \tag{3.1}$$

where r is the rate of disappearance of the TeCB (mass of TeCB reacted per mass of catalyst per time). $C_{\mathrm{TeCB}}^{\mathrm{cat}}$ and $C_{\mathrm{H2}}^{\mathrm{cat}}$ represent the concentration of TeCB sorbed on the catalyst surface and the concentration of H_2 sorbed on the catalyst surface, respectively.

Next, I assume that sorption and desorption of the TeCB and the hydrogen onto the catalyst surface are rapid processes since the reaction bottle is shaken vigorously. In other words, the rate-limiting step for the HDH reaction is surface reaction (step 3 in the list above), not mass transfer or sorption/desorption. Thus, the sorbed concentrations are in equilibrium with the dissolved concentration in the solvent. I further assume that these equilibrium sorption relationships are described by Langmuir isotherms. The hydrogen concentration is in the high region of the Langmuir isotherm, such that $C_{\mathrm{H2}}^{\mathrm{cat}}$ is a constant. (I have verified with experiments that the HDH reaction is not sensitive to the H_2 pressure in the reaction vessel as long as the pressure is at least 0.17 MPa; this finding supports the assumption that $C_{\mathrm{H2}}^{\mathrm{cat}}$ is constant.) Therefore, I may define

$$k_1 = k_2 \, C_{\mathrm{H2}}^{\mathrm{cat}} \tag{3.2}$$

where k_1 is an apparent first-order rate constant for the reaction on the catalyst surface.

However, I assume that the TeCB concentration in the water/ethanol solvent is in the low (linear) region of the Langmuir isotherm:

$$C_{\mathrm{TeCB}}^{\mathrm{cat}} \cong K_{\mathrm{d}} \, C_{\mathrm{TeCB}}^{\mathrm{solvent}} \tag{3.3}$$

where K_{d} is a partitioning coefficient describing the sorption equilibrium. Thus, equation (3.1) can be expressed as follows.

$$r = k_1 \, K_d \, C_{\mathrm{TeCB}}^{\mathrm{solvent}} \tag{3.4}$$

Next, I apply a mass balance for TeCB in the entire reaction vessel:

$$M^{\mathrm{cat}} \, \frac{dC_{\mathrm{TeCB}}^{\mathrm{cat}}}{dt} + V^{\mathrm{solvent}} \, \frac{dC_{\mathrm{TeCB}}^{\mathrm{solvent}}}{dt} = -M^{\mathrm{cat}} \, r \tag{3.5}$$

where M^{cat} and V^{solvent} are the mass of catalyst and the volume of solvent, respectively. Combining equations (3.3), (3.4), and (3.5) yields the following.

$$\left(V^{\text{solvent}} + M^{\text{cat}} K_d\right) \frac{dC_{\text{TeCB}}^{\text{solvent}}}{dt} = -M^{\text{cat}}\, k_1\, K_d\, C_{\text{TeCB}}^{\text{solvent}} \tag{3.6}$$

Finally, for my experimental conditions, the mass of catalyst is small compared to the volume of solvent: $V^{\text{solvent}} \gg M^{\text{cat}} K_d$. This enables me to arrive at the final result as follows.

$$\frac{dC_{\text{TeCB}}^{\text{solvent}}}{dt} \cong -k_1\, K_d\, \frac{M^{cat}}{V^{solvent}} C_{\text{TeCB}}^{\text{solvent}} = -k\, C_{\text{TeCB}}^{\text{solvent}} \tag{3.7}$$

Equation 3.7 shows that the rate of disappearance of TeCB in the water/ethanol solvent should exhibit first-order kinetics if the assumptions made above are valid. The apparent first-order rate constant k is given by

$$k = k_1\, K_d\, \frac{M^{cat}}{V^{solvent}}. \tag{3.8}$$

According to this conceptual and mathematical model, the apparent first-order rate constant k should depend upon the concentration of catalyst in the reactor ($M^{\text{cat}}/V^{\text{solvent}}$) and upon the partitoning coefficient K_d that describes the sorption of the contaminant onto the catalyst surface. The partitioning coefficient K_d is expected to depend upon the solvent composition: higher ethanol concentrations are expected to favor the TeCB remaining in liquid solution, as opposed to sorbing onto the catalyst surface. Therefore, the apparent rate constant k is expected to depend upon the solvent composition.

As shown in Table 3.2, I designed different sets of experiments to test the validity of this conceptual model. Results are reported below.

3.4. Results and discussion

3.4.1. Effect of solvent composition on the Pd-catalyzed HDH rate

The effect of solvent composition on the Pd-catalyzed hydrodehalogenation (HDH) kinetic rate of 1,2,4,5-tetrachlorobenzene (TeCB) over time in a batch reactor is presented in Fig. 3.1. The results show clearly that the Pd-catalyzed HDH rate increases as the fraction of water increases in the solvent. This was observed for both sets of experimental conditions (2 mg/L initial concentration of TeCB with 0.17 g/L catalyst, and 5 mg/L initial concentration of TeCB with 0.33 g/L catalyst). The apparent first-order rate constants k for each solvent composition are shown in Fig. 3.1 and are summarized in Table 3.3. Similar effects of solvent composition have been reported for the dehalogenation rate of polychlorinated biphenyls treated by bimetallic Pd/Fe (Korte et al., 2002), and for perchloroethylene treated by zero-valent iron (Clark et al., 2003). I attribute this to the effect of the solvent composition on the sorption of TeCB to the catalyst surface. As ethanol fraction increases in the solvent, the contaminant partitioning coefficient K_d decreases and apparent first-order kinetic constant k decreases, thereby resulting in a decrease in the overall HDH rate, as predicted by equation (3.7) and (3.8). Conversely, as the water fraction increases in the solvent, the amount of TeCB sorbed on the catalyst surface increases, and a higher kinetic rate is observed. These observations are consistent with the Langmuir-Hinshelwood framework adopted above.

Furthermore, the data shown on Fig. 3.1 appear to follow first-order kinetics, as predicted by equation (3.7). Therefore, the results shown in Fig. 3.1 are consistent with the conceptual and mathematical model I have developed above.

It is worth noting that, for a solvent composition of 67% water, the control experiments indicated poor recovery of TeCB, as described previously. I believe that some TeCB is lost due to volatilization for the experiments in 67% water. The data are included in Fig. 3.1, but should be interpreted appropriately. Despite this, I believe that there is a very clear trend indicating the strong effect of the solvent composition on the HDH kinetics.

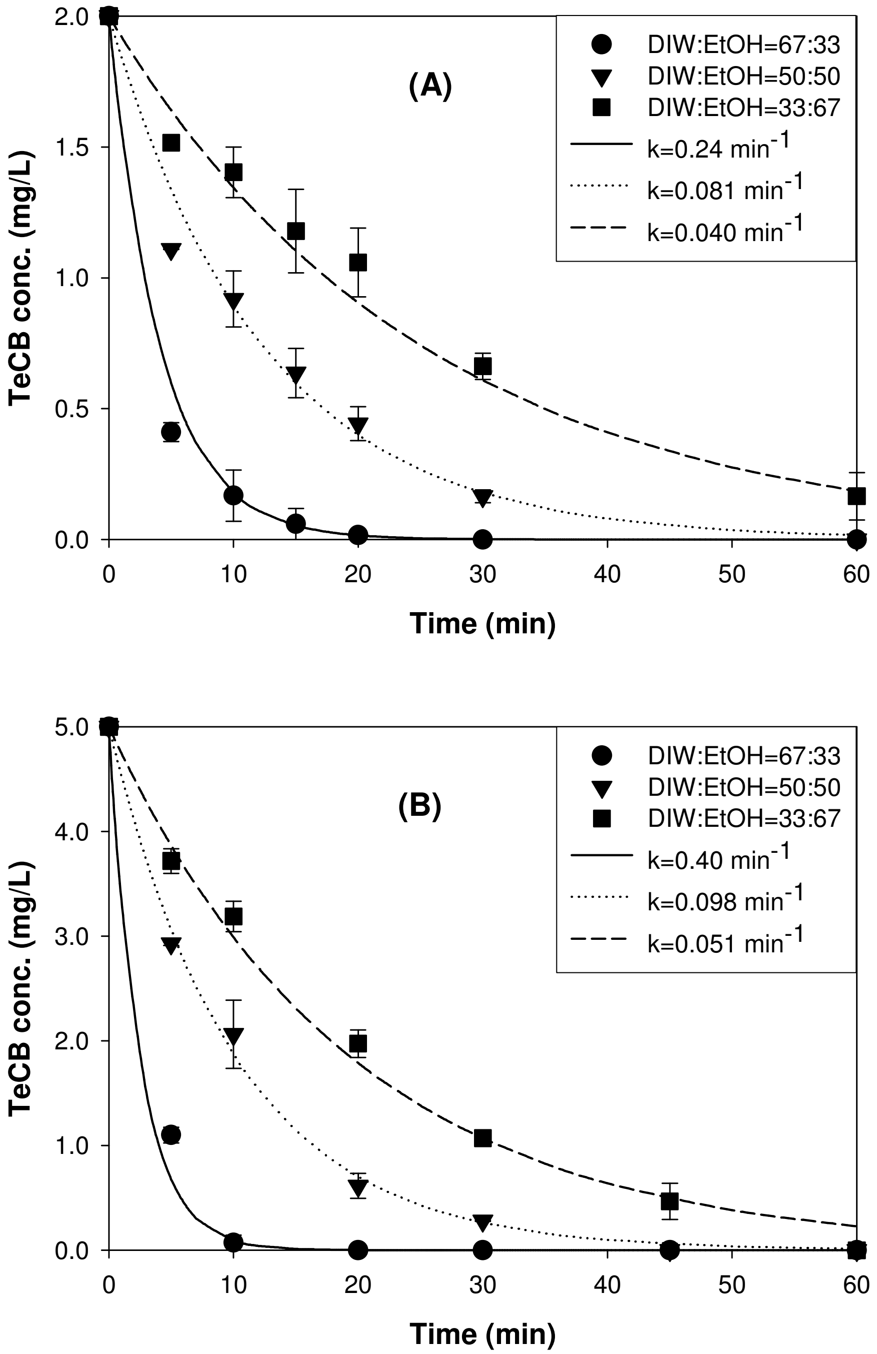

Fig. 3.1 - Effect of solvent composition on the Pd-catalyzed HDH rate of TeCB in a batch reactor: (A) catalyst conc. = 0.17 g/L and initial TeCB conc. = 2 mg/L; (B) catalyst conc. = 0.33 g/L and initial TeCB conc. = 5 mg/L. DIW and EtOH mean de-ionized water and ethanol, respectively. Symbols represent experimental data and lines represent first-order kinetic degradation model.

Table 3.3 - Summary of apparent first-order kinetic constants, recoveries in control, and pH change

Initial conc. of TeCB (mg/L)	Solvent composition (DIW(%):EtOH(%))	C_{cat}^* (g/L)	k (min^{-1})	R^2	TeCB recovery (%)**		pH change	
					Control 1	Control 2	initial	final
Effect of solvent composition								
2.0	67:33	0.17	0.24 ± 0.02	0.988	43		7.26	5.90
2.0	50:50	0.17	0.081 ± 0.007	0.985	95		7.53	6.49
2.0	33:67	0.17	0.040 ± 0.004	0.986	103		8.38	7.10
5.0	67:33	0.33	0.40 ± 0.15	0.968	47	33-64	7.26	4.59
5.0	50:50	0.33	0.098 ± 0.007	0.994	95	86-89	7.53	4.75
5.0	33:67	0.33	0.051 ± 0.002	0.995	99	103-107	8.38	4.81
Effect of catalyst concentration								
5.0	50:50	0.17	0.027 ± 0.004	0.983				
5.0	50:50	0.33	0.094 ± 0.003	0.999				
5.0	50:50	0.67	0.35 ± 0	1				
10.0	50:50	0.17	0.011 ± 0.004	0.918				
10.0	50:50	0.33	0.025 ± 0.003	0.990				
10.0	50:50	0.67	0.082 ± 0.005	0.998				
Effect of initial concentration of TeCB								
5.0	50:50	0.33	0.098 ± 0.007	0.994	95		7.53	4.75
10.0	50:50	0.33	0.087 ± 0.007	0.997	92		7.52	4.43

Note: * C_{cat} means catalyst concentration; **control 1 was conducted with no catalyst addition and control 2 conducted using nitrogen gas instead hydrogen gas; blank entry means value was not determined.

3.4.2. Effect of catalyst concentration on the Pd-catalyzed HDH rate

The effect of catalyst concentration ($M^{\mathrm{cat}}/V^{\mathrm{solvent}}$) on the Pd-catalyzed HDH rate is shown Fig. 3.2. All experiments in Fig. 3.2 were conducted in a 50:50 solvent composition. Fig. 3.2 shows clearly that an increase in catalyst concentration increases the HDH rate. This behavior is predicted by equations (3.7) and (3.8), and it indicates that the availability of Pd surface sites is a rate-limiting factor under the experimental conditions I tested.

According to equations (3.7) and (3.8), the apparent first-order rate constant k should increase linearly with the catalyst concentration. Instead, I observed that a four-fold increase in the catalyst concentration (from 0.17 g/L to 0.67 g/L) resulted in roughly a ten-fold increase in k. Therefore, k depends upon catalyst concentration more strongly than predicted by my mathematical model. My proposed explanation for this observation is that, at low concentrations of catalyst, it is not valid to assume that the TeCB is in the linear range of the Langmuir isotherm, because not enough sorption sites are available. Hence, the sorbed concentration $C_{\mathrm{TeCB}}^{\mathrm{cat}}$ is lower than would be predicted by equation (3.3), and the overall reaction rate is lower than its predicted value. This results in a non-linear dependence of k on the catalyst concentration. I believe that the observed data are consistent with this hypothesis.

Despite the non-linear dependence of k on the catalyst concentration, the results shown in Fig. 3.2 are in qualitative agreement with the Langmuir-Hinshelwood model for the HDH kinetics.

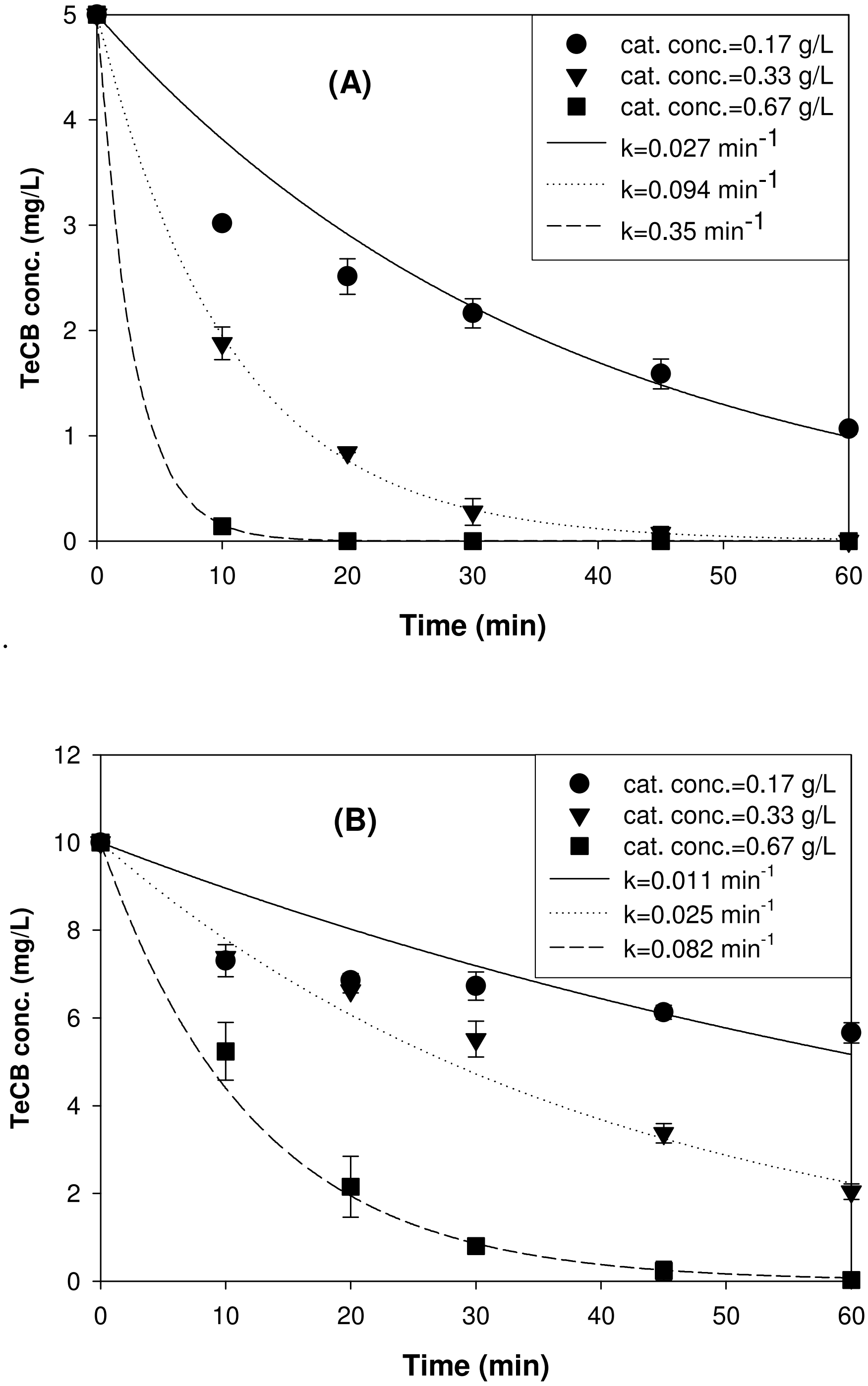

Fig. 3.2 - Effect of catalyst concentration on the Pd-catalyzed HDH rate of TeCB in a batch reactor: (A) initial concentration of TeCB = 5 mg/L; (B) initial concentration of TeCB = 10 mg/L. Solvent composition is 50:50 of de-ionized water:ethanol. Symbols represent experimental data and lines represent first-order kinetic degradation model.

3.4.3. Effect of initial concentration of TeCB on the Pd-catalyzed HDH rate

The effect of the initial concentration of TeCB on the HDH kinetic rate is shown in Fig. 3.3. The results with two initial concentrations of TeCB (5 mg/L and 10 mg/L) in the presence of a 50:50 mixture of water/ethanol and 0.33 g/L of catalyst concentration are shown in Fig. 3.3 (A). For each condition, experiments were conducted twice separately. Therefore, four data sets are shown. The HDH kinetic rates are very similar for three sets of data. The values of k of those similar sets of data are 0.12, 0.098, and 0.087 min^{-1}. However, a significantly different k value, 0.023 min^{-1}, was obtained under the same conditions. A possible explanation is that the duplicate experiments were conducted about 14 months apart, and the catalyst surface may have changed due to exposure to the atmosphere.

I also compared the results with three initial concentration of TeCB (2, 5, and 10 mg/L) with a 50:50 mixture of water/ethanol and 0.17 g/L of catalyst concentration. The effect of initial concentration of TeCB on the HDH rate was apparent as shown Fig. 3.3 (B). As the initial concentration increased, slower degradation of TeCB was observed. In addition, the first-order mathematical model described in section 3.3 does not predict the experimental data well in case of 5 and 10 mg/L. Therefore, at high TeCB concentration compared to the catalyst concentration in the solvent (or at low concentration of catalyst compared to the TeCB concentration in the solvent), the mathematical model may break down since the assumption of linear isotherm is not valid. As a relationship between the concentration of TeCB sorbed on the catalyst surface and the TeCB concentration in the

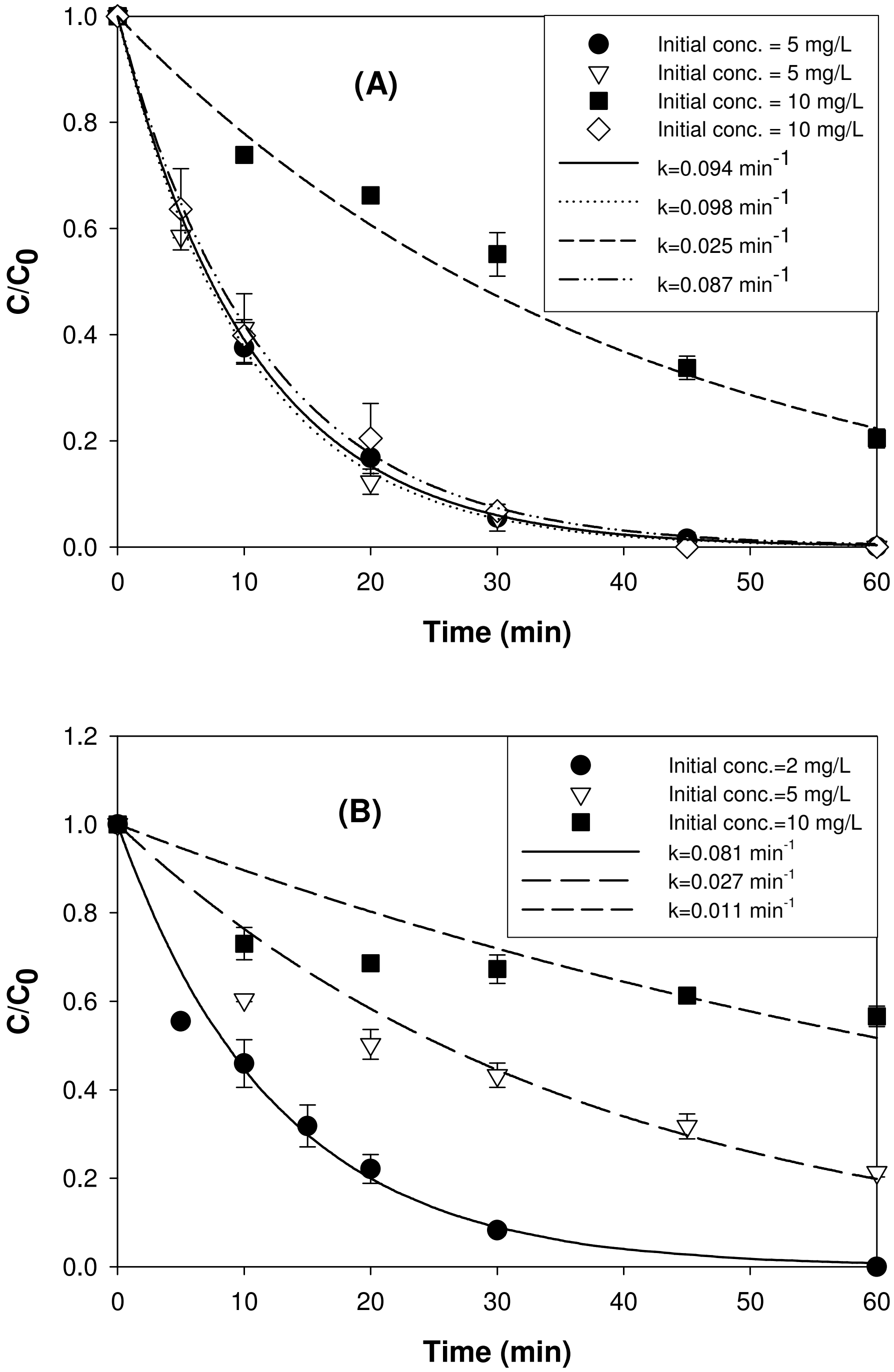

Fig. 3.3 - Effect of initial concentration of TeCB on the Pd-catalyzed HDH rate in a batch reactor: (A) catalyst conc. = 0.33 g/L; (B) catalyst conc. = 0.17 g/L. Solvent composition of both (A) and (B) is 50:50 of de-ionized water:ethanol. Symbols represent experimental data and lines represent first-order kinetic degradation model.

solvent is shown in equation (3.3), the use of a linear partitioning coefficient K_d indicates that the concentration is in the low (linear) region of the Langmuir isotherm. Therefore, the model may require revision to describe cases of high TeCB concentrations with low catalyst concentrations.

In summary, the effect of initial concentration of TeCB on the HDH kinetic rate may or may not be significant depending on the catalyst concentration in the reactor.

3.4.4. Transformation of TeCB by the Pd-catalyzed HDH

The experimental data presented in Figures 3.1–3.3 show clearly that the concentration of TeCB in the water/ethanol solvent decreases over time. However, one might still question whether the observed disappearance of TeCB is due to Pd-catalyzed HDH, or due to some other process (e.g., slow volatilization into the reactor head space, slow sorption onto the catalyst surface). A mass balance is required to ascertain that the observed disappearance of TeCB is due to conversion to a reaction product. Furthermore, for development of the full-scale REACH process, it is important to know the chemical products of the HDH reaction. For instance, do chlorinated by-products accumulate in the system? To answer these questions, and to determine a proposed reaction pathway, a mass-balance study was performed.

Experiments were conducted as described above, but samples were analyzed by purge-and-trap gas chromatography with mass spectrometry in order to quantify the concentrations of all reaction products.

Experimental results are presented in Fig. 3.4. Minor amounts of 1,2,4-trichlorobenzene (TCB) as an intermediate chlorinated by-product were formed, but the TCB did not persist or accumulate. The concentration of benzene, which is the end product of the HDH reaction, increased as the TeCB was removed. This finding is consistent with that of previous research (Alonso et al., 2002; Balko et al., 1993; Urbano and Marinas, 2001). Fig. 3.4 shows excellent closure of the mass balance, meaning that all TeCB originally present in the system is accounted for by conversion to TCB or to benzene. This verifies that any observed loss of TeCB is due to hydrodehalogenation, not due to any other loss process. Analyses were performed by Advanced Technologies and Testing Laboratories, Inc., in Gainesville, Florida.

A possible reaction pathway for the transformation of TeCB to benzene by the Pd-catalyzed HDH method is:

$$\text{1,2,4,5 - TeCB} \xrightarrow{k^{*}} \text{1,2,4 - TCB} \xrightarrow{k^{**}} \text{benzene} \tag{3.9}$$

where k^{*} and k^{**} are kinetic constants and k^{**} is much larger than k^{*}. Accordingly, an intermediate product is formed, but it reacts very quickly, so effectively it appears that 1,2,4,5-TeCB is converted to benzene via a direct transformation.

3.4.5. Discussion of significance

The formation of benzene as an end product would not necessarily represent a significant environmental clean-up, because benzene is a regulated contaminant. In certain

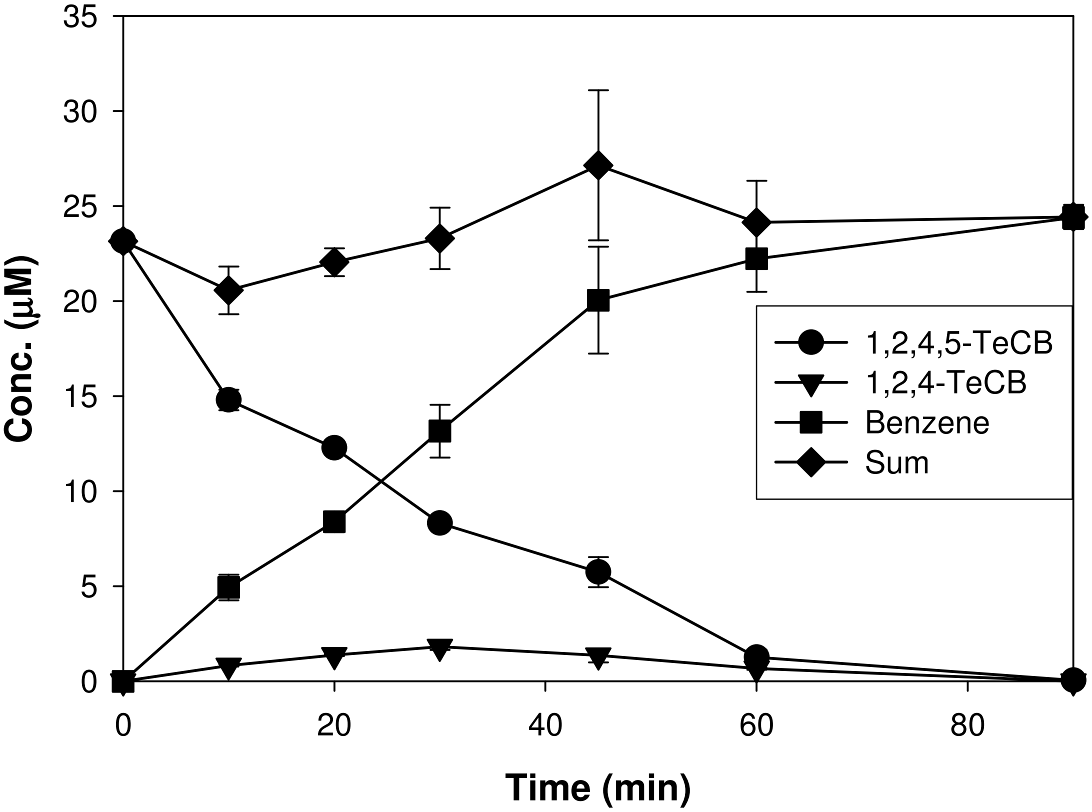

Fig. 3.4 - Transformation of 1,2,4,5-tetrachlorobenzene in a batch reactor: Solvent composition is 50:50 of de-ionized water:ethanol. Initial concentration of TeCB is 23 μM. Catalyst concentration is 0.33 g/L. Symbols represent experimental data.

circumstances, conversion of TeCB to benzene might be considered a significant improvement, but that may not be the case generally. Future investigations might employ both palladium catalyst and rhodium (Rh) catalyst, because Rh is known to catalyze hydrogenation of the aromatic ring (Coq et al., 1986). Hence, I expect that TeCB could be converted to cyclohexane, which would likely represent an acceptable environmental endpoint.

Despite the fact that benzene is formed as an end product in this investigation, the results of this study are significant because they have allowed me to determine the effect of solvent composition on the HDH reaction, and have allowed me to formulate a conceptual and mathematical model for the HDH process. Finally, I note that the information gained in this study will be helpful for the treatment not only of TeCB, but also other candidate contaminants such as PCBs, chlorinated phenols, pesticides, etc. Thus, overall I believe the results of this investigation are essential to the development of the full-scale REACH process, despite the fact that benzene is formed as an end product in this investigation.

3.5. Conclusions

In this Chapter, I have investigated the Pd-catalyzed HDH of a selected target contaminant, 1,2,4,5-tetrachlorobenzene (TeCB), in mixtures of water and ethanol. The goals of this Chapter were (1) to demonstrate the feasibility of the REACH technology, (2) to determine the effect of the solvent composition (i.e., the water:ethanol ratio) on the

HDH process, and (3) to develop a model for the kinetics of the dehalogenation process. These goals were accomplished through a series of experiments conducted in a batch reactor.

I found that TeCB can be completely dehalogenated at room temperature under mild hydrogen pressure (0.21 MPa). Therefore, I believe that the proposed REACH technology is feasible for treatment of soils contaminated by HHOCs. Other significant findings of this Chapter are:

- the Pd-catalyzed HDH rate decreases as the fraction of ethanol increases in the solvent;
- the Pd-catalyzed HDH rate increases as the concentration of catalyst increases in the reaction vessel;
- the initial concentration of TeCB might or might not affect the apparent HDH rate constant depending on the concentration of catalyst in the solvent; and
- the kinetics of the TeCB disappearance are apparently first-order.

All of these findings can be interpreted within the framework of a Langmuir-Hinshelwood model for heterogeneous catalysis. This framework has enabled me to formulate a mathematical model in which the TeCB disappearance follows first-order kinetics:

$$\frac{dC_{\mathrm{TeCB}}^{\mathrm{solvent}}}{dt} = -k\, C_{\mathrm{TeCB}}^{\mathrm{solvent}}$$

with the apparent first-order rate constant, *k*, given by the following:

$$k = k_1 K_d \frac{M^{cat}}{V^{solvent}}$$

where K_d is a distribution coefficient describing TeCB sorption onto the catalyst surface, M^{cat} is the mass of catalyst in the reaction vessel, and $V^{solvent}$ is the volume of solvent in the reaction vessel.

Thus, with regard to the effect of the solvent composition, I suggest that as the ethanol concentration increases, the TeCB resides preferentially in the liquid solvent, rather than sorbing to the surface of the catalyst. The decreased concentration of TeCB on the catalyst surface results in a decreased overall reaction rate. Other experimental findings (e.g., the dependence of *k* on the catalyst concentration) are also interpreted within the Langmuir-Hinshelwood framework.

TeCB was converted stoichiometrically to benzene by the Pd-catalyzed HDH reaction. I observed low concentrations of a transient intermediate, 1,2,4-trichlorobenzene (TCB). The disappearance of TCB was rapid enough that one could consider TeCB is converted directly to benzene. Future work could involve the use of both Pd catalysts and Rh catalysts to convert the benzene to cyclohexane, which is less toxic than benzene.

Overall, the findings of this study are important towards the full development of the proposed REACH process as described in subsequent Chapters. These findings may also be useful to the treatment of other liquid waste streams containing TeCB or other halogenated hydrophobic organic contaminants.

CHAPTER IV

PALLADIUM-CATALYZED HYDRODEHALOGENATION OF PENTACHLOROPHENOL IN WATER-ETHANOL MIXTURES

4.1. Introduction

Since the degradation kinetics observed for PCP studies are different from those for TeCB in water/ethanol mixtures which were described in the previous Chapter III, this separate Chapter is prepared for the comparison purposes.

In this Chapter, the effects of solvent composition, catalyst concentration, and hydrogen pressure in the reactor are discussed with respect to their effect on PCP degradation. The Langmuir-Hinshelwood model is again employed to interpret the three effects. A sequential reductive dehalogenation of PCP by Pd-catalyzed HDH was also studied. A hypothesis why the catalytic degradation of PCP does not follow first-order kinetics is offered.

4.2. Materials and methods

4.2.1. Chemicals and catalyst

Table 4.1 shows the chemicals and catalyst used in this research. More detailed physical properties of the catalyst can be found elsewhere (Lowry and Reinhard, 1999). Stock solution of pentachlorophenol (PCP) at 1000 mg/L was prepared by dissolving 0.02 g of chemical into 20 mL ethanol in a 20-mL clear borosilicate glass vial. The vial was sealed using a PTFE-lined septum and stored in a freezer to minimize any loss due to the volatilization.

4.2.2. Pd-catalyzed HDH kinetics studies

General experimental procedures for the studies of the effects of solvent composition, catalyst concentration, and H_2 gas pressure on the Pd-catalyzed hydrodehalogenation (HDH) reactions can be found in the previous Chapter. Except where noted subsequently, the total volume of solvent used in each experiment was 100 mL and the reaction bottle used was a 250-mL Pyrex glass bottle. Table 4.2 shows the detailed sets of experimental conditions for the Pd-catalyzed HDH reaction studies.

The analytical method is a modified version of the method described in a published paper (Khodadoust et al., 1999). A sample is acidified with 6N hydrochloric acid. This acidification is conducted to ensure that the hydroxyl group of the PCP is fully protonated, to allow PCP to be extracted by a non-polar solvent. An appropriate amount of acidified sample is mixed with 1 mL toluene in a 2-mL screw thread glass vial. Then, the vial is placed on a mechanical shaker and is shaken for 1 hour. For the analysis, 0.5 mL of the toluene is transferred to a 2-mL vial and loaded on the auto-sampler of a gas chromatograph (GC). The instrument employed is a Perkin-Elmer Clarus 500 GC equipped with an electron capture detector (ECD) and a 30 m × 0.32 mm i.d. DB-5ms

Table 4.1 - Chemicals and catalyst used in experiments

Chemical or catalyst	Specification	Company
Pentachlorophenol	98%	Sigma-Aldrich
2,3,4,6-Tetrachlorophenol	99%	Supelco
2,3,5,6-Tetrachlorophenol	99%	Supelco
2,3,4,5-Tetrachlorophenol	99%	Supelco
2,3,4-Trichlorophenol	99%	Sigma-Aldrich
2,3,5-Trichlorophenol	99%	Supelco
2,3,6-Trichlorophenol	99%	Supelco
2,4,5-Trichlorophenol	99%	Supelco
2,4,6-Trichlorophenol	99%	Supelco
3,4,5-Trichlorophenol	99%	Supelco
Phenol	99+%	Sigma-Aldrich
Ethanol	99.5%	Sigma-Aldrich
Toluene	99.9%	EMD Chemicals
2,5-Dibromotoluene	98%	Sigma-Aldrich
Pd-on-Al_2O_3 catalyst	1% Pd by weight	Sigma-Aldrich
De-ionized water	> 17.5 MΩ·cm	Barnstead

Table 4.2 - Experimental conditions for Pd-catalyzed HDH reactions

Initial concentration of PCP in reactor (mg/L)	C_{cat} (g/L)	Solvent composition (DIW(%):EtOH(%))	H_2 gas pressure (MPa)
Effect of solvent composition			
5.0	0.5	67:33	0.17
5.0	0.5	50:50	0.17
5.0	0.5	33:67	0.17
10.0	0.5	67:33	0.17
10.0	0.5	50:50	0.17
10.0	0.5	33:67	0.17
Adsorption isotherm			
6 different concentrations	1.0	67:33	N.A.
6 different concentrations	1.0	50:50	N.A.
6 different concentrations	1.0	33:67	N.A.
Effect of catalyst concentration			
5.0	0.1	50:50	0.17
5.0	0.5	50:50	0.17
5.0	1	50:50	0.17
10.0	0.1	50:50	0.17
10.0	0.5	50:50	0.17
10.0	1	50:50	0.17
Effect of H_2 gas pressure			
10.0	0.5	50:50	0.17
10.0	0.5	50:50	0.24
10.0	0.5	50:50	0.31
Mass balance studies			
20.0	1.0	50:50	0.17

Note: C_{cat} means concentration of catalyst; DIW and EtOH indicate de-ionized water and EtOH, respectively, v/v ratio; N.A. means not caplicable.

capillary column (J&W). Injector and detector temperatures are 250 and 300°C, respectively. The oven of the GC is operated at 100°C for 1 minute, then the temperature is increased to 200°C at a rate of 10°C/min, then the temperature is held for a period of 4 minutes. The toluene extractant contains 2,5-dibromotoluene as an internal standard for quality control.

4.2.3. Adsorption isotherm studies

All adsorption isotherm experiments were performed in a batch type mode in the pH range of 6.0 to 6.5. Twenty mL of a desired solvent, which is a pre-mixed water/ethanol mixture, was added into a 20-mL EPA glass vial. A desired volume of 1000 mg/L PCP stock solution was spiked to the vial to make a targeted initial concentration. The PCP spiked vials were shaken vigorously for 30 minutes. A sample (0.2 mL) was taken from each vial for measuring the initial concentration of PCP, C_{in}. Twenty mg of 1% (wt) Pd on Al_2O_3 powder was added into the vials. Then, the vials were securely tightened with a Teflon-line cap and shaken at 300 rpm using a mechanical shaker for 24 hours for the adsorption. After that, the caps were unscrewed and a sample was taken from each vial. The sample was filtered using a 0.2-µm membrane to remove any particles. In order to quantify the equilibrium concentration of PCP, C_{eq}, the filtered sample was then extracted with toluene for GC analysis as described in previous section. The concentration of PCP adsorbed onto the catalyst surfaces was determined by the following equation.

$$q = (C_{in} - C_{eq}) / C_{cat} \tag{4.1}$$

The units of q are mass of PCP sorbed per mass of catalyst.

4.2.4. Mass balance studies

The identification of transformation behavior of PCP during dehalogenation by the Pd-catalytic treatment is critical. Therefore, mass balance studies were conducted in order to distinguish between a sequential pathway through lesser chlorinated compounds or a direct pathway to phenol. The experimental conditions for these studies were shown in Table 2.

PCP concentrations in samples were analyzed by the same patterns as described in section 4.2.2. A Perkin-Elmer Clarus 500 GC equipped with flame ionization detector (FID) was employed to quantify phenol concentrations. Dichloromethane was used to extract phenol from a sample and ready for the GC analysis. The column used was a DB-5ms capillary column (30 m length × 0.25 mm i.d.) (J&W). The daughter chlorinated compounds of PCP were identified by comparing their elution times to those of standards injected on the GC-ECD. The analytical procedures for the daughter compounds of PCP followed the one developed for the PCP analysis.

4.2.5. Control experiments

In order to make sure that any observed disappearance of PCP was due to the Pd-catalytic HDH, two sets of control tests were performed. Detailed experimental procedures can be found in the previous Chapter. No significant loss occurred due to volatilization, with recoveries greater than 98% for all conditions tested. In the sorption controls, recoveries of PCP were in the range 86-110%. Therefore, I trust that any observed removal of PCP is due to catalytic HDH.

4.3. Results and discussion

4.3.1. Effect of solvent composition on the Pd-catalyzed HDH rate

The primary object of this part of the study is to determine the effect(s) of solvent composition on the Pd-catalyzed destruction of the target contaminant. I measured the catalytic hydrodehalogenation (HDH) of PCP in three different water/ethanol mixtures. The water:ethanol ratios were 67:33, 50:50, and 33:67 (vol:vol, before mixing).

As shown in Fig. 4.1, at both 5 and 10 mg/L of PCP initial concentration, the rate of PCP degradation by Pd-catalyzed HDH increases as the fraction of water increases in the solvent composition. It is clearly shown that the solvent composition has a strong effect on the HDH rates. The same trend of the solvent effect on the HDH rate was observed in previous studies for 1,2,4,5-tetrachlorobenzene (TeCB) with Pd/Al_2O_3 in Chapter III, and for polychlorinated biphenyls (PCBs) with Pd/Fe (Korte et al., 2002). For the dehalogenation experiments of 2,4,4'-trichloro-2'-hydroxydiphenylether (TCPE) with Pd/Carbon (Xia et al., 2003), the rate was promoted by the addition of water but the volume ratios of water to ethanol insignificantly affected the turnover frequency (TOF) of the dehalogenation.

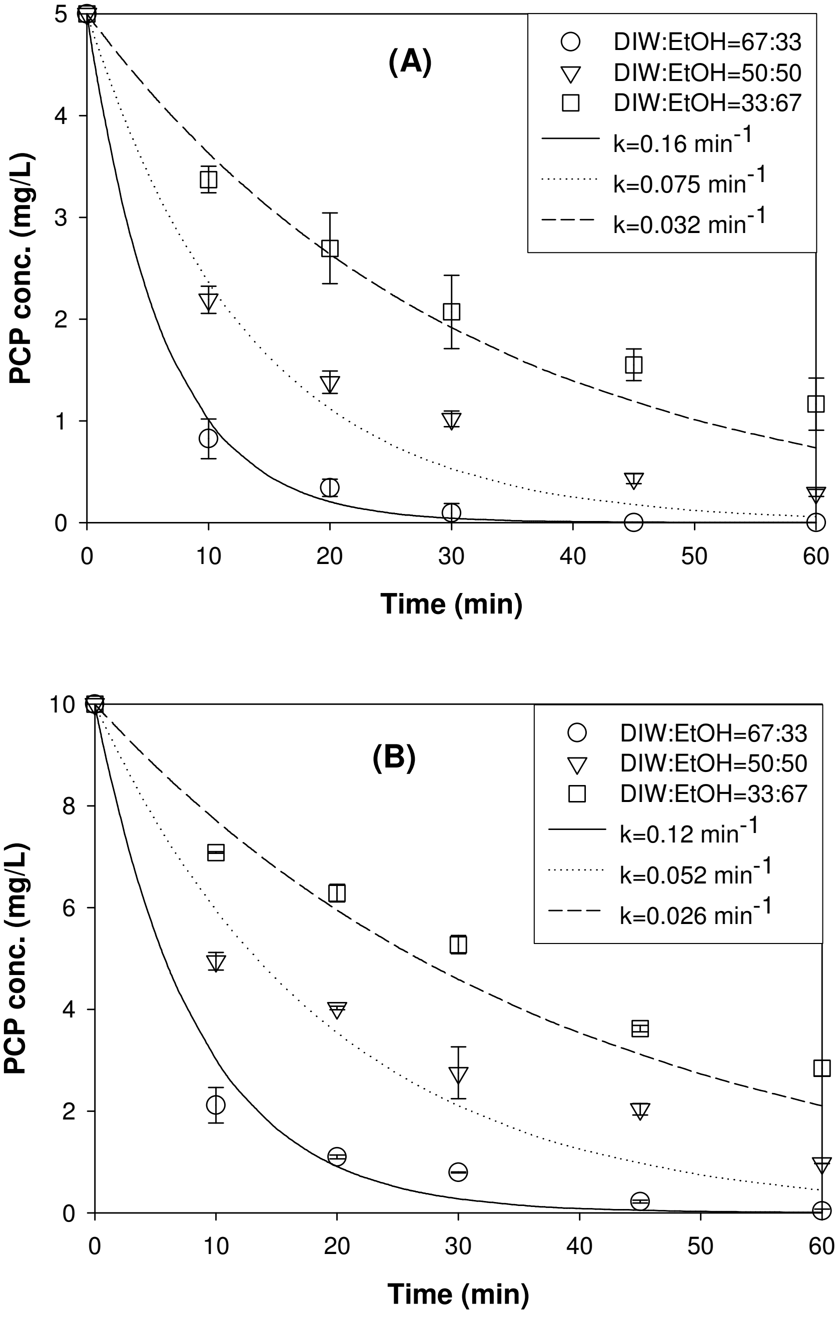

Fig. 4.1 - Effect of solvent composition on the Pd-catalyzed HDH rate of PCP in a batch reactor: catalyst conc. and hydrogen gas pressure were 0.5 g/L and 0.17 MPa, respectively, in both sets of experiment. DIW and EtOH mean de-ionized water and ethanol, respectively. Symbols represent experimental data and lines represent first-order degradation model.

In the previous Chapter, it was observed that the HDH reactions of TeCB follow first-order reaction kinetics. However, based on visual inspection, the catalytic HDH of PCP does not follow first-order kinetics in this study as shown Fig. 4.1. The feasible explanations for this will be described in section 4.3.6., below.

I believe that the observed effect of solvent composition on the rate of the HDH is due to the equilibrium partitioning of the target contaminant between the liquid solvent and the solid catalyst surfaces. When the solvent is mostly water, the hydrophobic contaminant, PCP, partitions more strongly to the catalyst surface, increasing the catalytic reaction rate. As the ethanol fraction increases, PCP is more "comfortable" in the solvent, and partitions less strongly to the solid catalyst surface, thereby slowing the rate.

4.3.2. Adsorption isotherms

The study of the adsorption isotherm was performed to confirm further the effect of solvent composition on the HDH rate. Fig. 4.2 shows the adsorption isotherms of PCP onto Pd/Al_2O_3 in three different solvent compositions. In order to calculate the isotherm parameters, the following Langmuir isotherm model was employed:

$$q = (q_{\max} K C_{eq}) / (1 + K C_{eq}) \tag{4.2}$$

where, q (mol/g) is the concentration of PCP adsorbed onto catalyst surface, C_{eq} (mol/L) is the equilibrium concentration of PCP in the liquid solvent, $q_{\max}$ (mol/g) is the

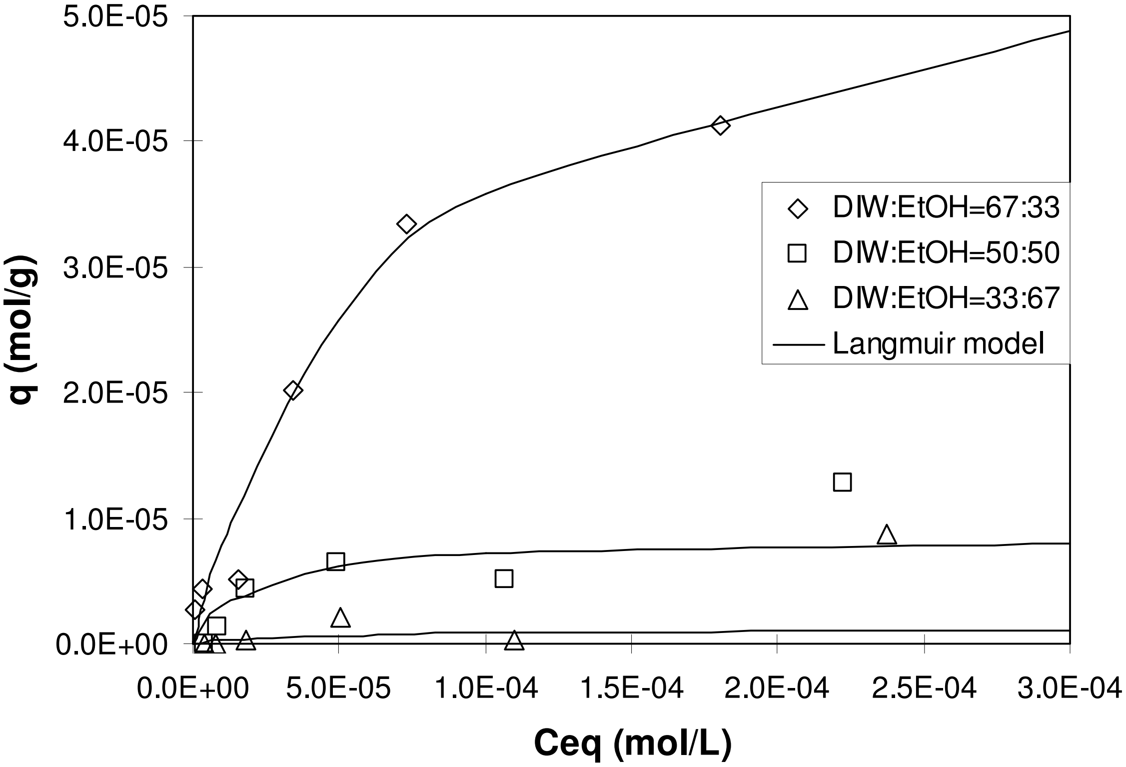

Fig. 4.2 - Adsorption isotherms of PCP onto Pd/Al_2O_3 in different solvent compositions.

Table 4.3 - Adsorption parameters calculated from isotherm experiments

Solvent composition (DIW:EtOH)	q_{max} (mol/g)	*K* (L/mol)
67:33	5.94E-05	1.53E+04
50:50	8.50E-06	5.54E+04
33:67	1.27E-06	2.18E+04

maximum concentration of PCP that can be adsorbed onto the catalyst surface, and K (L/mol) is the adsorption equilibrium constant. The adsorption parameters calculated by the Langmuir model, equation (4.2), are summarized in Table 4.3.

Larger amounts of PCP adsorbed onto the catalyst surfaces are allowed as the water fraction increases in the solvent, clearly illustrated in Fig. 4.2. The adsorption behaviors of PCP onto Pd/Al_2O_3 are successfully predicted by the Langmuir model. I expected that since same adsorbent, Pd/Al_2O_3, and adsorbate, PCP, were used, the adsorption capacity, $q_{\max}$, should be similar for all solvent compositions. The adsorption equilibrium constant, K, could be different in the three different solvent compositions. However, higher $q_{\max}$ was observed at higher fraction of water in the solvent, and similar values of K were shown in all three solvent compositions, confirmed in Table 4.3. I do not have a scientific explanation for this disagreement. It is demonstrated from this isotherm experiment that the water fraction in the solvent is a very important operational parameter for Remedial Extraction and Catalytic Hydrodehalogenation (REACH).

4.3.3. Effect of catalyst concentration on the Pd-catalyzed HDH rate

Fig. 4.3 shows the effect of catalyst concentration on the HDH reaction rate of PCP. The HDH rate increases with increasing catalyst concentration. Since the degradation of PCP by the Pd-catalyzed HDH does not appear to follow first-order kinetics, the degradation rate constant cannot be calculated, and I cannot explain mathematically if the effect is linear.

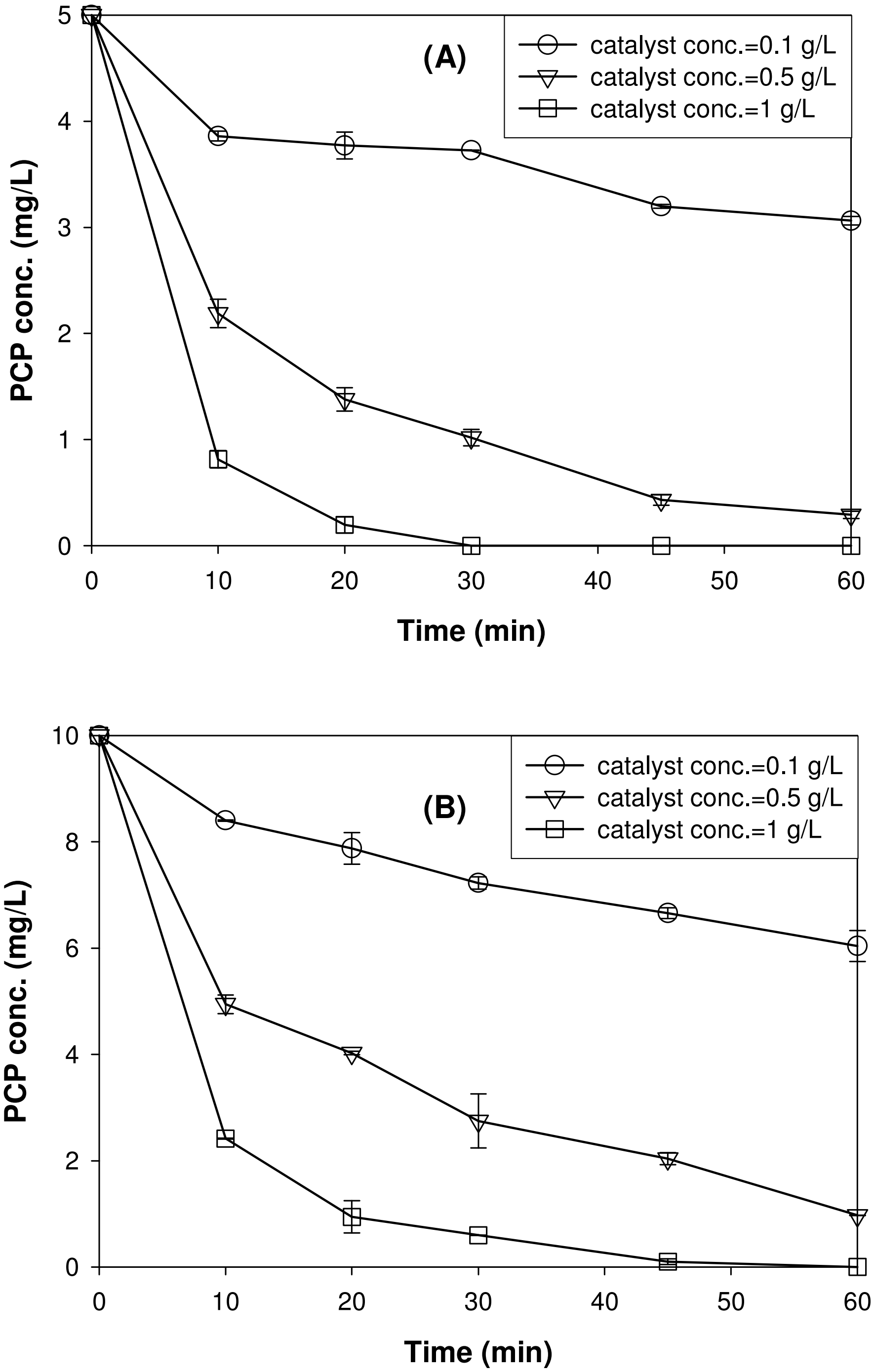

Fig. 4.3 - Effect of catalyst concentration on the Pd-catalyzed HDH rate of PCP in a batch reactor: solvent composition is 50:50 of de-ionized water:ethanol.

4.3.4. Effect of H_2 pressure on the Pd-catalyzed HDH rate

The HDH reaction typically follows a stoichiometry along the lines of the following (Urbano and Marinas, 2001):

$$R\text{-}X_n + nH_2 \rightarrow R\text{-}H_n + nH^+ + nX^- \qquad (4.3)$$

where X represents a halogen atom, e.g., chlorine or bromine. As described by the above equation, hydrogen is a reactant in the HDH of the halogenated compounds. Therefore, one might expect that the HDH reaction rate would be sensitive to the hydrogen pressure in the reactor. It was reported that the degradation rate of nitrate by Pd/Cu bimetallic catalyst could be enhanced by increasing hydrogen partial pressure (Pintar et al., 1996). I also verified that, in the absence of hydrogen, no reaction occurs, describing control experiments where nitrogen was used in stead of hydrogen.

Fig. 4.4 shows the effect of hydrogen pressure on the dehalogenation of PCP. Surprisingly, the hydrogen pressure had no effect on the HDH reaction of PCP when the pressure was varied between 10 and 30 psig under the experimental conditions I considered. To explain this finding, I hypothesize that the sorption of hydrogen gas onto the catalyst surface follows a Langmuir isotherm. Thus, once the hydrogen pressure in the reactor is above a certain level, no additional sorption can take place, and the reaction ceases to be sensitive to the pressure. I have not attempted to determine the pressure at which this threshold resides. However, it is clearly somewhere between 0 psig (at which point no reaction occurs) and 10 psig (at which point the reaction

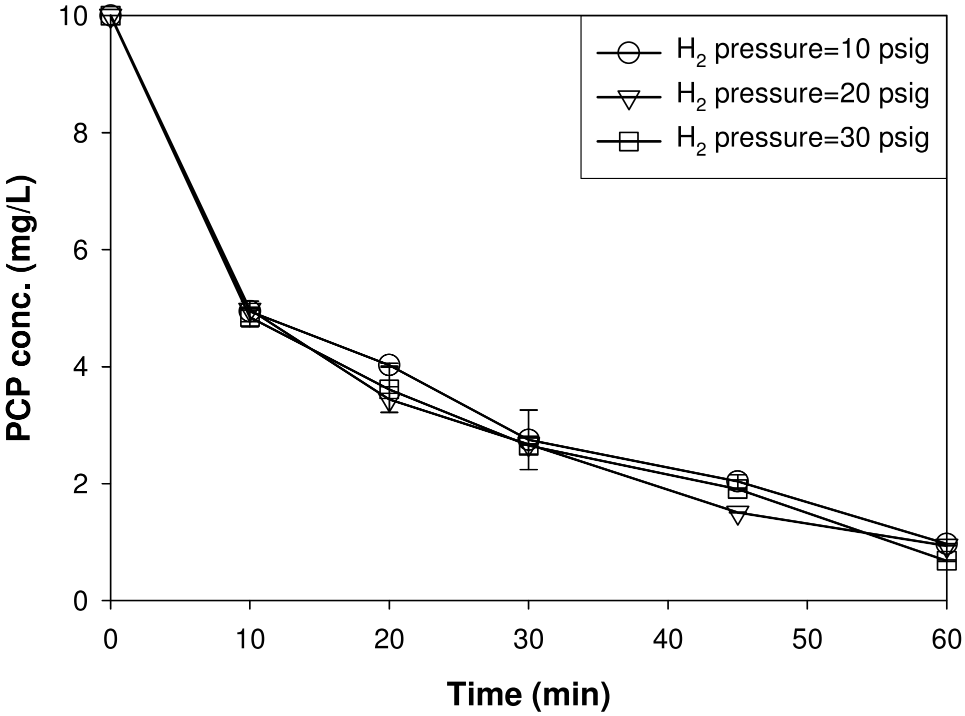

Fig. 4.4 - Effect of H_2 gas pressure on the Pd-catalyzed HDH rate of PCP in a batch reactor: solvent composition is 50:50 of de-ionized water:ethanol; catalyst concentration is 0.5 g/L.

proceeds at its maximum rate).

From this experiment, it is inferred that dissolved molecular hydrogen, [H_2(aq)], does not compete for adsorption sites on the catalyst surfaces with PCP, and the H_2 concentration on the catalyst is constant during the reaction when above 10 psig of hydrogen gas is delivered.

4.3.5. Transformation of PCP by the Pd-catalyzed HDH

A mass balance study was performed to examine if PCP is transformed sequentially or directly by the Pd-catalyzed HDH, to identify intermediate and final products, and finally to propose a possible transformation pathway. As shown in Fig. 4.5, substantial amounts of daughter chlorinated compounds of PCP as intermediates are generated. As PCP concentration decreases, the phenol concentration increases continuously over time. Therefore, it is likely that phenol is the final product of PCP HDH reaction. The concentration of 2,3,4,6-tetrachlorophenol (TeCP) increases up to 60 min, and then decreases. A negligible concentration of 2,3,5,6-TeCP was formed. The concentrations of 2,3,4- and 2,3,6-trichlorophenol (TCPs) initially increase and stay at a certain level within 2 hours under the experimental conditions. The complete dehalogenation of 2,4,5-TCP with Pd/Al_2O_3 (Hoke et al., 1992) and 2,4,6-TCP with Pd/Mg (Morales et al., 2002) were reported previously. Therefore, 2,3,4- and 2,3,6-TCP are probably not stable products and they should be further dechlorinated if longer reaction periods are given or if more fresh catalyst is added. The dichlorophenols and chlorophenols were not detected.

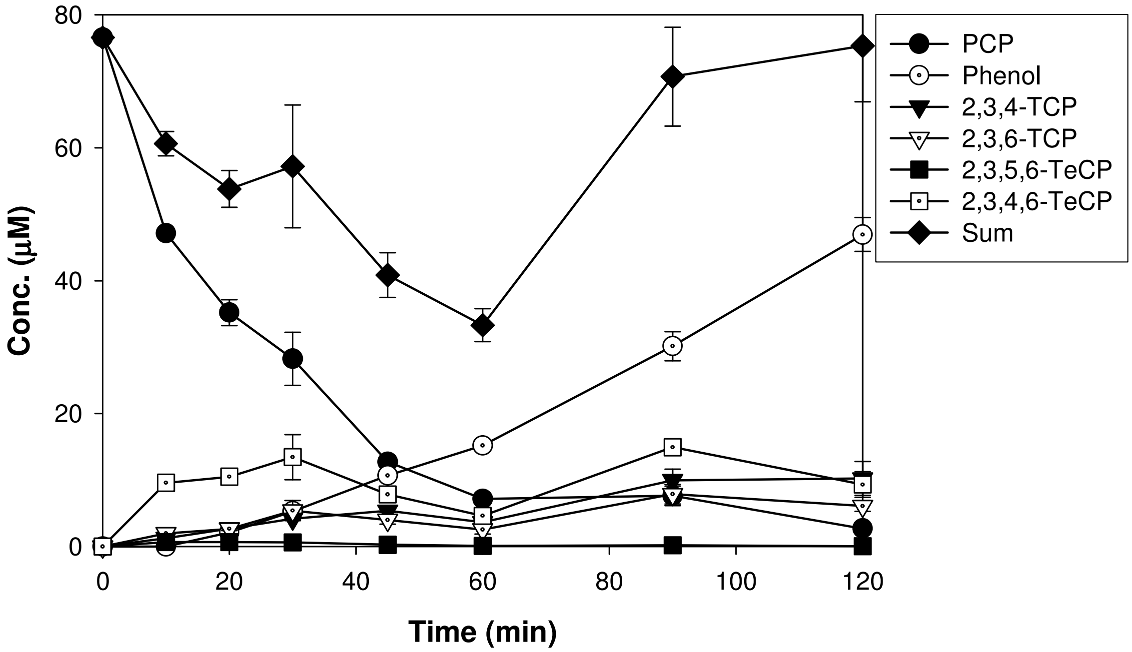

Fig. 4.5 - Transformation of pentachlorophenol by Pd-catalyzed HDH in a batch reactor: solvent composition is 50:50 of de-ionized water:ethanol. PCP, TCP, and TeCP mean pentachlorophenol, trichlorophenol, and tetrachlorophenol, respectively.

Generally, a total mass balance at each time point meets the expected one. However, the summation values of compounds between 10 and 60 min are lower than the expected one. I believe that chlorinated compounds are adsorbed on the catalyst surface, not released to the solvent. Since any catalyst particles in samples were removed by the filtration with a 0.2-μm membrane before ready to be analyzed, the chlorinated compounds adsorbed on catalyst surfaces are not detected.

In summary, PCP treated with the Pd-catalytic HDH is transformed to phenol by sequential reductive dehalogenation to tetrachlorophenols, then to trichlorophneols, then to phenol. Therefore, a dehalogenation pathway of PCP can be proposed as shown Fig. 4.6. No 2,3,4,5-tetrachlorophenol was detected, so I do not believe it is part of the reaction pathway.

4.3.6. Degradation kinetics of PCP by the Pd-catalyzed HDH

The Langmuir-Hishelwood (L-H) mechanism is defined by the following steps (Carberry, 1976): (i) two species adsorb onto the catalyst surface, (ii) reaction between two adsorbed species occurs, and (iii) products are formed and desorb. In the previous paper Chapter III, a first-order kinetic model was developed based on the L-H kinetics and successfully used to represent the 1,2,4,5-tetrachlorobenzene HDH data.

However, the first-order kinetic model failed to predict the PCP HDH data as shown Fig.4.1. Initially, the degradation rate of PCP is fast, but it slows down over time. The failure of first-order kinetics to describe the degradation of PCP is probably due to

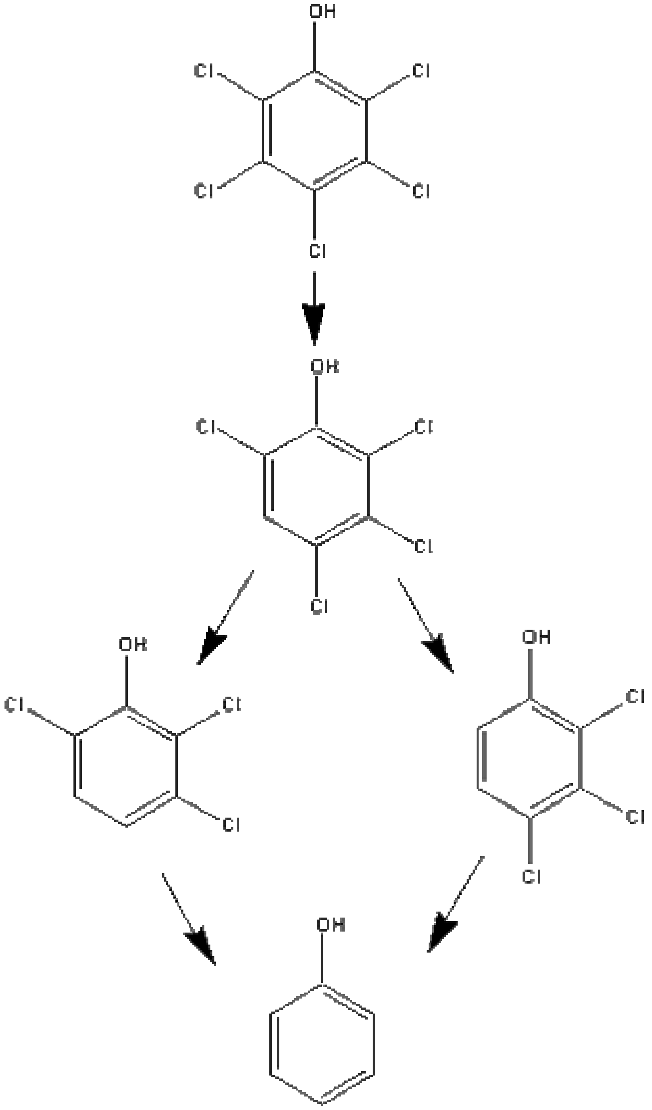

Fig. 4.6 - Proposed transformation pathway of PCP by Pd-catalyzed HDH in a water/ethanol mixture.

the competitive reactions with intermediate products which are generated during PCP degradation. As explained in section 4.3.5., substantial mass of intermediate products are generated during PCP degradation. The concentration of the intermediates adsorbed onto the catalyst cannot be ignored compared to that of PCP. In other words, PCP probably must compete with intermediates for sorption sites on the catalyst. Since intermediate products are accumulated over time, the kinetic rate of PCP decreases as reaction time proceeds.

Because of this competition, I have not developed a mathematical model based on the L-H kinetics to successfully describe the degradation profiles of PCP HDH. However, I believe that the degradation of PCP by Pd-catalyzed HDH reaction follows the L-H mechanism, as confirmed by adsorption isotherms, effect of catalyst concentration, effect of hydrogen pressure, and mass balance experiments.

4.4. Conclusions

PCP can be reductively dehalogenated through Pd-catalyzed HDH. The rate of the HDH reaction is a strong function of the solvent composition and the concentration of catalyst in the reactor. The hydrogen pressure is not important as long as it is above some critical level. The transformation of PCP using Pd on Al_2O_3 powered catalyst in water/ethanol mixtures occurs sequentially by dehalogenation to tetrachlorophenols, then to trichlorophenols, then to phenol. The degradation rate of PCP does not follow first-order kinetics, probably because competition for reactive sites occurs between PCP and intermediate products which are generated during PCP degradation. The experimental results obtained here are useful when the Pd-catalytic HDH technology is practically applied to the remediation of contaminated sites.

CHAPTER V

STUDIES OF THE REACH TECHNOLOGY IN CONTINUOUS MODE: SYNTHETICALLY CONTAMINATED SOILS IN THE LABORATORY

5.1. Introduction

In Chapter II, the extraction of 1,2,4,5-tetrachlorobenzene (TeCB) and pentachlorophenol (PCP) from contaminated soils in batch mode was discussed. In Chapters III and IV, Pd-catalyzed hydrodehalogenation (HDH) reactions of TeCB and PCP in batch mode were described. Now, I am going to discuss the studies of the remedial extraction and catalytic hydrodehalogenation (REACH) in continuous mode to treat soils synthetically contaminated by HHOCs in the laboratory. In other words, I combined contaminant extraction and contaminant destruction in a closed-loop system as suggested in Chapter I.

5.2. Materials and methods

5.2.1. Chemicals

Ethanol (99.5%, ACS grade, Aldrich), acetone (≥99%, ReagentPlus grade, Aldrich), hexane (98.5%, HPLC grade, EMD chemicals), toluene (99.9%, HPLC grade, Aldrich), 1,2,4,5-tetrachlorobenzene (98%, Sigma-Aldrich), pentachlorophenol (98%, Sigma-

Adrich), 2,5,-dibromotoluene (98%, Sigma-Aldrich), ammonium hydroxide (TraceMetal grade, Fisher), and sodium hypochlorite (Purified grade, 4-6% NaOCl, Fisher) were used without further purification. The solvent selected for the closed-loop treatment system was a 50:50 mixture of water and ethanol (vol:vol, before mixing) and it was prepared using deionized water and 200 proof (99.5%) ethanol. In this project, 1,2,4,5-tetrachlorobenzene (TeCB) and pentachlorophenol (PCP) were selected as the two target contaminants. TeCB and PCP stock solutions of 1000 mg/L were prepared by dissolving 0.02 g of TecB and PCP powdered chemical, respectively, into 20 mL ethanol in a glass via and closed with a PTFE-lined septum.

A commercially available supported palladium (Pd) was used in this research. It is Pd, 1.01% (wt) on 1-2 mm alumina spheres, manufactured by Alfa Aesar and the catalyst was prereduced when supplied. The information regarding to the catalyst was trusted as the manufacturer provided. The catalyst was employed for my experiments as it was supplied. No attempt was given to protect the catalyst from air contact which may result in oxidation of Pd and decrease in performance.

5.2.2. Lab contaminated soils

Uncontaminated soil was obtained from College Station, TX. The soil was classified as a sandy loam with 78% sand, 6% silt, and 16% clay which was determined by the Soil, Water, and Forage Testing Laboratory at Texas A&M University. The fraction of soil organic matter was 0.30%.

I contaminated the soil with TeCB and PCP separately for this continuous experiment. The contamination procedures of the soil with TeCB and PCP were described in Chapter II. To determine how the contaminant mass was extracted from soil and removed by Pd-catalyzed treatment, I first had to know the concentration of TeCB or PCP in the contaminated soil. I determined the soil concentration by a "shaker" method, which was also described in Chapter II. The TeCB and PCP concentrations were determined to be 55.5±2.5 and 86.9±3.7 mg/kg, respectively. The contaminated soil was aged nearly three months before being subjected to the continuous mode experiment.

5.2.3. Closed-loop treatment system

The closed-loop treatment system was constructed and operated under "baseline" conditions to demonstrate that REACH is suitable for the soils contaminated by HHOCs for long periods. Fig. 5.1 shows the schematic diagram of the closed-loop flow-through system as it has been constructed in the laboratory. Two identical systems were constructed in order to be able to run two experiments side-by-side. Table 5.1 shows the experimental (baseline) conditions of the system operation.

Important specifications of the equipment used in the flow-through system are as follows.

- The reservoir is a 2.3-L glass bottle, sealed with a three hole cap (manufactured from PTFE with a TFE/propylene o-ring and a polypropylene screw collar,

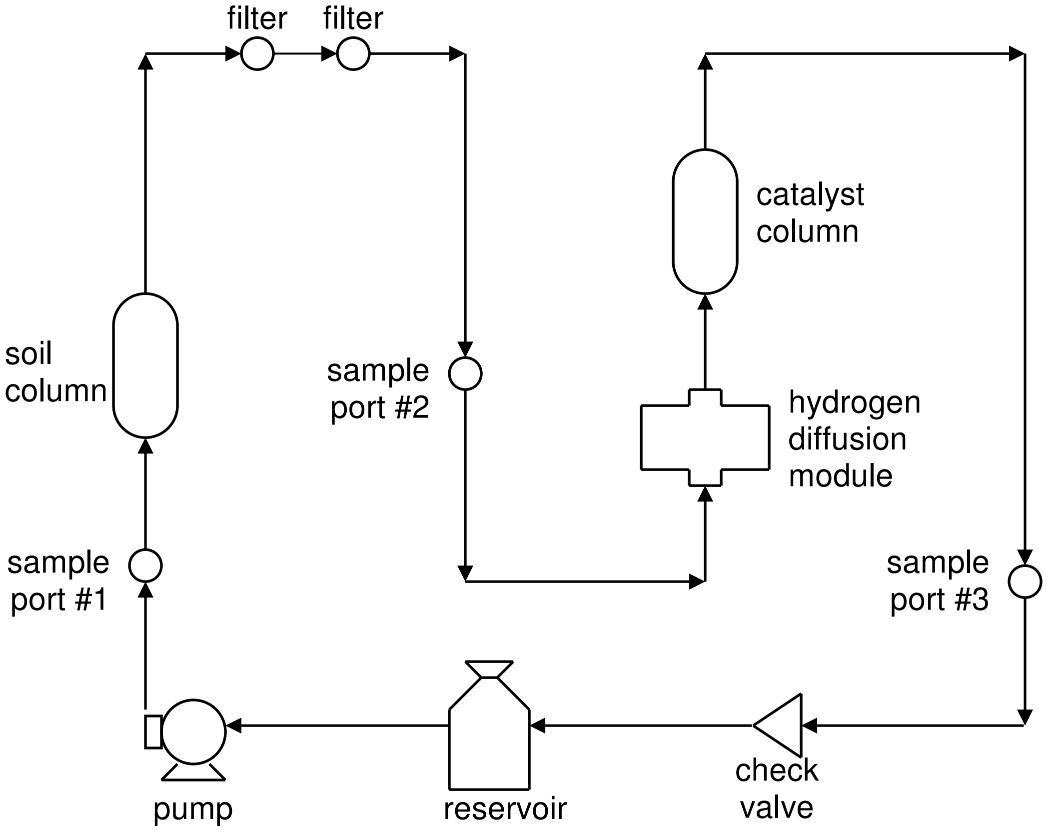

Fig. 5.1 - Schematic diagram of closed-loop flow-through system as conducted in the laboratory.

Table 5.1 - Experimental (baseline) conditions of closed-loop flow-through system.

Catalyst	10 g of catalyst Palladium, 1.01% on 1-2 mm alumina spheres, reduced
Glass bead	3 mm borosilicate glass
Column for catalyst	25 cm^3 stainless steel tubular cylindrical reactor
Amt of contaminated soil	200 g
Column for soil	150 cm^3 stainless steel tubular cylindrical reactor
Pressure of H_2 injected	10 psig (69.0 kPa above atmospheric pressure)
Solvent	50:50 of water:ethanol mixture
Solvent volume	2.2 Liters
Solvent flow rate	1 mL/min
Check valve	10 psig (69.0 kPa above atmospheric pressure)
Pore size of filter	0.5 μm

Kimble) to minimize volatilization of the solvent or of the target contaminants from the solvent. One of the holes is for the inlet line, another for the outlet line, and the other for a base addition which was sealed with a plug under normal conditions.

- The pump is an Eldex Optos metering pump, model 2SM (Eldex Laboratories, Napa, CA). Typical flow rate is 1 mL/min. The Optos series of pumps is designed to provide high accuracy at that flow rate.
- The catalyst column is Swagelok miniature sample cylinder. The approximate internal volume is 25 cm^3. The column is constructed of corrosion-resistant 316 stainless steel.
- The soil column is Swagelok sample cylinder. The internal volume of the cylinder is 150 cm^3. The column is manufactured with 304L stainless steel, which resists intergranular corrosion.
- The filters are 0.5-μm Swagelok tee-type filters, TF series, with sintered filter media.
- The sample ports are Swagelok three-way valves. For normal flow conditions, the valves are oriented as shown in Fig. 5.1. When a sample is desired, the valve is switched, and the flow is directed into a Hamilton gas-tight syringe. The syringes are attached to the three-way valves by securing a 16-gauge syringe needle into a 1/16” Swagelok fitting.

- The hydrogen diffusion module is a SuperPhobic mini-module from Membrana (Charlotte, NC). Hydrogen is supplied to the model through gas-impermeable flexible plastic tubing.
- The catalyst reactor is filled approximately one-third with glass beads on the bottom, then one-third with 1% Pd-on-Al_2O_3 catalyst in the middle, then one-third with glass beads on the top as shown in a previous paper (Lowry and Reinhard, 2000).
- The check valve is a 10-psig check valve from Swagelok.
- All tubing is 1/8” stainless steel, except for the tubing between the reservoir and the pump. That tubing is 1/16” flexible plastic, provided by Eldex to be used with the pump.
- All fittings are stainless-steel Swagelok compression-type fittings.
- The solvent used is a 50/50 mixture of water and ethanol (vol/vol, pre-mixing).

5.2.4. System operation

The systems were run for 7 weeks. One system had TeCB-contaminated soil and the other had PCP-contaminated soil. Every week, I removed the treated soil from the column, and re-packed the column with “fresh” contaminated soil. Note that soil did not actually move through the treatment system. Rather, soil was treated batch-wise, one column at a time.

Samples were collected once per day from three sample locations, which are shown in Fig. 5.1. These samples were extracted with hexane for TeCB samples and with toluene for PCP samples, and analyzed with a Perkin-Elmer Clarus 500 GC equipped with an electron capture detector (ECD) and a 30 m × 0.32 mm i.d. DB-5ms capillary column (J&W).

After 5 weeks of running the treatment system for PCP-contaminated soil, the Pd catalyst had partially deactivated and was regenerated with dilute sodium hypochlorite solution (Lowry and Reinhard, 2000). Regeneration was performed as described in the following. The spent catalyst was taken out from the catalyst column and placed in a 50-mL plastic centrifuge tube. 20 mL of 20 mM NaOCl was poured into the tube. The tube was slowly shaken for 30 min. Then, I put the washed catalyst back in the column.

Because protons are released during the hydrodehalogenation (HDH) reaction (Urbano and Marinas, 2001), it is possible that the pH of the solvent would drop over time, and this could potentially affect the solvent's interactions with the catalyst (Alonso et al., 2002). Therefore, I spiked 0.2 mL of ammonium hydroxide into the reservoir each time I changed the soil, i.e., every 7 days. Then, I monitored the pH of the solvent in the reservoir. At the starting time, the pH was around 10.2 and at the end of each run, it was around 7.20.

5.2.5. Evaluation of system performance

The contaminant extraction rate, contaminant reaction rate, contaminant mass percent conversion, and apparent first-order rate constant, k, were calculated to evaluate the closed-loop system for TeCB-contaminated soil and for PCP-contaminated soil.

By comparing the concentrations upstream and downstream of the soil column, I can determine the flux of the contaminants from the contaminated soil to the solvent. The contaminant extraction rate (mass/time) is equal to the solvent flow rate (volume/time) multiplied by the concentration difference (mass/volume) across the soil column.

$$R_{\text{extract}} = Q_{\text{solvent}}\,(C_{\text{column out}} - C_{\text{column in}}) \qquad (5.1)$$

Also, by comparing the concentrations upstream and downstream of the catalyst column, I can calculate the rate of contaminant destruction. The contaminant reaction rate (mass/time) is equal to the solvent flow rate (volume/time) multiplied by the concentration difference (mass/volume) across the catalyst column.

$$R_{\text{react}} = Q_{\text{solvent}}\,(C_{\text{reactor in}} - C_{\text{reactor out}}) \qquad (5.2)$$

The measured concentrations were used to calculate the contaminant mass that was extracted from the soil and catalytically destroyed. The contaminant mass percent (%) conversion in each set of treatment was calculated by following equation.

$$\%\ conversion = \frac{\left\{\left(C_{in}^{soil} \times M_{soil} + C_{in}^{solvent} \times V_{solvent}\right) - \left(C_{out}^{soil} \times M_{soil} + C_{out}^{solvent} \times V_{solvent}\right)\right\}}{\left(C_{in}^{soil} \times M_{soil} + C_{in}^{solvent} \times V_{solvent}\right)} \times 100 \qquad (5.3)$$

where, C_{in}^{soil} (mg/kg) is an initial contaminant concentration in soil, M_{soil} (kg) is mass of soil, $C_{in}^{solvent}$ (mg/L) is an initial contaminant concentration in solvent at the beginning of each set, and $V_{solvent}$ (L) is volume of solvent.

Apparent first-order rate constant, *k*, was calculated with the assumption of ideal plug flow reactor using equation (5.4),

$$k = \frac{\ln\left(C_I / C_E\right)}{\bar{t}} \tag{5.4}$$

where, *k* is apparent first-order rate constant, C_I (mg/L) is a concentration entering the Pd reactor, C_E (mg/L) is a concentration exiting Pd reactor, and $\bar{t}$ (min) is the solvent residence time. The solvent residence time can be calculated by equation (5.5)

$$\bar{t} = f\frac{nV}{Q} \tag{5.5}$$

where, f is fraction occupied by catalyst, n is the column porosity, V is the volume of catalyst reactor, and Q is the flow rate. f was about 0.33 and n was 0.42. Therefore, calculated $\bar{t}$ was 3.5 min.

5.2.6. Control experiment

Control experiments of the closed-loop system for the treatment of TeCB and PCP were conducted to confirm that no loss of contaminants occur due to volatilization. A desired concentration of TeCB or PCP was amended in the reservoir. The soil column was empty, but 10 g of the Pd catalyst was packed in the catalyst column. Nitrogen gas was used instead of hydrogen gas and its pressure was 10 psig. The other operating conditions were the same as shown in Table 5.1. A sample was taken from the reservoir daily and the control experiments were run for 5 days.

The results of control experiments for TeCB and PCP are shown in Fig. 5.2. For the TeCB control, around 0.6 mg/L of TeCB disappeared within 1 day, but then very similar concentrations of TeCB were observed for the remaining time. For the PCP control, a similar trend was observed as shown in TeCB control. Around 0.2 mg/L of PCP decreased within 1 day, and then PCP concentrations remained similarly. Therefore, it is suspected that the mass of TeCB or PCP dropped within 1 day was adsorbed onto the catalyst surfaces. Overall, the mass balance suggests that the system was properly constructed to verify the performance of REACH technology.

5.3. Results and discussion

5.3.1. Contaminant extraction rate

Fig. 5.3 (A) and (B) show the results for the contaminant extraction rate over time of TeCB-contaminated soil and PCP-contaminated soil, respectively. Note that, every

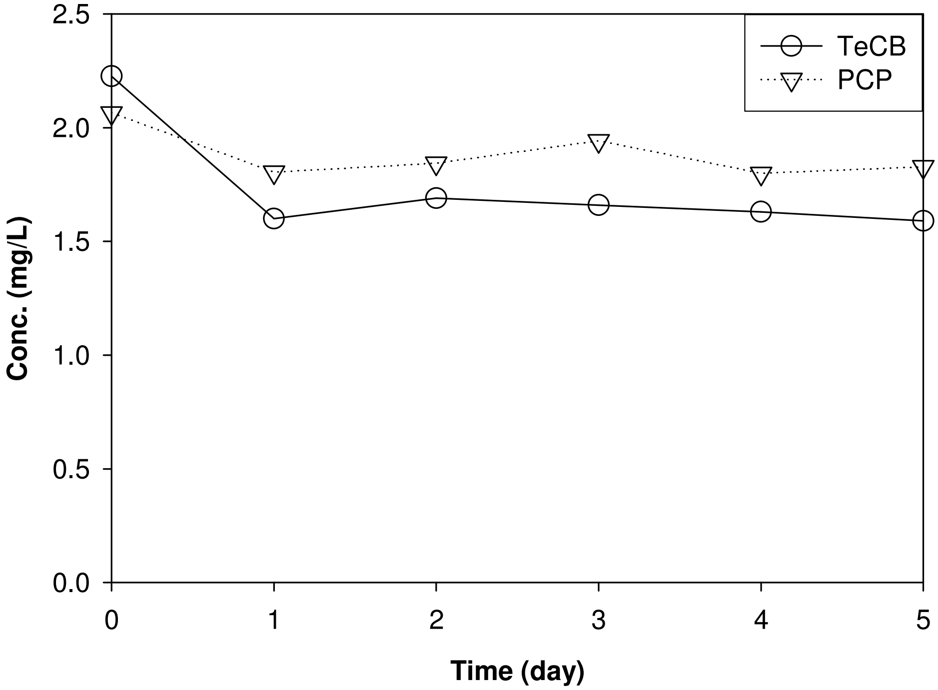

Fig. 5.2 - Control experiments for closed-loop flow-through system: Symbols represent concentrations in reservoir; solvent pumped at 1.0 mL/min; soil column was empty; N_2 gas used instead of H_2 gas.

week, I changed soil columns. That means treated soil was taken out and contaminated soil was repacked in the column. I found that contaminant extraction rate was high within 1-day period and, afterward, it decreased in both TeCB- and PCP-contaminated soils. My observed results have good agreement with previous findings of pentachlorophenol with water-ethanol mixtures (Khodadoust et al., 1999), PAHs with water miscible co-solvents (Khodadoust et al., 2000), and non-aqueous phase liquids (NAPLs) mass with chemical flushing (US EPA, 2006a). When contaminated soil was packed newly, the same trend of extraction rate was observed. It is concluded that extraction of both target contaminants from soils was almost completed by a 50:50 mixture of water and ethanol within 2 days.

A central feature of this research is that the solvent can be re-used in a closed loop, as illustrated in Fig. 5.1. It was expected that the solvent might degrade over time, losing some of its ability to extract contaminants from the contaminated soil. In a span of 7 weeks, I found that the solvent extraction ability was not degraded over time in either TeCB- or PCP-contaminated soil, as shown Fig. 5.3. I tested 1.4 kg of contaminated soil (0.2 kg of soil treated in every week) over 7 weeks. I have not verified whether an effect between solvent extraction longevity and catalytic destruction of contaminants is present. Since final products such as benzene and phenol are accumulated, the solvent might eventually need to be replaced. However, it was shown that the solvent had enough contaminant extraction ability from soil in the closed-loop system and it could be re-used under my experimental conditions and periods. Future work may consider the limits of solvent longevity.

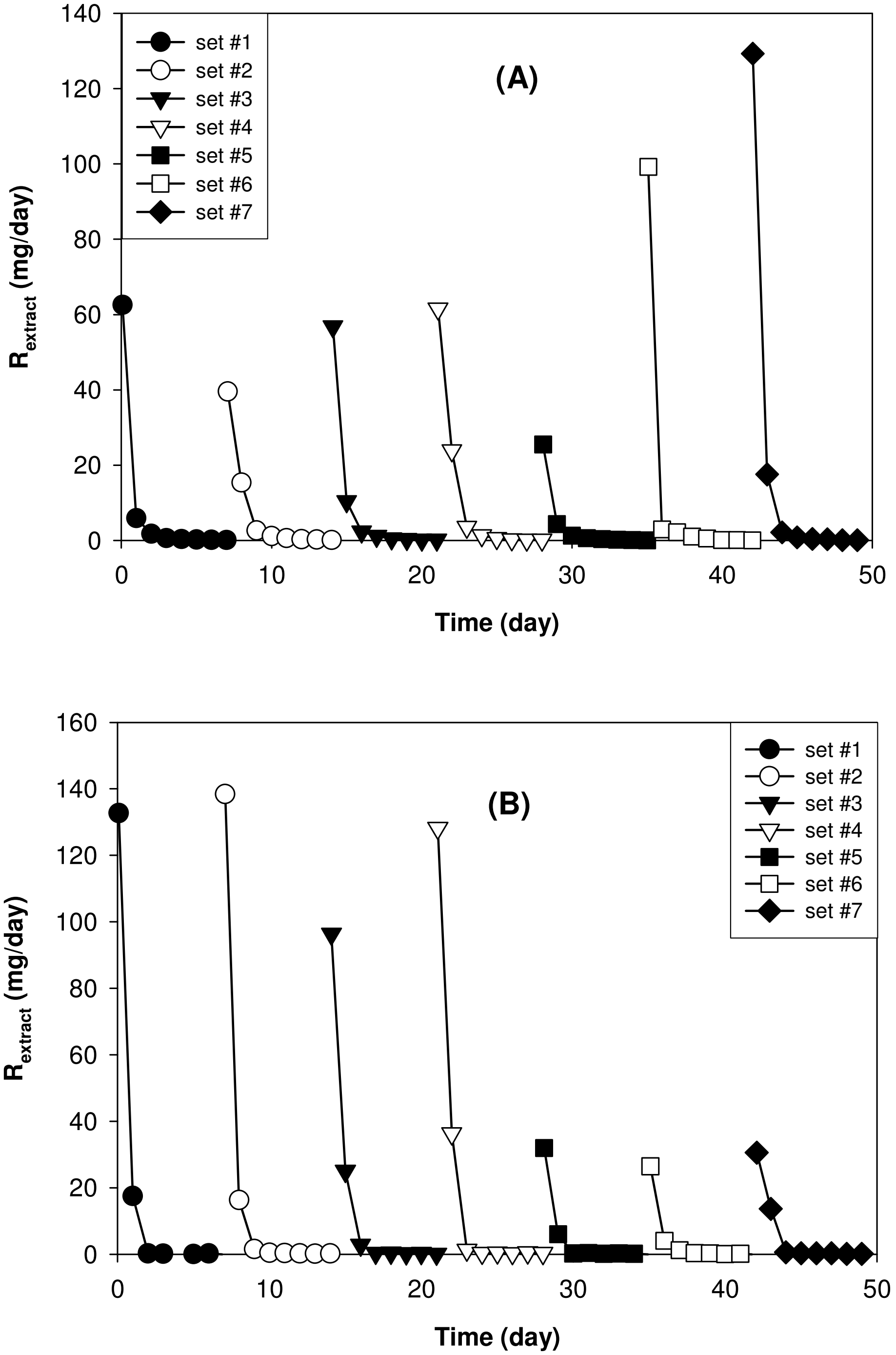

Fig. 5.3 - Contaminant extraction rate over time: (A) TeCB-contaminated soil, (B) PCP-contaminated soil.

5.3.2. Contaminant reaction rate

Fig. 5.4 shows the TeCB reaction rate by Pd-catalyzed HDH in the closed-loop system. TeCB concentrations at sample port #2, which are entering the Pd reactor, and at sample port #3, which are exiting Pd reactor, are shown in Fig. 5.4 (A). Based on these TeCB concentrations, TeCB reaction rates are calculated using the equation (2), and shown in Fig. 5.4 (B). Note that each set was run for 1 week and fresh contaminated soil was repacked. Higher reaction rates, which are degradation of TeCB mass per time, were observed in early stages of each set and the rates decreased over time. This observation can be explained as follows. Higher concentrations of TeCB in the solvent were present in early stages when the mass of TeCB extracted from soil was high. As TeCB was destroyed by the Pd-catalytic HDH reaction, the available mass of TeCB in the solvent was depleted. Therefore, less mass of TeCB is adsorbed and reacted on the catalyst surface, even though almost the same active sites of the catalyst are present, assuming that deactivation rate of catalyst can be ignored in span of 1 week. This explanation is also supported by the apparent first-order rate constant, k, over time as shown Fig. 5.5. In each set, a higher value of k is detected in early stages and the value decreased afterward.

The results of the PCP reaction rate by Pd-catalyzed HDH in the closed-loop system are shown in Fig. 5.6 (A) and (B), which indicate PCP concentrations in samples and calculated reaction rate, respectively. A similar trend of reaction rate for PCP was observed as shown for TeCB. However, lower reaction rates were observed for PCP than

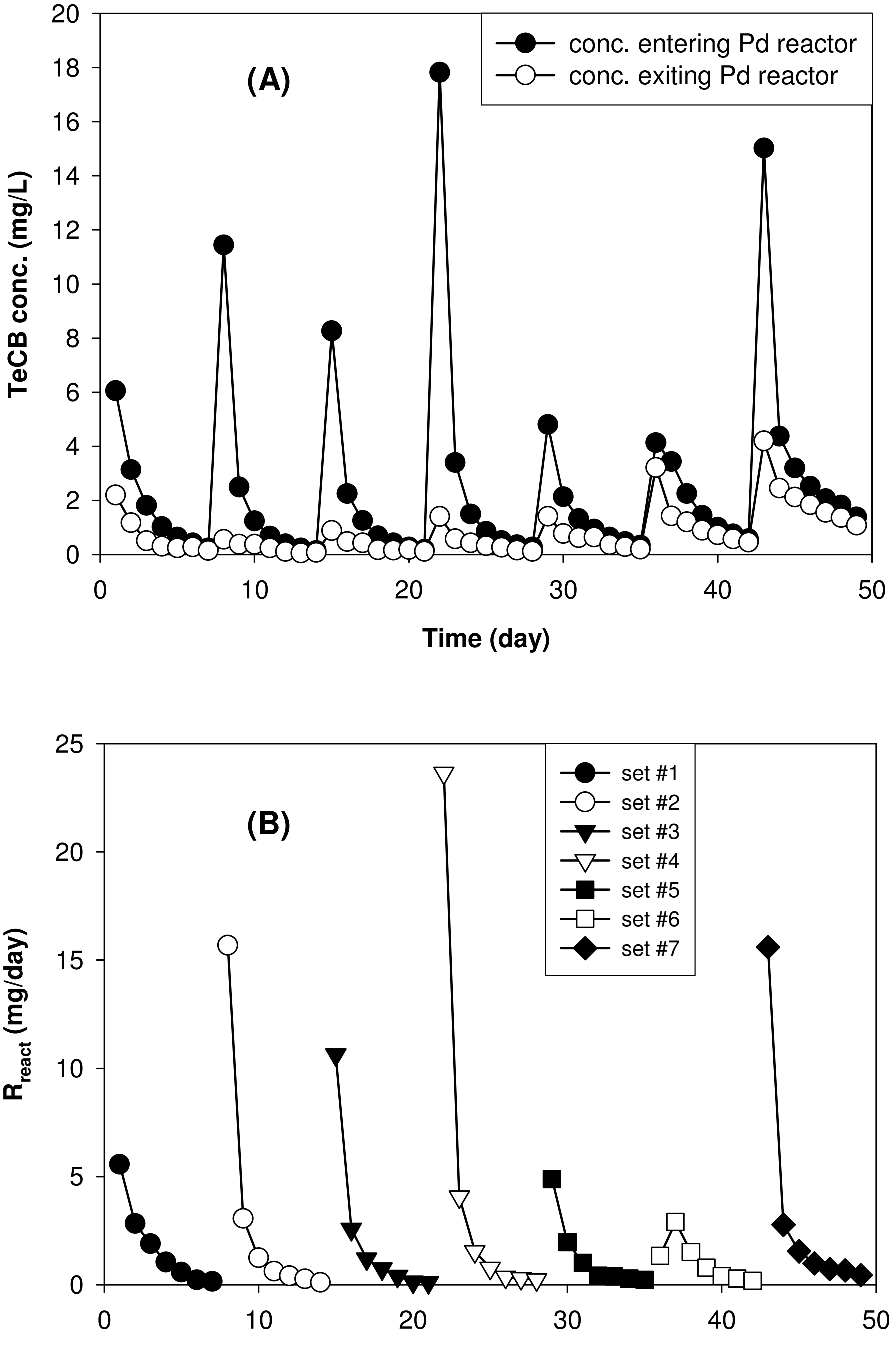

Fig. 5.4 - TeCB reaction rate by Pd-catalyzed hydrodehalogenation in closed-loop system.

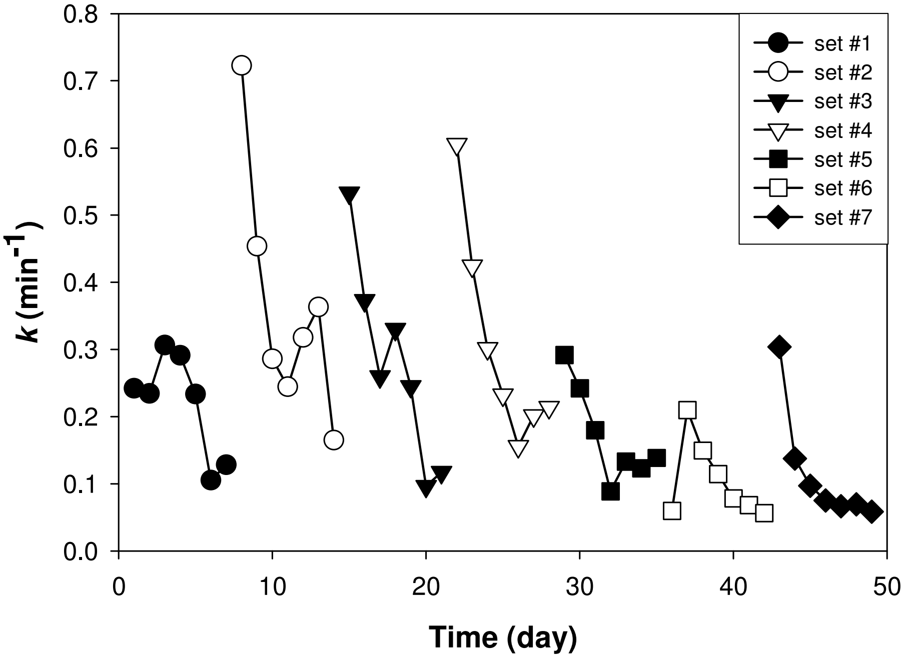

Fig. 5.5 – Apparent first-order rate constant (*k*) over time in TeCB-contaminated soil.

for TeCB. This is consistent with results from Chapters IV and V. Fig. 5.6 does not indicate properly the effect of catalyst regeneration on the PCP destruction rate. This will be explained in the next section.

5.3.3. Contaminant mass destruction

Table 5.2 shows the contaminant mass percent (%) conversion in each set of REACH treatments. For TeCB treatment, over 90% mass conversion was observed for the first 6 soil batches using only 10 g of catalyst and 2.2 L of solvent. However, the mass conversion decreases as the amount of contaminated soil treated increases. For the last soil batch, the TeCB mass conversion was down to 76%. This is likely due to the deactivation of catalyst.

The change of TeCB concentration in the reservoir over time is shown in Fig. 5.7 (A). The TeCB concentration increased as mass of TeCB was extracted from soil, and then decreased as the process performed in each set. Over the span of 7 weeks, the TeCB concentration remaining in the reservoir increased. This observation can also be explained by the deactivation of catalyst.

The mass conversion of PCP in the contaminated soil was somewhat lower than that of TeCB as shown in Table 5.2. However, in general, the PCP mass conversion was acceptably high, over 80% for each soil batch. The catalyst regeneration with dilute hypochlorite was performed before starting set #6. After that, the conversion increased considerably. This suggests that the catalyst slowly deactivated during treatment, causing the decrease of contaminant mass conversion over time.

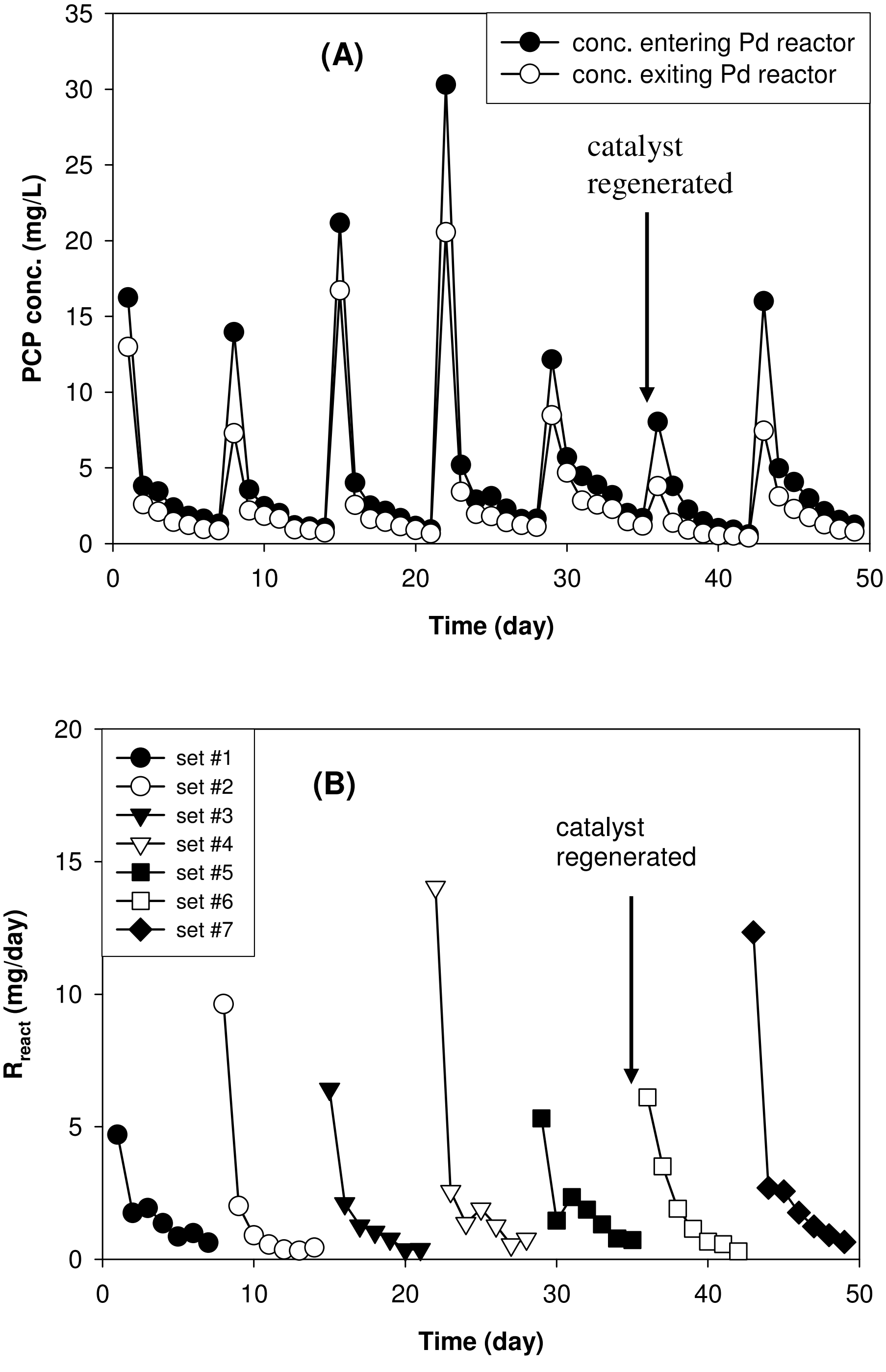

Fig. 5.6 - PCP reaction rate by Pd-catalyzed hydrodehalogenation in closed-loop system.

Table 5.2 - Contaminant mass percent (%) conversion in each set of REACH treatment

Set #	TeCB conversion (%)	PCP conversion (%)
1	96.5	83.2
2	98.7	90.5
3	98.3	90.2
4	96.5	83.7
5	94.4	81.8
6	90.0	93.2 *
7	76.1	86.1

Note: each set operated for 7 days. * Catalyst was regenerated before starting set #6.

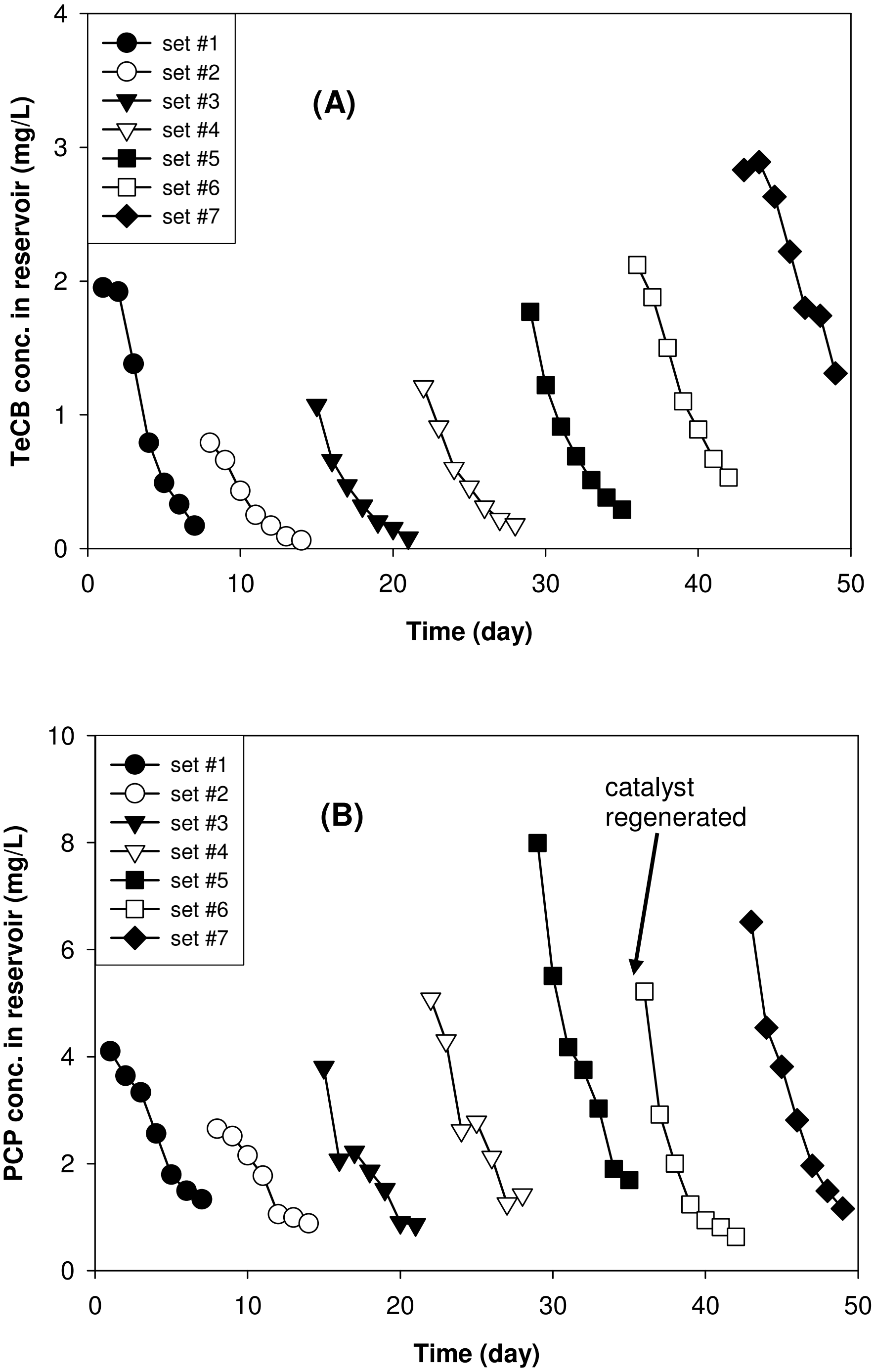

Fig. 5.7 - Contaminant concentrations in reservoir over time: (A) TeCB contaminated soil, (B) PCP contaminated soil.

For each soil batch treated, a higher concentration of PCP in the reservoir was observed in the early stage and then the concentration decreased as the HDH process performed, as shown in Fig. 5.7 (B). This trend was also shown for TeCB-contaminated soil. The effect of catalyst regeneration on the PCP mass destruction is also confirmed in Fig. 5.7 (B). The concentrations in the reservoir dropped after catalyst regeneration.

5.3.4. Intermediate products of PCP

Fig. 5.8 shows the gas chromatograms of samples taken from reservoir at the end of each treatment for all 7 soil batches. In Chapter IV, I proposed the sequential reductive transformation of PCP, converting to tetrachlorophenols (TeCPs), to trichlorophenol (TCPs), and finally to phenol. The peaks for TeCPs and TCPs are located between peaks for internal standard and PCP. It is confirmed that the final product of PCP degradation by Pd-catalyzed HDH in the solvent is phenol, not any other chlorinated phenols, since TeCPs and TCPs were not significantly accumulated in the solvent stream.

I did see some accumulation of TeCP and TCP over the span of 7 weeks. The peak areas of TeCP and TCP increased up to the first 5 batches. However, after catalyst regeneration , those areas decreased at the end of set #6 and increased again at the end of set #7. However, the amount of TeCP and TCP appears very small compared to the amount of PCP treated. Therefore it appears the conversion of PCP was almost completely to phenol, with only small accumulation of TeCP or TCP.

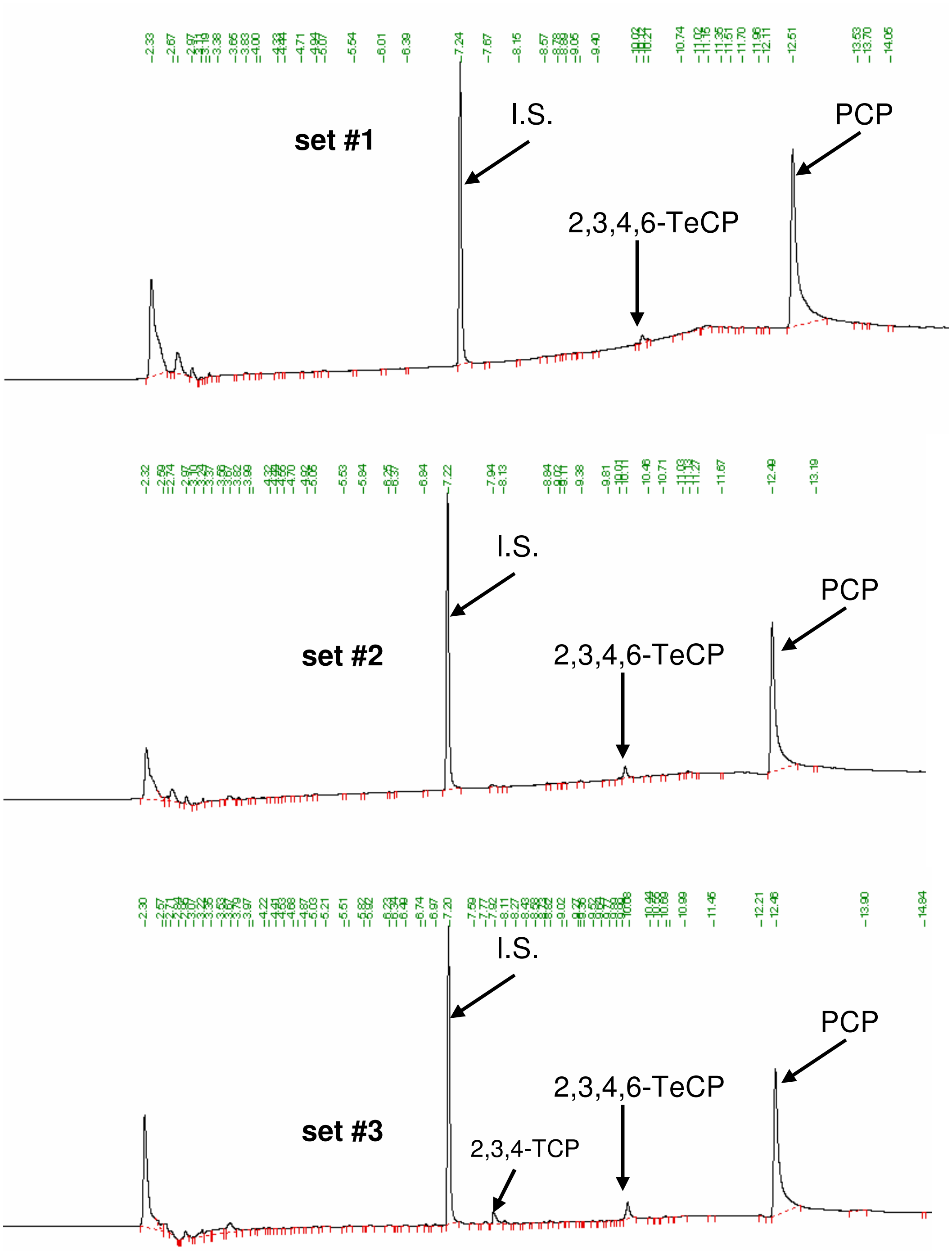

Fig. 5.8 - Gas chromatograms of samples taken from the reservoir of the system for the treatment of PCP-contaminated soil at the end of each treatment for all 7 soil batches.

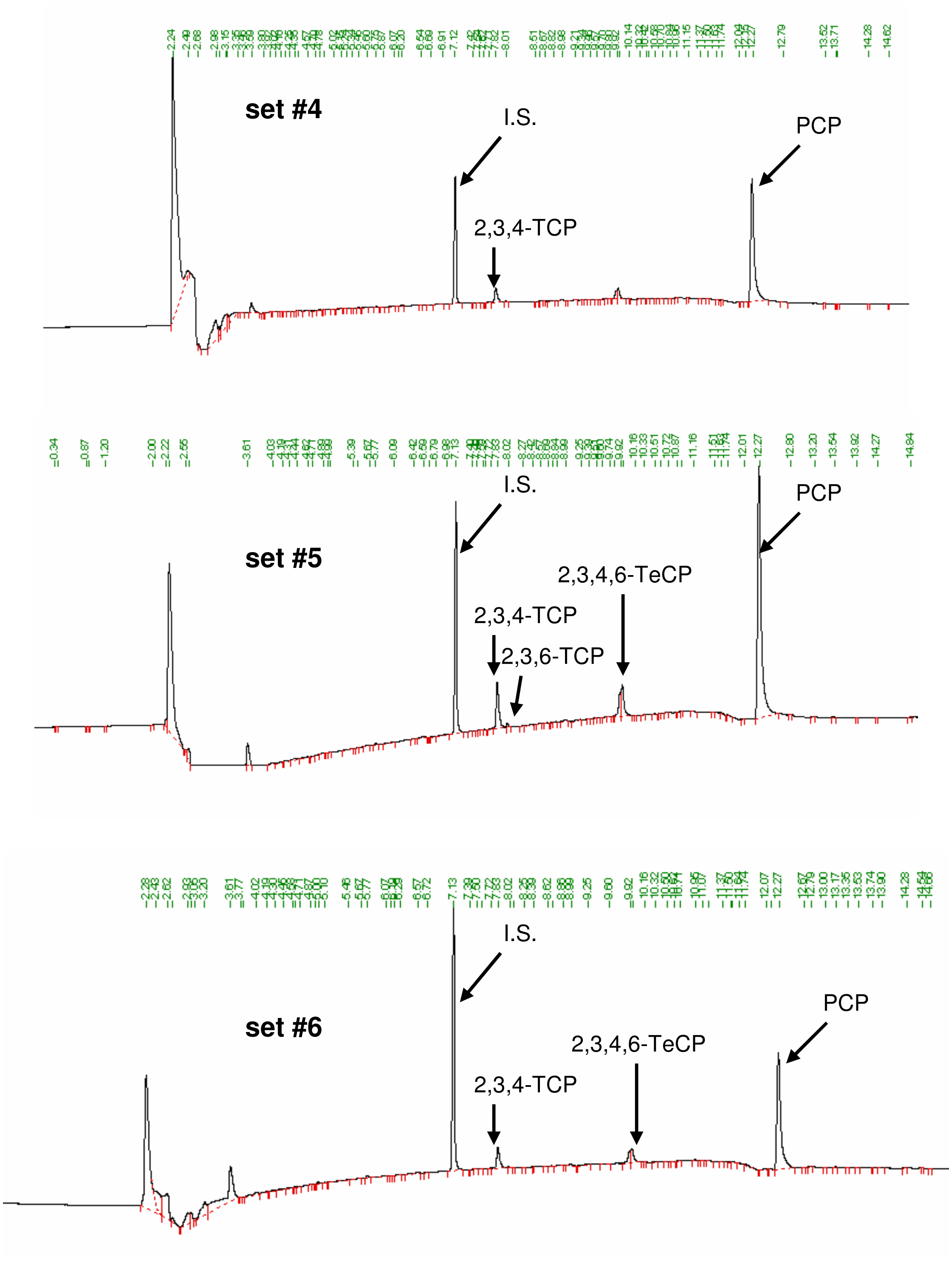

Fig. 5.8 – continued.

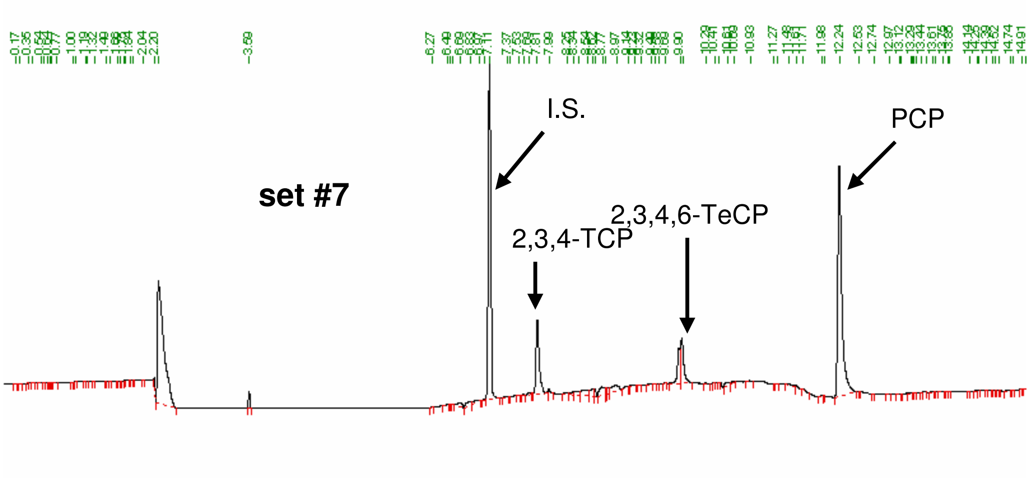

Fig. 5.8 – continued.

5.4. Conclusions

The REACH system was built in a lab-scale and tested on soils contaminated by 1,2,4,5-tetrachlorobenzene (TeCB) and by pentachlorophenol (PCP). In my lab system, I pump 1 mL/min solvent (a 50:50 mixture of water and ethanol) through a packed bed of contaminated soil for the extraction step, and then through a packed bed of catalyst for the hydrodehalogenation step. In a span of 7 weeks, I treated 1.4 kg of contaminated soil: 7 columns of contaminated soil, each with 0.2 kg soil, each treated for 1 week. This was accomplished with just 10 g of catalyst and 2.2 L of solvent. Extraction of both TeCB and PCP mass from soils was almost completed within 2 days using the solvent. Higher reaction rate, which is mass removed per time, was observed for TeCB than for PCP. The efficiency of the REACH process slowly decreased as the amount of contaminated soil subjected to treat increased. This is either because by-products build up in the solvent stream or because the catalyst slowly deactivates. Regeneration of the catalyst by treatment with dilute hypochlorite appears to restore the overall efficiency of the process.

In a period of 7 weeks, it appeared that the solvent maintained its ability to extract contaminants from soil under our experimental conditions in this research. However, it is possible that the solvent might degrade over time, losing some of its ability to extract contaminants from the contaminated soil. If this occurs, the solvent would need to be replaced. This represents a periodic operating cost that would need to be factored into the overall cost for this technology. Therefore, the longevity of the solvent’s ability to extract contaminants from the soil should be investigated in the future.

CHAPTER VI

STUDIES OF THE REACH TECHNOLOGY IN CONTINUOUS MODE: A FIELD SOIL CONTAMINATED BY PENTACHLOROPHENOL

6.1. Introduction

Pentachlorophenol (PCP) is an important contaminant that was widely used as a fungicide and insecticide in commercial wood treatment (Cirelli, 1978). The soil contaminated by PCP in an actual field site, in which operations of pressure-treating posts and other lumber ceased in the mid-1980's, was supplied by an environmental consulting company in Orlando, FL. The contaminated site is named the Post & Lumber Preserving Co. (PLP) site, after the company that operated there.

I tested the applicability and performance of the remedial extraction and catalytic hydrodehalogenation (REACH) technology for the treatment of the PCP-contaminated field soil. In particular, I have done three different types of experiments: (1) REACH system with field-contaminated soil for 11 days, (2) REACH system with no soil, used solvent, and fresh catalyst for 24 hours to test how rapidly the catalyst deactivates, and (3) Regeneration experiments to determine if the catalyst activity can be regained after deactivation.

A rapid extraction of PCP from the soil by a 50:50 mixture of water and ethanol was observed although the contaminant had aged over 20 years. However, fast catalyst deactivation was shown, resulting in no hydrodehalogenation (HDH) reaction for destroying PCP. I have not yet identified the chemical causing the catalyst deactivation in the extractant solvent. The deactivated catalyst was successfully regenerated with dilute hypochlorite solution. However, the catalyst deactivation rate was so fast as to prevent successful dechlorination of PCP. Therefore, the application of REACH technology to treat the PCP-contaminated soil was ceased. In this Chapter, proposed research is discussed to make up for REACH's failing to treat the contaminated field soil.

6.2. Contaminated soil

6.2.1. Site description and history

The Post & Lumber Preserving Co. site (PLP) is on the northeast corner of State Road 12 and Post Plant Road, approximately 3.5 miles east of Quincy, Florida, near Tallahassee. PLP is an 18-acre facility in an area that is predominantly rural residential, pasture and undeveloped land (Florida Department of Environmental Protection, 2006).

Beginning in 1948, this 18-acre site was used for pressure-treating posts and other lumber using both wolmanizing salts (copper, chromium, and arsenic) and pentachlorophenol (PCP). The PCP wood preservative was made of a 5 to 7 percent solution of PCP with diesel fuel and/or water. Pressure treating operations ceased in the mid-1980's. Currently the site is used only as a distribution center for pressure-treated posts and lumber (Florida Department of Environmental Protection, 2006).

6.2.2. Field soil handling and analysis

The soil contaminated by PCP at the PLP site was supplied by an environmental company in Orlando, FL. The field soil was collected from 15 to 30 cm below land surface and stored in an amber glass bottle. When the soil arrived in our laboratory, I air-dried the soil over night under room temperature. The air-dried field soil was mixed thoroughly to get homogeneous conditions and kept in the amber glass bottle until subjected to experiments.

A part of the field soil was shipped to the Soil, Water, and Forage Testing Laboratory at Texas A&M University for characterization. The textural class of the soil was a sandy clay loam with 58% sand, 22% silt, and 20% clay. The fraction of organic matter and pH were 2.11% and 6.5, respectively. The concentration of sulfur was 23 mg/kg but the species of sulfur were not reported.

In order to know the initial concentration of PCP in the field soil, a shaker extraction method was conducted. Detailed procedures of the method were described in Chapter II. The PCP concentration was determined to be 416±11 mg/kg. From the values, I know that the soil was severely contaminated by PCP.

6.3. REACH operation with field-contaminated soil

6.3.1. Experimental method

The treatment of field soil at the PLP site using the closed-loop system was conducted. Detailed specifications for the system and operating conditions for the closed-loop treatment can be found in Chapter V. The only exception here is that the flow rate of solvent was 0.5 mL/min, not 1 mL/min. My intention was to give more residence time in particular for the extraction step since the soil had aged more than 20 years, so that much longer time is expected to extract PCP from the soil.

6.3.2. Results and discussion

<u>*Contaminant extraction rate*</u>

It has been widely reported that the extractability of contaminants, such as PAHs, from soil changes with the age of the contamination (Northcott and Jones, 2001). Since the PCP had aged over 20 years at the PLP site, I expected that extraction would be done at a slow rate, resulting in a limiting step for the overall performance of REACH.

The PCP extraction rate from the field-contaminated soil with a 50:50 mixture of water and ethanol is shown in Fig. 6.1. The highest extraction rate was observed within the first 2 days, consistent with the laboratory-contaminated soil in Chapter V. Three days after starting the operation, no or negligible extraction was observed. This observation could be either because equilibrium between soil and solvent is reached or because equilibrium is not reached, but the rate is very slow. An average concentration of PCP in the reservoir between 3 days and 11 days is 31.1±3.1 mg/L, which corresponds to about 85% of PCP mass in the field soil. It is suspected that the last 15% of PCP mass was still sorbed on the soil because the experimental system was constructed well to prevent any loss of mass due to volatilization or sorption.

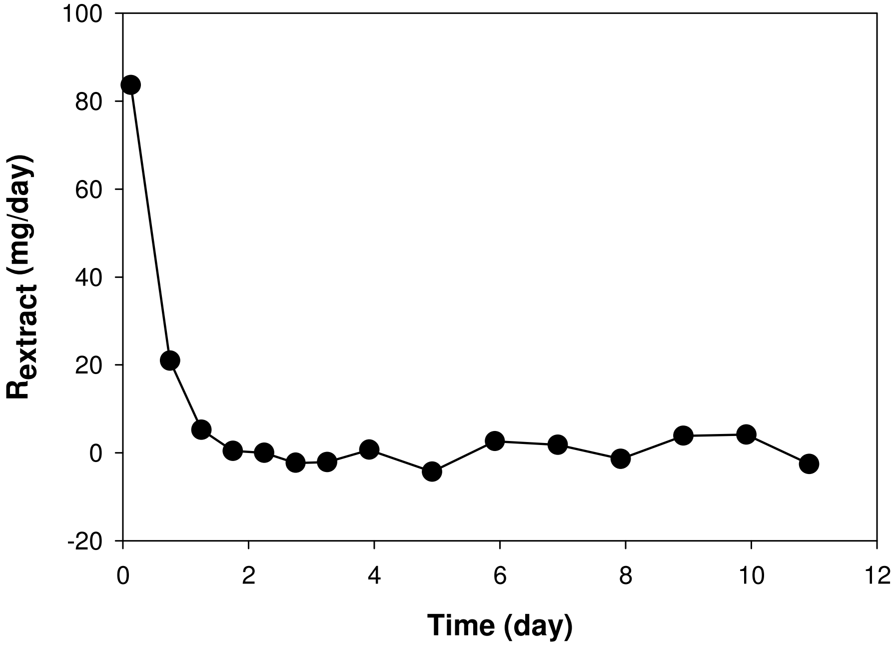

Fig. 6.1 - PCP extraction rate from PLP field contaminated soil over time in closed-loop system.

During the operation of the REACH system, the color of the solvent turned yellow as it circulated through the system. I suspect that the solvent extracted some chemical agent(s) from the soil that imparted the color. It may be some form of natural organic matter (NOM) which has yellow to black in color (Sparks, 1995).

Contaminant reaction rate

The PCP reaction rate by Pd-catalyzed HDH in the closed-loop system is shown in Fig. 6.2. Severely low reaction rates were observed, as shown in Fig. 6.2. Initially, some reaction rate is observed. However, I am not sure that the disappearance of PCP is due to the HDH reaction, because PCP could be adsorbed onto the Pd/Al_2O_3 surface. Recall that the amount of catalyst used was 10 g. Two days after starting the REACH system for the field-contaminated soil, almost no PCP reaction (degradation) by Pd-catalyzed HDH was observed. As shown in Fig. 6.2, regeneration of the Pd catalyst with 20 mM sodium hypochlorite solution was conducted on day 8 and 9, separately. The regeneration procedures were performed as introduced in Chapter V. However, no improvement of reaction rate was observed. Even after all catalyst was replaced with fresh catalyst on day 10, the concentration of PCP remained almost constant.

Based on these observations, I suspected that the field soil contains some chemical that rapidly deactivates the Pd catalyst when it is extracted. Therefore, I conducted experiments to determine how fast the deactivation occurs, and if the deactivation is reversible. Theses are described below.

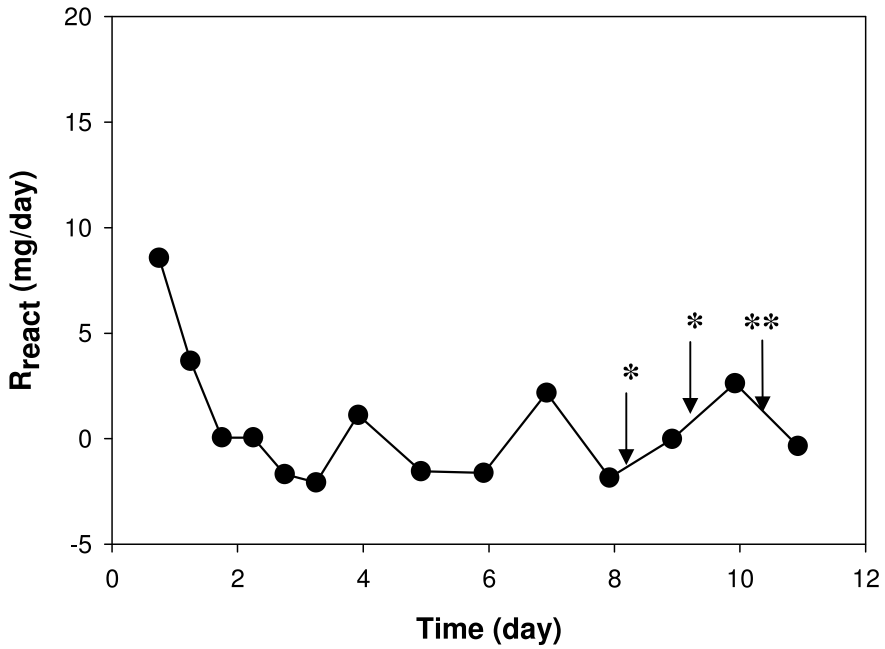

Fig.6.2 - PCP reaction rate by Pd-catalyzed HDH in closed-loop system for the treatment of PLP field-contaminated soil: * catalyst was regenerated with a dilute hypochlorite, ** fresh catalyst was repacked.

6.4. Catalyst deactivation experiment

6.4.1. Experimental method

Following attempted treatment by REACH, a deactivation experiment was conducted to know how fast the Pd catalyst deactivates over time. I assumed that the chemicals responsible for deactivation are present in the solvent in the reservoir after the operation of closed-loop system for the field soil for 11 days, since disappearance of PCP was negligible during the period. The soil column was taken out from the system and "fresh" Pd catalyst was packed in the catalyst column. The solvent that had been used for extraction of the field soil was still in the reservoir and was employed for this deactivation experiment. The system was turned on and samples were collected both at the sample port entering the catalyst column and at the sample port exiting the catalyst column at desired time intervals. Since two 0.5 μm filters were installed in the system, collected samples were not filtered further for gas chromatography (GC) analysis. Detailed analytical method is described in Chapter IV.

6.4.2. Results and discussion

As seen in Fig. 6.3, no HDH reaction was observed, indicating that the deactivation of Pd catalyst occurred very fast. Therefore, the REACH technology is not technically applicable to remediate the contaminated soil from the PLP site since the catalyst loses its activity quickly within 1 hr and the catalyst regeneration process may not be done frequently enough to maintain activity.

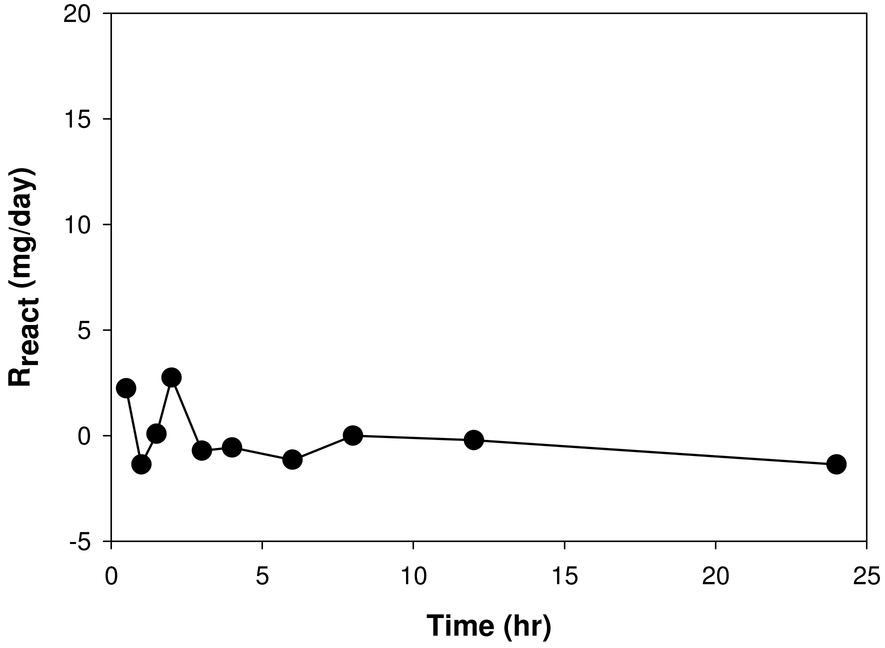

Fig. 6.3 - Pd catalyst deactivation rate with solvent used for extraction of contaminated soil at PLP site.

As seen in Fig. 6.3, there was essentially no HDH activity even after just 1 hr of operation. It was not clear if the catalyst deactivated in that time, or if perhaps some chemical agent was hindering the HDH reaction through a different mechanism (e.g., competition for surface sites). To determine this and to determine if the catalyst could be regenerated, I conducted a regeneration experiment as described below.

6.5. Catalyst regeneration experiment

6.5.1. Experimental method

Two different batch-mode experiments were conducted with and without catalyst regeneration with a dilute sodium hypochlorite solution.

I took out from the REACH reactor the deactivated catalyst which had been used for 1 day since all catalyst was replaced with fresh catalyst on day 10, from the closed-loop system. The mass of the deactivated catalyst was measured and found to be more than 10 g. Half of it was regenerated with 20 mM sodium hypochlorite solution following the procedures described in Chapter V. The other half was not regenerated.

A 50:50 mixture of water and ethanol was prepared freshly. 100 mL of the 50:50 mixture of water and ethanol was added into a 250-mL batch-type reaction bottle and a desired volume of 1000 mg/L stock solution of PCP was spiked into the bottle. Then, the solution in the bottle was stirred using a magnetic stirrer for 2 min and 1 mL of sample was taken to quantify an initial concentration of PCP. After that, I added the half of catalyst not regenerated into the reaction bottle and placed it in the hydrogenation reactor. A batch type HDH reaction was performed as described in Chapter IV. Then, for the half of catalyst that was regenerated, a batch type HDH reaction was carried out following the method described above.

6.5.2. Results and discussion

The results of HDH reaction with and without catalyst regeneration are shown in Table 6.1 indicating that the Pd catalyst could recover its activity by regeneration with 20 mM hypochlorite solution.

The results also indicate that the catalyst had, in fact, been deactivated by exposure to the used solvent. The catalyst that had no regeneration exhibited no activity, suggesting that it was completely deactivated by 1 day of operation in the REACH system. Therefore, the lack of activity seen in Fig. 6.3 is probably due to rapid deactivation, not due to any other reasons.

6.6. Hypothesis for catalyst deactivation

I hypothesize that Pd catalyst active surface sites were coated with chemicals that were extracted from the field-contaminated soil, resulting that no HDH reaction of PCP was observed in the closed-loop system. The deactivated catalyst could be regenerated with a dilute hypochlorite solution. However, regeneration did not lead to removal of PCP in the REACH system, because the chemicals causing the deactivation were still present

Table 6.1 - Pd catalyst activity with and without regeneration with a dilute hypochlorite solution

	Initial PCP concentration (mg/L)	1 hr HDH reaction later (mg/L)
Without catalyst regeneration	4.55	4.53
With catalyst regeneration	4.19	0.45

and rapidly deactivated the catalyst again. Hypotheses regarding the catalyst deactivation are discussed below.

6.7. Summary and proposed research for the future

The REACH process was applied for treating the highly PCP contaminated field soil from the PLP site. PCP in the soil was extracted rapidly with a 50:50 mixture of water and ethanol. However, no HDH reaction was observed because Pd catalyst lost its activity quickly, probably caused by chemicals extracted simultaneously from the field soil with PCP. The deactivated catalyst can be regenerated with a dilute hypochlorite solution. The experimental result of Pd catalyst deactivation rate indicated that the deactivation was done within an hour. Therefore, The REACH technology is not applicable to treat the field-contaminated soil unless the fast deactivation of catalyst is resolved.

Here, I propose two category of research in the future to improve the REACH technology. First, we need to identify which chemical(s) in the solvent cause the deactivation of Pd catalyst. The suspected chemicals for Pd catalyst deactivation are sulfide species and NOM. It was reported that Pd catalyst lost its performance by coating with sulfide species in groundwater (Lowry and Reinhard, 2000). It was also presented that NOM can affect adversely photocatalytic reactions (Doll and Frimmel, 2005) and zero-valent iron performance (Klausen et al., 2003).

The second proposed line of research is aimed to eliminate or minimize the catalyst deactivation, which was found in this current research and mainly caused that the REACH performance was inactive for treating PCP in the field soil. A different catalyst, which is less susceptible to deactivation compared to Pd catalyst, can be employed in the REACH technology. Alternative catalysts exist such as platinum or nickel. The HDH reaction performance and economic analysis for overall cost should be studied as well. Another method is to avoid the contact of Pd catalyst with deactivation-causing chemicals by constructing the closed-loop system shown in Fig. 6.4.

A basic idea of the process shown in Fig. 6.4 is that HHOCs extracted from contaminated soil in the solvent are stripped by N_2/H_2 mixed gas and then are dehalogenated in Pd catalyst reactor. The destruction of halogenated compounds by catalytic HDH reaction in gas phase has been studied previously (Ordonez et al., 2002; Jujjuri et al., 2006).

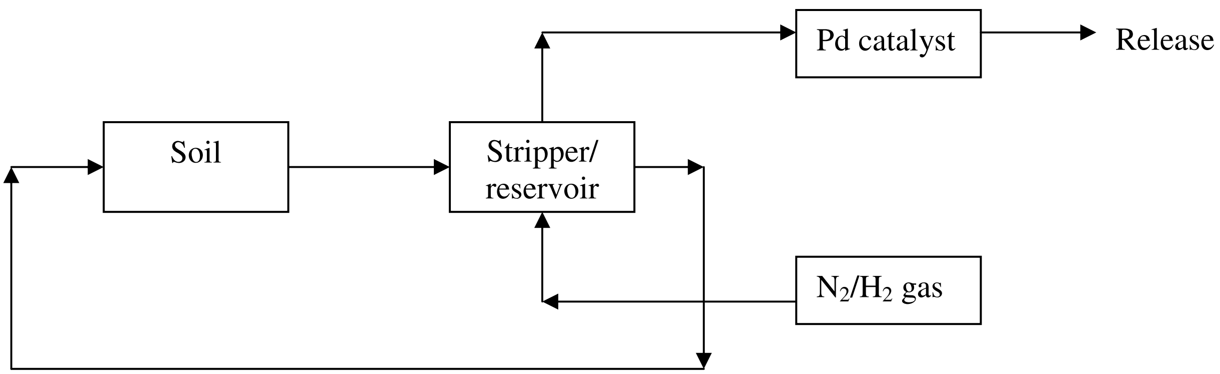

Fig. 6.4 - Schematic diagram for the REACH technology with avoiding contact of solvent with Pd catalyst.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The results shown in this research demonstrate that the remedial extraction and catalytic hydrodehalogenation (REACH) technology has the potential to be a significant improvement over existing techniques, such as solvent extraction, to remediate the soil contaminated by halogenated hydrophobic organic compounds (HHOCs). In the REACH system proposed here, HHOCs are catalytically dehalogenated and transformed to less or non-toxic forms. The findings of this research provide basic knowledge about the extraction of HHOCs from contaminated soils, Pd-catalyzed hydrodehalogenation (HDH) reaction in different water-ethanol mixtures, and operating parameters of HDH reaction. In addition, a model closed-loop system of the REACH technology was built at the laboratory scale, and that system can provide field engineers with a schematic system design idea when this technology is applied to treat HHOCs in soil and other waste streams in practice. The specific findings of this research are as follows:

7.1.1. Dependence on the key parameters for the extraction of selected HHOCs from soil

- Mixtures of water and ethanol are shown to be good candidates to extract TeCB and PCP from contaminated soil.
- Solvent composition strongly affects the contaminant extraction efficiency. At least 50% ethanol (by volume, before mixing) in the solvent is required to effectively remove TeCB from contaminated soil. PCP could be effectively extracted by mixtures with as little as 33% ethanol.
- The ratio of solvent volume to soil mass has very little effect on the extraction efficiency of both TeCB and PCP under my experimental conditions.
- For short extraction times, the mass of TeCB or PCP extracted is very sensitive to extraction time. However, for long extraction times, the removal efficiency is not sensitive to extraction time, suggesting an approach to equilibrium.
- During continuous closed-loop operation, contaminants could be removed from 200 g of soil within about 2 days at a solvent flow rate of 1-5 mL/min.

7.1.2. Dependence on the key parameters for the Pd-catalyzed HDH of selected HHOCs

- TeCB and PCP can be completely and reductively dehalogenated at room temperature under mild hydrogen pressure (0.21 MPa) in batch mode.

- For both TeCB and PCP treatment, the rate of the Pd-catalyzed HDH reaction is a strong function of the solvent composition and the concentration of catalyst in the reactor. The Pd-catalyzed HDH rate decreases as the fraction of ethanol increases in the solvent. The Pd-catalyzed HDH rate increases as the concentration of catalyst increases in the reaction vessel.
- The effect of solvent composition appears to be caused by its effect on the partitioning of the target contaminants between the liquid and solid phases.
- The initial concentration of TeCB might or might not affect the apparent HDH rate constant under my experimental conditions.
- The hydrogen pressure supplied into the reaction bottle did not affect the degradation rate of PCP as long as the pressure was above some critical level.
- The kinetics of the TeCB disappearance are apparently first-order.
- A mathematical model was developed based on a Langmuir-Hinshelwood model to describe first-order kinetics of TeCB under various operational conditions.
- TeCB was converted stoichiometrically to benzene by the Pd-catalyzed HDH reaction. Low concentrations of a transient intermediate, 1,2,4-trichlorobenzene (TCB), were observed. The disappearance of 1,2,4-TCB was rapid enough that I may consider TeCB is converted directly to benzene.
- The degradation rate of PCP does not follow first-order kinetics, probably because competition for surface active sites occurs between PCP and intermediate products which are generated during PCP degradation.

- The transformation of PCP by Pd-catalyzed HDH reaction in water/ethanol mixtures occurs sequentially by dehalogenation to tetrachlorophenols, then to trichlorophenols, then to phenol. .

7.1.3. Demonstration of the REACH technology for a long period of time in a closed-loop system

The REACH system was built in a lab-scale and tested on soils synthetically contaminated by TeCB and by PCP in our laboratory. In a span of 7 weeks, 1.4 kg of contaminated soil was treated: 7 columns of contaminated soil, each with 0.2 kg soil each treated for 1 week. This work was accomplished with just 10 g of catalyst and 2.2.L of solvent, which is a 50:50 mixture of water and ethanol.

- Extraction of both TeCB and PCP mass from soils was almost completed within 2 days using the solvent at a solvent flow rate of 1-5 mL/min.
- Higher reaction rate, which is mass removed per time, was observed for TeCB than for PCP.
- The efficiency of the REACH process slowly decreased as the amount of contaminated soil subjected to treat increased. This is either because by-products build up in the solvent stream or because the catalyst slowly deactivates.
- Regeneration of the catalyst by treatment with a dilute hypochlorite solution appears to recover the overall efficiency of the process.

The REACH process was applied for treating field soil, which was highly contaminated by PCP and aged over 20 years.

- At least 85% of the PCP in the soil was extracted rapidly with a 50:50 mixture of water and ethanol.
- No HDH reaction was observed because Pd catalyst lost its activity quickly, apparently because of chemicals extracted simultaneously from the field soil with PCP.
- The deactivated catalyst could be regenerated with a dilute hypochlorite solution.
- Pd catalyst was deactivated completely but reversibly within an hour when it was tested with the solvent that had been used for extraction of the field soil.

7.2. Recommendations for future research

A number of opportunities for future research are recommended here.

- The longevity of the solvent's ability to extract contaminants from the soil should be quantified since replacement and disposal of solvent are related to the overall cost for this technology. It is possible that the solvent might degrade over time, losing some of its ability to extract contaminants from the contaminated soil.
- The longevity of catalyst should be tested since it is also associated with the overall cost of the technology. As shown in this research, the deactivated Pd

catalyst can be regenerated with a dilute hypochlorite solution. However, the overall activity of catalyst might slowly decrease as the amount of treated soil increases.

- Pd catalyst was quickly deactivated for the treatment of the field contaminated soil. Therefore, it is worthwhile identifying which chemical(s) in the solvent used for extraction of the field soil cause the deactivation of Pd catalyst.
- In order to eliminate or minimize the catalyst deactivation in the REACH system, two topics of research are proposed. The first one is to use a different catalyst, which is less easily deactivated compared to Pd catalyst. The Second one is to build a system to avoid the contact of Pd catalyst with the chemicals that cause deactivation in the solvent stream as shown Fig. 6.4.

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VITA

Hun Young Wee was born in Cheongwon, Chungbuk, Republic of Korea. He received a Bachelor of Engineering degree in environmental engineering from Chungbuk National University in 1999. He attended Texas A&M University from August 2000 and received a Master of Science degree and a Ph.D. degree in civil engineering from Texas A&M in August 2003 and in May 2007, respectively.

Permanent address: 1136-Bongmyung-dong
Hungduk-Gu, Cheongju-City, Chungbuk
Republic of Korea
361-818