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TCE and PCB Degradation by Zero-Valence Iron in the Presence of Surfactants

B. Gu; L. Liang; P. Cameron; O. R. West
Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA
D. Davenport
University of Wisconsin, Madison, Wisconsin, USA

Surfactants and cosolvents are being used to enhance the removal of dense non-aqueous phase liquids (DNAPL) such as trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) from contaminated soils. However, the waste surfactant solution containing TCE and PCBs must be treated before it can be disposed. This study evaluated the use of zero-valence iron and palladized iron fillings in the dechlorination of TCE and a PCB congener (2,3,2',5'-tetrachlorobiphenyl) in a dihexyl-sulfosuccinate surfactant solution. Batch experimental results indicated that TCE can be rapidly degraded by palladized iron filings with a half-life of ~27.4 min. PCB was degraded at a slower rate than TCE with a half-life ranging from ~100 min to ~500 min as the concentration of surfactant increased. In column flow-through experiments, both TCE and PCB degrade at an enhanced rate with a half-life about 1.5 and 6 min respectively because of an increased solid to solution ratio in the column. Results of this work suggest that Fe-Pd filings can be potentially applicable for ex-situ treatment of TCE and PCBs in the surfactant solutions that are generated during surfactant washing of the contaminated soils.

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Authors:

B. Gu; L. Liang; P. Cameron; O. R. West
Environmental Sciences Division
Oak Ridge National Laboratory
P. O. Box 2008, MS 6038
Oak Ridge, TN 37831-6038, USA
Phone: (423)-574-7286; Fax: (423)-576-8543

D. Davenport
The University of Wisconsin
1415 Johnson Drive #1218
Madison, WI 53706

Technical Focus Area = Barrier Materials

Presenter = B. Gu

Platform Presentation

DISCLAIMER

Degradation of Trichloroethylene (TCE) and Polychlorinated biphenyls (PCBs) by Fe and Fe-Pd Bimetals in the Presence of Surfactants and Cosolvents

Baohua Gu*, Liyuan Liang, Paula Cameron, Olivia R. West, and D. Davenport

ABSTRACT

Surfactants and cosolvents are being used to enhance the removal of dense non-aqueous phase liquids (DNAPL) such as trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) from contaminated soils. However, the waste surfactant solution containing TCE and PCBs must be treated before it can be disposed. This study evaluated the use of zero-valence iron and palladized iron fillings on the dechlorination of TCE and a PCB congener (2,2',3,5'-tetrachlorobiphenyl) in a dihexyl sulfosuccinate surfactant solution. Batch experimental results indicated that TCE can be rapidly degraded by palladized iron filings with a half-life of ~27.4 min. PCB was degraded at a slower rate than TCE with a half-life ranging from ~100 min to ~500 min as the concentration of surfactant increased. In column flow-through experiments, both TCE and PCBs degrade at an enhanced rate with a half-life about 1.5 and 6 min because of an increased solid to solution ratio in the column than in the batch experiments. Results of this work suggest that Fe-Pd filings may be potentially applicable for ex-situ treatment of TCE and PCBs in the surfactant solutions that are generated during surfactant washing of the contaminated soils.

INTRODUCTION

Enhanced soil washing with surfactants has been proposed as an alternative method for remediating soils that are contaminated with polychlorinated biphenyls (PCBs) and nonaqueous-phase liquids (NAPLs) such as trichloroethylene (TCE). Surfactants can dramatically increase the solubility of organic compounds in groundwater and lower their interfacial tensions; both effects can significantly increase the extraction efficiency of pump-and-treat systems (Pennell et al., 1993; Fountain et al., 1991; Abdul and Ang, 1994). Previous studies (Pennell et al., 1993; Fountain et al., 1991) have successfully applied this technique to remove various hydrocarbons, PCBs, and polycyclic aromatic hydrocarbons (PAHs) from soil. For example, surfactants have been used extensively in enhance oil recovery to increase the mobility of crude oil (Gogarty, 1983; Nelson, 1989). In this process, surfactants and cosolvents are blended to reduce interfacial tension between oil and water to less than 0.01 dynes/cm (10^{-6} N/m), a reduction of over four orders of magnitude. In both laboratory and field experiments, Abdul and Ang (1994) reported that PCBs can be effectively removed from soils by the surfactant washings. They observed more than 85% of PCB removal from a laboratory soil column after 105 pore volume washings.

However, one of the problems associated with the surfactant washing is the generation of large quantities of secondary wastes that must be properly treated or disposed of. Although many treatment techniques are available and known to be effective to degrade TCE and PCB contaminants in the absence of surfactants, few studies have evaluated the treatment techniques to degrade these contaminants in the presence of surfactants and cosolvents. Among various treatment techniques, the use of zero-valence iron metal for reduction of chlorinated organic compounds such as TCE has been an area of significant recent research (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Liang et al., 1996). Field demonstration of this treatment technology at the Borden site in Ontario (O'Hannesin, 1993) and subsequent detailed

*Corresponding author. Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS-6036, Oak Ridge, TN 37831-6036.

laboratory studies have been reported (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Campbell and Burris, 1995; Liang et al., 1995; Sivavec and Horney, 1995; Mackenzie et al., 1995). Several investigators also discovered that a bimetallic preparation of Fe with a small amount of Pd (0.05% by weight) can substantially enhance the dechlorination rate of the chlorinated volatile organic compounds (Muftikian et al., 1995; Korte et al., 1995; Liang et al., 1995). The bimetallic system provided faster (about 1-2 orders of magnitude) dechlorination kinetics and more complete dechlorination than reduction by iron alone. As an example, the reported half-life for 1,2-*cis*-dichloroethylene (*cis*-DCE), when exposed to zero valence iron is over 30 hours. In contrast, the half-life is only several minutes when the iron is properly treated with palladium (Korte et al., 1995). In addition, dichloromethane (DCM) and PCB compounds that do not react with zero valence iron are also dechlorinated by palladized iron (Liang et al., 1995; West et al., 1996).

The present study was undertaken to evaluate if zero-valence Fe and Fe-Pd bimetals can degrade TCE and PCBs in the presence of surfactants and cosolvents. It is hoped that zero-valence Fe and Fe-Pd bimetals can be potentially applied for in-situ and/or ex-situ treatment of surfactant wastes that may be generated during the surfactant washing of soils contaminated with TCE and/or PCBs.

MATERIALS AND METHODS

TCE and PCB [2,3,2',5'-tetrachlorobiphenyl (PCB)] were the two target contaminants used for the present study. The surfactant (dihexyl sulfosuccinate or Aerosol MA-1) was obtained from Cytec Industries Inc. (West Paterson, NJ) and was used without further purification. Both ethanol and isopropanol were used as cosolvents for the study. Additionally, the surfactant itself contains ~5% isopropanol and methyl isobutylcarbinol. All chemicals used were analytical reagents except the surfactant solution.

Dechlorination of TCE was first studied in batch experiments using zero-headspace extractors (or ZHEs) to prevent TCE volatilization losses (Associate Design & Manufacturer Co., Alexandria, VA). The essential components of the ZHE are composed of a stainless steel cylinder and a piston (Gu and Siegrist, 1996). The upward movement of the piston is controlled by applying a positive pressure at the bottom of the piston. At a given time of reaction, sample can be taken or displaced by slowly raising the piston so that no headspace is left in the ZHE as a result of sample withdrawal. Two reactive or reductive materials were studied on their effects in degrading TCE in the presence of surfactants and cosolvents. They were 40-mesh iron filings obtained from Fisher Scientific (Pittsburgh, PA) and 40-mesh Pd-coated iron filings (0.05% Pd) obtained from Johnson Matthey Inc. (West Deptford, NJ). Experimentally, 20 g of Fe or Fe-Pd filings were added to ZHEs, to which 100 mL of aqueous solution containing TCE, surfactant (2% or 4%), and cosolvent (2%) was added. The initial TCE concentration was 2 mg/L. A ZHE without the addition of Fe or Fe-Pd filings was prepared similarly as a control. All ZHEs were then mounted on a rotary shaker and rotated at 30 rpm. At various time intervals of reaction, 4 mL of aqueous sample was taken through the sampling valve on ZHEs and immediately injected into 4 mL of hexane for the extraction of TCE. The extraction of TCE was accomplished by shaking the samples in hexane for 24 h; the samples were then allowed to settle for at least 1 h so that a clear hexane layer can be observed and sampled for analysis.

Degradation of PCBs was studies in 5-mL glass vials with 2 g 100~200-mesh Fe-Pd filings (with 0.1% Pd) because our preliminary studies showed that PCBs degrade very slowly with Fe-filings alone or coated with a relatively low amount of Pd. The experimental procedures were similar to those described for TCE degradation studies except that 5-mL glass vials were used because PCBs are semi-volatile organic compounds, and the extraction of PCBs was accomplished with a mixture of methanol-hexane (1:2).

The concentration of TCE or PCB was analyzed by means of a gas chromatograph (GC) (Hewlett-Packard, 5890 Series II) equipped with a HP-5 fused-silica column (0.32 mm × 50 m) and an electron capture detector (ECD). TCE in hexane or PCB in methanol-hexane (1–2 μL) was directly injected into the GC column, and its concentration was determined in reference to TCE or PCB standards prepared in hexane or obtained from Ultra Scientific Inc. (North Kingston, RI). For biphenyl analysis, a flame ionization detector (FID) was used on the same GC.

Column experiments were performed to evaluate the reaction kinetics between TCE or PCB and Fe or Fe-Pd filings under the flow-through conditions. Two columns of 1x5 cm were used for TCE degradation studies whereas two columns of 2.5x5 cm were used for the PCB degradation studies because of a slower reaction kinetics of PCBs in comparison with that of TCE. The two columns were wet-packed with Fe or Fe-Pd filings and connected in series through a three-way valve so that a sample can be withdrawn between the two columns. After flushing the packed columns with several pore volumes (>10) of the reactant solution, samples were taken at the inlet, outlet, and between the two columns for the analyses of TCE, PCB, or their byproducts, as described earlier. This sampling process was repeated at different time intervals and at three different flow rates which determine the residence time of TCE or PCB in the column.

RESULTS AND DISCUSSION

Degradation of TCE in the presence of 2% Aerosol surfactant and 2% ethanol is shown in Fig. 1. TCE degraded much faster (~2 orders of magnitude) on Fe-Pd filings than on Fe-filings. The degradation of TCE appeared to follow the pseudo-first-order rate law with an estimated half-life of 27.4 min in Fe-Pd system and ~1200 min in Fe-filing system. Results of TCE degradation in Fe-Pd is comparable with TCE degradation in the same system without the presence of surfactants and cosolvents (Liang et al., 1995) and suggest that the presence of surfactants (2%) and cosolvents (2%) did not significantly influence the dechlorination kinetics of TCE.

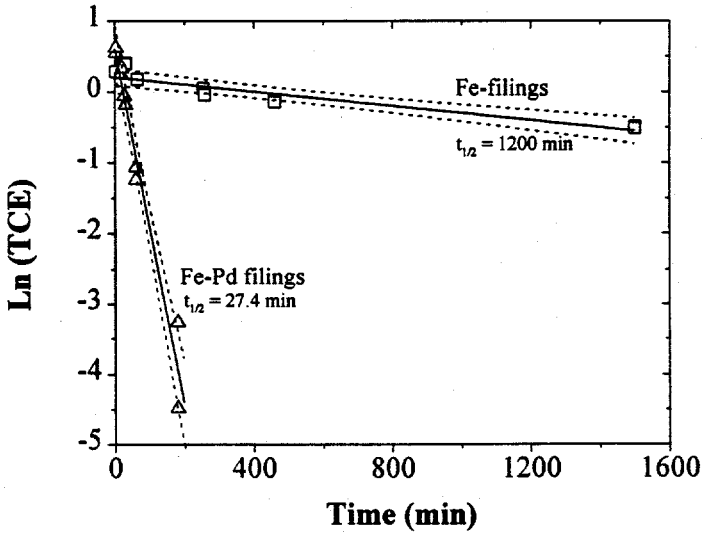

Fig. 1. Reactions between trichloroethylene (TCE) and iron and palladized iron filings in the presence of 2% Aerosol surfactant and 2% ethanol. Dashed lines show 95% confidence limits.

The formation of byproducts during TCE degradation in Fe or Fe-Pd filings were not observed by direct analysis of TCE in hexane by the GC-ECD. Attempts were made to analyze byproducts by the purge-and-trap system but were unsuccessful because of the foaming of surfactants during the purging process. In the absence of surfactant, however, Liang et al. (1995) have reported the formation of byproducts such as *cis*-DCE and vinyl chloride. In particular, these byproducts persisted at a relatively high concentration in the system with Fe-filings only. On the other hand, no DCE isomers were observed and about an order of magnitude less amount of vinyl chloride was observed in the Fe-Pd system.

Degradation of PCBs was studied in 100~200-mesh Fe-Pd filings (with 0.1% Pd) because our preliminary studies have shown that PCBs do not degrade appreciably with Fe-filings alone or with a low amount of Pd coated on Fe filings (West et al., 1996). Results (Fig. 2) indicated that PCB degraded slowly in comparison with TCE, particularly in the presence of a relatively high concentration of surfactant. The degradation half-lives were about 100 and 306 min in the presence of 2% and 4% Aerosol surfactant. These observations suggest that surfactant reduced the degradation rates of PCB by Fe-Pd filings. In the absence of surfactant, West et al. (1996) reported that PCBs degraded rapidly under similar conditions with a half-life on the order of ~10 min.

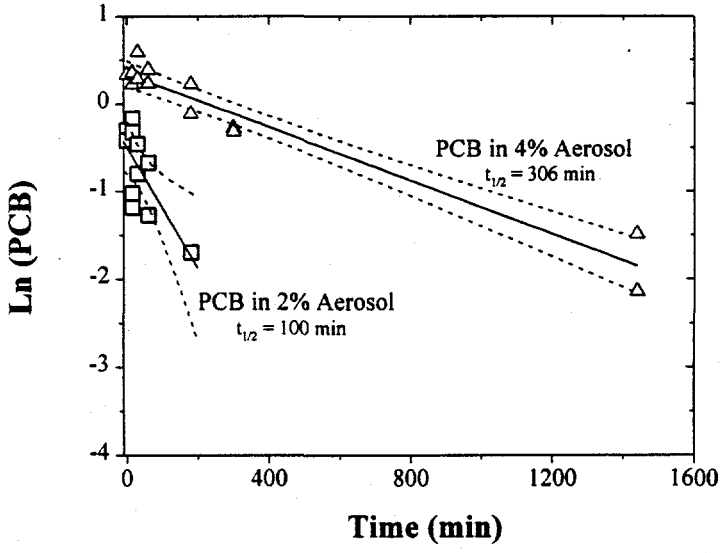

Fig. 2. Reactions between 2,3,2',5'-tetrachlorobiphenyl (PCB) and palladized iron filings in the presence of 2% and 4% Aerosol surfactant. Dashed lines show 95% confidence limits.

Major reaction byproducts during PCB degradation were identified as 2,2'-dichlorobiphenyl (DCB), 2,3,2'- and 2,5,2'-trichlorobiphenyl (TCB) (Fig. 3). Low amounts of biphenyl were also identified for PCB degradation in the 2% Aerosol surfactant but were not in the 4% surfactant solution. These results again indicate that the presence of high concentrations of surfactant could have influenced the degradation rate of PCBs. On the basis of these reaction byproducts, the degradation of 2,3,2',5'-PCB by Fe-Pd filings appears to follow a step-wise dechlorination process as evidenced by the appearance of less chlorinated byproducts, which are 2,3,2'-TCB followed by 2,5,2'-TCB and 2,2'-DCB.

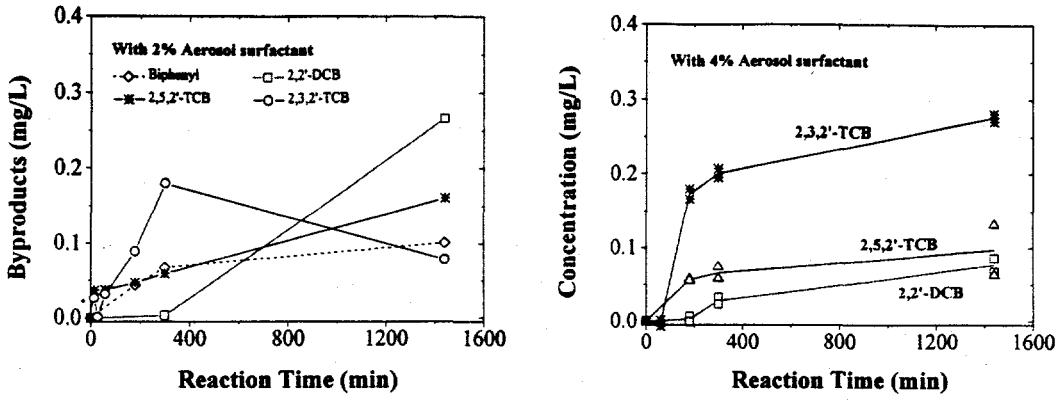

Fig. 3. PCB degradation byproducts with 100-200-mesh Fe-Pd filings in 2% and 4% Aerosol surfactant.

It should be indicated, however, that a mass-balance analysis indicated a relatively low recovery of PCBs (<60%), suggesting that other processes such as adsorption may also play a role in removing PCBs from the solution phase. It is known that PCBs can be strongly adsorbed or partitioned by various media such as minerals and the walls of many containers (Nkedi-Kizza et al., 1985; Baker et al., 1986). In this case, the Fe-Pd filings may act as adsorbents followed by the dechlorination of PCB on the Fe-Pd surfaces. Adsorption of PCBs on Fe-Pd filings can be evidenced when only Fe-filings were used as a reactive media. A substantial amount of PCB can be removed or adsorbed by the Fe-filings alone but no detectable amounts of byproducts can be identified in the system (data not shown). This is because Fe-filings don not degrade PCBs.

In laboratory column studies (Fig. 4), both TCE and PCB appear to degrade much faster than that were observed in the batch experiments. The degradation half-life for TCE was only about 1.5 min and was ~6 min for the degradation of PCB in the presence of 2% Aerosol surfactant and cosolvent. These observations are primarily attributed to the fact that a much higher solid to solution ratio is used in the column experiments than in the batch experiments. This increased solid to solution ratio greatly increased the available surface area of Fe-Pd filings to react with TCE or PCB. As has been indicated by other investigators (Matheson and Tratnyek, 1994; Muftikian et al., 1995), the dechlorination of these chlorinated organic compounds is a surface-controlled reaction process. The higher is the specific surface area, the faster is the reaction kinetics. Similar observations were also reported by Liang et al. (1995). An additional contributing factor to an increased reaction rate in the column experiments may be attributed to an initial adsorption process, particularly in the case of PCBs, as discussed earlier. The column experiments for the PCB was run for ~9 h. We observed a consistently increased C/C_0 with the reaction time in the effluent of the first column (Fig. 4b, PCB). These results may well illustrate that surfaces of Fe-Pd filings became relatively saturated with PCB or surfactant as the PCB-surfactant solution was continuously displaced into the column. PCB removal as a result of the partitioning into and degradation on the Fe-Pd surfaces decreased with time. On the other hand, this reaction-rate dependence on the reaction time was not observed for the degradation of TCE within the experimental error and within the limited reaction time period (Fig. 4a). These results are consistent with the batch experiments that the degradation of PCBs appears to be more strongly influenced by the presence of surfactant and by the adsorption process than that of TCE.

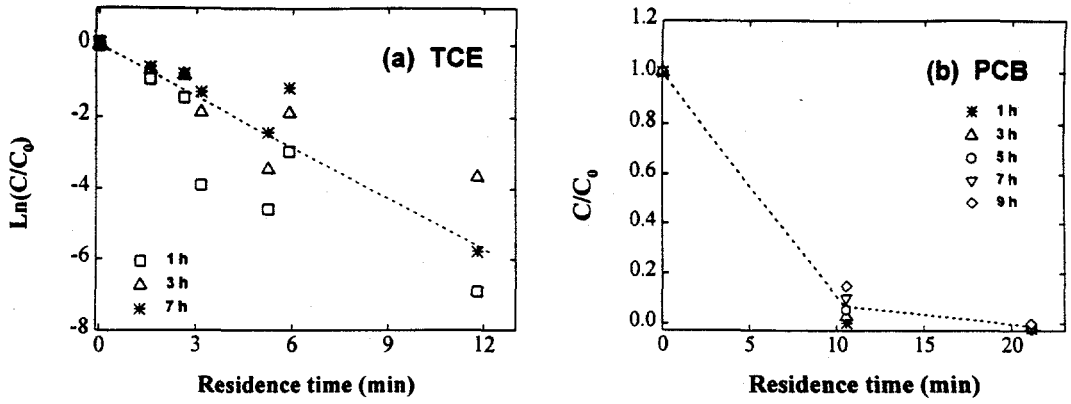

Fig. 4. Degradation of TCE (a) and PCB (b) in two packed columns (connected in series) with Fe-Pd filings in 2% Aerosol surfactant and 2% isopropanol. Samples were taken at the inlet, outlet, and between the two columns at various time intervals.

In summary, both laboratory batch and column experiments showed that TCE can be rapidly dechlorinated by Fe-Pd filings despite the presence of surfactants and cosolvents. PCBs can also be degraded by Fe-Pd filings but are at a reduced rate. A high concentration of surfactant may further reduce the rate of PCB degradation. The degradation of PCBs appears to follow a step-wise dechlorination process to less chlorinated byproducts such as 2,3,2'-TCB, 2,2'-DCB, and biphenyl. Results of this work suggest that Fe-Pd bimetal may be potentially applicable for ex-situ treatment of surfactant washing solutions containing chlorinated organic compounds such as TCE and PCBs, as long as a sufficient residence time is provided for their reactions with Fe-Pd filings. Fe-filings alone may be used to degrade TCE in the surfactant solution but a longer residence time is required for the process.

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