

# The Exploration of Conditions in Which Chlorinated Benzenes Are Degraded by Zero-Valent Iron

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## Introduction

Chlorinated benzenes have been used to manufacture pesticides, herbicides, dyestuff and rubbers for over 60 years (Environmental Health Criteria, 1997). Twelve chlorobenzene isomers exist and exhibit a wide range of physical and chemical properties. Chlorinated benzenes enter the environment through industrial discharge, agricultural use and improper disposal. Hexachlorobenzene (HCB), a hydrophobic and strongly sorbing chemical, is the most toxic and has been banned in the United States since 1966. It has been found to be animal carcinogen and is considered a probable carcinogen to humans (IARC, 2001). HCB poisoning may induce liver, kidney and thyroid cancer along with liver disease, skin lesions, ulceration, and photosensitivity (Environmental Health Criteria, 1997). Biomagnifications of HCB has been observed beginning with deposition in the lipid tissues of stream biota. Several contaminated sites contain chlorinated benzene contamination; including the Bayou d'Inde in Lake Charles, Louisiana.

The Bayou d'Inde is a tributary of the Calcasieu River near Lake Charles that has received discharge of industrial pollutants including metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlorinated benzenes, and many other chlorinated organics. A largest fraction of chlorinated benzene present in the Bayou d'Inde resides as HCB. Due to HCB's high organic carbon partition coefficient ( $K_{oc}$ ) and slow rate of desorption, the bioavailability to microorganisms is extremely small and natural attenuation has been found to be ineffective at reducing contamination (Yeh and Pavlostathis, 2004). A limited number of remediation options remain for the management of HCB in the Bayou d'Inde.

There are five possible remediation options for sediment sites contaminated with chlorinated benzenes, including (1) cover and contain; (2) remove and landfill; (3) physical sequestration; (4) chemical; and (5) biological treatment. Dredging the sediment is very expensive and may not eliminate the contamination completely or reduce the net flux of contaminants into the overlying water. Similarly the low bioavailability of HCB to microorganisms makes biodegradation impracticable without the use of experimental surfactants. One remaining option is to incorporate a cap along with a mechanism to treat the mobile fraction of HCB that desorbs. Capping consists of the placement of a one to three foot layer of sand or any of a variety of active capping materials (i.e. coke breeze, apatite) between the sediment-water interface. The new capping layer;

- prevents biomagnification of HCB by shifting the bioturbation zone out of the contaminated sediment which prevents the uptake of HCB to first level organisms,
- contains the sediment such that they cannot be re-suspended,
- and provides a barrier to advection and diffusion process responsible for chemical migration.

The use of caps has been shown to effectively reduce bioaccumulation and the transfer of contaminants up the food chain while containing hydrophobic organic compounds below the sediment surface (Reible et al., 2003). However, a small mobile fraction will still exist that slowly desorbs over time and in which presents a threat to the environment. Therefore the placement of an active capping material to treat the mobile fraction of the contaminant would decrease future risk.

A system that would be ideal to limit the material necessary for the active capping treatment would be to incorporate a funnel and gate setup. This system utilizes a non-active capping material with a very low permeability to block and funnel the groundwater advection through the active capping zone which ensures the treatment of the mobile contaminant. However, the contaminant must react quickly because residence times through the active cap are on the order of 1-2 days.

The proposed active capping material is zero-valent iron (ZVI). The application of zero-valent iron towards remediation of chlorinated organic contaminants has become increasingly favorable due to the successes found in laboratory experiments with chlorinated alkanes and alkenes (Matheson and Tratnyek, 1994). Iron is a cost effective and nontoxic metal that can donate electrons for chlorinated organic reduction.

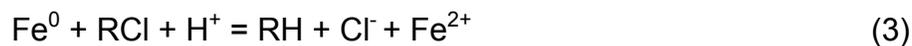
Zero-valent iron can be oxidized by a number of electron accepting compounds through the corrosive half reaction displayed in Equation 1. Water, hydrogen ion, carbonate, sulfate, nitrate and oxygen are common electron acceptors capable of out competing chlorinated organics for iron's electrons (Matheson and Tratnyek, 1994).



In the presence of a proton donor, reductive dechlorination of chlorinated organics (R) can take place through the reduction half reaction according to Equation 2.



If Equations 1 and 2 are combined then Equation 3 results, with the chlorinated organic acting as the oxidizing agent.



Matheson and Tratnyek (1994) have hypothesized two other mechanisms for anaerobic reductive dehalogenation. They include reduction by  $\text{Fe}^{2+}$  and catalyzed hydrogenolysis by  $\text{H}_2$ . Dissolved  $\text{Fe}^{2+}$  can be formed from the corrosion of iron and subsequently be oxidized to  $\text{Fe}^{3+}$ , providing one electron available for the reduction of chlorinated organics. However this reaction is presumed to be slow and the speciation of ferrous iron can affect its ability as a strong reductant (Matheson and Tratnyek, 1994).

The third reductive pathway requires anaerobic oxidation of iron by water as written in Equation 4.  $\text{H}_{2(g)}$  is produced in that reaction and with the presence of an effective catalyst (another metal) rapid dehalogenation can occur following Equation 4.



In the absence of an effective catalyst  $\text{H}_2$  can act as a dechlorination inhibitor as  $\text{H}_2$  will accumulate on the surface of the iron preventing any further iron corrosion and compound degradation (Matheson and Tratnyek, 1994).

Regardless of the reduction mechanism, the goal of this research is to reduce HCB to lesser chlorinated benzenes so that they can be biodegraded. The lesser chlorinated benzene species exhibit increased bioavailability, due to their increased solubility and lower organic carbon partition coefficient ( $K_{oc}$ ) and are less toxic to the environment. Therefore the proposed remediation option is to employ a funnel and gate system with ZVI as the active capping material to reduce the HCB. This option was explored by conducting batch tests with several chlorinated benzene isomers to identify the ideal conditions in which chlorobenzenes can be reduced by ZVI.

### Experimental Setup

Iron was weighed out and placed inside 40 ml volume amber vials. 20 ml of solution (99.8% water, 0.2 % 1 M HCl by volume) was added to each vial containing iron and additional control vials without iron. 20 ml of solution was chosen to provide sufficient headspace such that the generation of hydrogen gas formed from water oxidation of the iron would not impede the reduction of chlorobenzene by sorbing to reactive iron surfaces as shown by Chen et al., 2001. The solution was made by mixing Millipore water with 1 M HCl to achieve desired pH. The solution was boiled for five minutes to eliminate dissolved oxygen and then allowed to cool in an anaerobic chamber.

After the solution had cooled and 20 ml had been pipetted into each vial, the desired chlorobenzene was injected. The experiment was started by spiking the solution with 0.05 - 0.1 ml of a chlorinated benzene standard prepared in methanol. The vials were capped and placed in a rotary mixer to await sampling. Samples were prepared at predetermined sampling times for analysis in a gas chromatograph coupled with a micro electron capture device (GC/ECD).

### Preliminary Experiments

1,2,4-Trichlorobenzene (1,2,4-TCB) was found to undergo no reductive dehalogenation with ZVI. The experiment was conducted at neutral pH without a buffer and 20 ml of headspace. Lu et al. (2004) found that pH greatly affected the reduction potential of chlorinated benzenes with the greatest reduction at low pH. Therefore 1,2,4-TCB was again tested at a pH of 2.7 and the results are shown in Figure 1. Unfortunately no degradation by ZVI was observed. Previous data suggested that such conditions would result in dechlorination so Hexachloroethane (HCA) was used to test the effectiveness of the experimental procedure. Presented in Figure 2 is HCA reduction by ZVI.

HCA was reduced completely to dechlorination byproducts within 30 minutes at an order of magnitude faster than reported in the literature by Johnson et al. (1996). The increased rate of reduction seen is likely from the lower pH conditions. The HCA experiment demonstrates that lower pH conditions do yield greater reduction of chlorinated organics and

that the experimental procedure employed is sufficient to test whether chlorinated benzenes can be reductively dechlorinated.

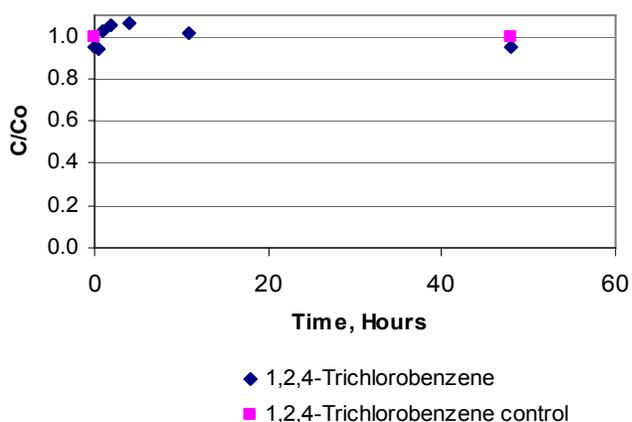


Figure 1. 1,2,4-TCB reduction by ZVI at pH 2.7

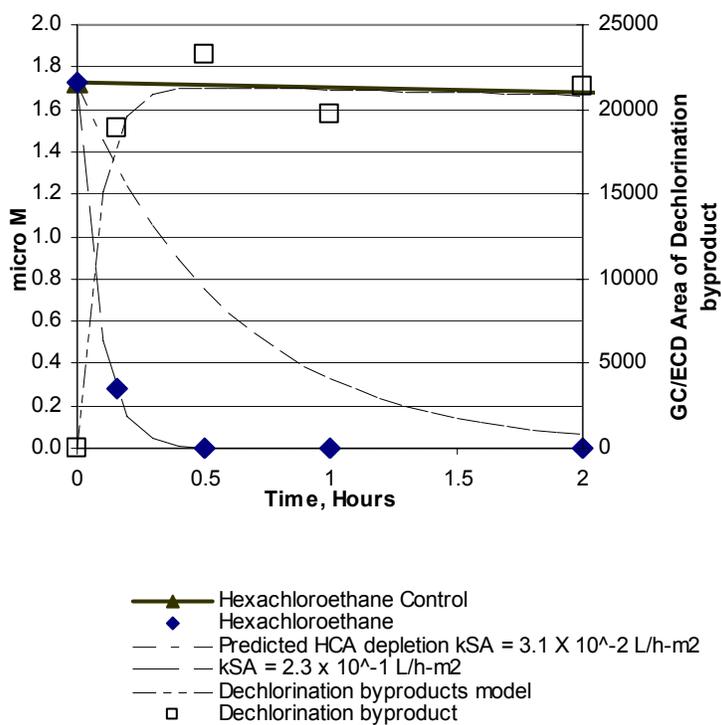


Figure 2. HCA reduction by ZVI at pH 2.7 and predicted HCA reduction

## Results

Experiments were then conducted on HCB, Pentachlorobenzene (PeCB), 1,2,3,4-Tetrachlorobenzene (1,2,3,4-TeCB), 1,2,3,5-Tetrachlorobenzene (1,2,3,5-TeCB), and 1,2,4,5-

Tetrachlorobenzene (1,2,4,5-TeCB) . Presented in Figures 3 and 4 are HCB and PeCB reduction by ZVI.

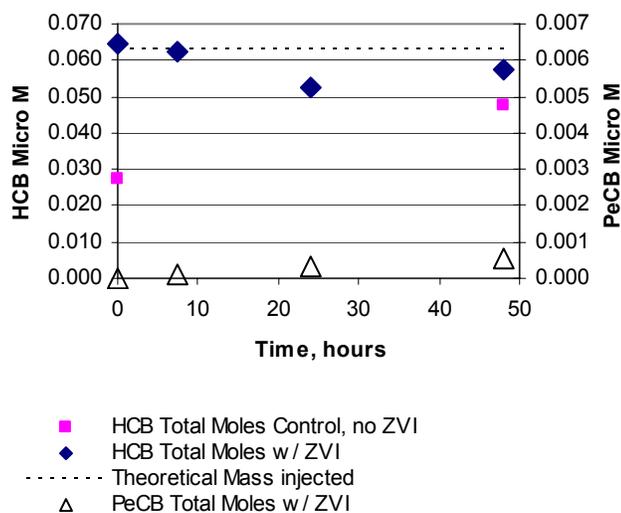


Figure 3. HCB reduction by ZVI at pH 2.7

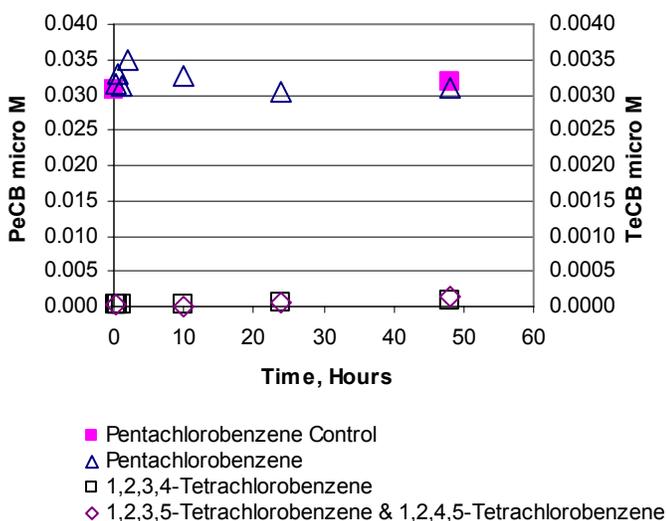


Figure 4. PeCB reduction by ZVI at pH 2.8

The results for HCB reduction showed less than 1% molar formation of PeCB in 48 hours. No lesser chlorinated benzenes were detected with the GC/ECD. PeCB reduction was even less effective as only 0.7% molar formation of tetrachlorobenzenes was detected. The reduction pathway seemed to favor each tetrachlorobenzene isomer equally; however, the method employed with the GC/ECD could not separate the peaks of 1,2,3,5-TeCB and 1,2,4,5-TeCB and the preferential pathway of PeCB reduction could not be deciphered. Results on TeCBs are not shown due to their lack of reduction. No statistical difference could be made between the experiments on TeCBs and their controls.

## Conclusion

The results from batch experiments suggest that chlorobenzene dehalogenation has limited reactivity with ZVI even under optimum conditions. With the understanding that environmentally relevant conditions would lead to further decreased reactivity, it can be concluded that implementing ZVI as a reactive capping material for degradation of chlorinated benzenes is infeasible at this time. Further work is also under way on whether nanoiron, 1 to 100 nanometer diameter iron particles, would be more effective in degrading chlorobenzenes than ZVI powder.

## Reference

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