Admicelle-Catalyzed Reductive Dechlorination of Perchloroethylene (PCE) by Zero Valent Iron

Project Completion Report

By

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Project Summary

Title: Admicelle-Catalyzed Reductive Dechlorination of Perchloroethylene (PCE) by Zero Valent Iron

Project ID: R/UW-REM-002

Investigator: Dr. Zhaohui Li, Assistant Professor of Geology and Assistant Professor of Chemistry, Geology Department and Chemistry Department, University of Wisconsin – Parkside

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Background/Need: Chlorinated solvents are a major groundwater contaminant at industrial sites, U.S. Department of Energy facilities, and military installations. Recent discovery of using zero valent iron (ZVI) as permeable barriers to degrade chlorinated solvents dissolved in groundwater has attracted great attention. Numerous researches on using ZVI for groundwater remediation have been focused on increasing the degradation rate constant of chlorinated solvents. However, most of them involve in coating the metals with noble metals such as Pt or Pd. Thus a search for an inexpensive, yet effective material, to enhance the rate of degradation of chlorinated solvents becomes more imminent.

Objectives: The objectives of this research are to further study a novel observation made by the PI on enhanced perchloroethylene degradation by ZVI under the catalysis of a cationic surfactant hexadecyltrimethylammonium (HDTMA). The influence of surfactant chain length of several quaternary ammonium surfactants, the surfactant coverage and the surfactant surface configuration on ZVI, the initial PCE concentrations, and initial solution pH and ionic strength on PCE reduction kinetics will be studied in batch scale. Column experiments will be conducted as a function of initial PCE concentrations and contaminant injection rates to verify the batch results and to provide further justification for future pilot scale and/or field tests.

Methods: Laboratory batch sorption was performed to determine the sorption maxima of surfactants with different hydrophobic chain lengths (8, 12, and 16 carbons in the tail group, respectively). Batch reduction kinetic study was performed to determine the rate constants of PCE degradation and trichloroethylene (TCE) generation due to the degradation of PCE. For column studies, both modified and unmodified ZVIs were packed in duplicates to glass columns of 30 cm long and 2.5 cm in diameter. Contaminant solutions were made in a 12-L collapsible Teflon bags and were delivered by a precision syringe pump with four 10-mL gas-tight syringes attached at different flow rates and different initial PCE and TCE concentrations to verify the enhancement of PCE reduction catalyzed by HDTMA on ZVI surfaces.

Results and Discussion:

Batch results indicate that the longer the surfactant tail group, the more hydrophobic the surfactant is, thus the higher the surfactant sorption. Compared to unmodified ZVI, the rate constants of PCE dechlorination increased by 15 to 20 folds when ZVI was modified by HDTMA. A six to nine fold increase in rate constants was found for ZVI modified with dodecyltrimthylammonium, while a five to seven fold increase was found for ZVI modified with octyltrymethylammonium. The half-life of PCE in the presence of unmodified ZVI was about 10 days, but reduced to 0.4 day when HDTMA-ZVI was used. Solutions with ionic strengths of 0.001, 0.01, and 0.1 M of NaCl, and with initial pHs at 3, 5, and 7 had little effect on PCE reduction rates. Significant slowdown of PCE reduction was found at an initial pH of 11, maybe due to the inhibition of iron corrosion.

Column results show that a 10-fold reduction in effluent PCE concentrations was achieved when HDTMA-ZVI was used compared to unmodified ZVI. With an initial PCE concentration of 20 mg/L and a flow rate of 0.25 mL/min, the effluent PCE concentrations were 0.08-0.1 mg/L and 1.1-2.4 mg/L for modified and unmodified columns, respectively. As the flow rate increased to 2 mL/min, the effluent PCE concentrations increased to 1.5-1.7 mg/L and 13-14 mg/L for modified and unmodified columns, respectively. As the input concentration reduced to 6 mg/L, at a flow rate of 2 mL/min, the effluent PCE concentrations was 0.1-0.2 mg/L and 3.0-3.3 mg/L for modified and unmodified columns, respectively.

Conclusions/ Implications/ Recommendations:

The research shows that the sorbed cationic surfactant, particularly HDTMA, drastically increase the PCE degradation rate. In addition, the pathway of PCE degradation could be predominant by reductively dechlorination when surfactant was present compared to β-elimination when surfactant was absent. Due to the superior enhancement of PCE reduction under the influence of surfactant, it is recommended for a pilot scale test, which will be proposed to US DOE.

Related Publications:

Alessi, D. S. and Li, Z. (2001) Synergistic Effect of Cationic Surfactants on Perchloroethylene Degradation by Zero Valent Iron, *Environ. Sci. Technol.*, in press.

Key Words: Perchloroethylene, Reductive Dechlorination, Trichloroethylene, Surfactant, Zero-Valent Iron

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Introduction

Zero-valent iron (ZVI) as an inexpensive and effective material of permeable reactive walls for destruction of chlorinated solvents has attracted great attention in recent years (Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994). Laboratory studies indicated that ZVI was able to degrade carbon tetrachloride (CT) at a very fast rate with a half-life $t_{1/2}$ of approximately 15 minutes based on pseudo first-order kinetics (Matheson and Tratnyek, 1994). Compared to degradation of CT, the degradation of perchloroethylene (PCE) by ZVI was relatively slow and the half-life was 20 to 40 days (Schreier and Reinhard, 1994). In general, chlorinated ethanes could be degraded more easily than chlorinated ethenes (Gillham and O'Hannesin, 1994).

Because of slower reduction rates of chlorinated ethenes with ZVI, researchers have been focusing on increasing their degradation rates by modifying ZVI. Coating iron with Pd resulted in more than an order of magnitude increase in rate constant for TCE reduction (Liang *et al.* 1997). Reducing the particle size, such as using nanometer scale Pd/Fe, further increased the TCE reduction rate (Wang and Zhang, 1997). Combination of ZVI with other metals such as Ni and Zn enhanced the degradation of TCE (Cheng and Wu, 2000). In a preliminary study, it was found that hexadecyltrimethylammonium (HDTMA), a cationic surfactant, enhanced the PCE dechlorination rate constant by ZVI by a factor of three (Li, 1998).

Surfactants have long been used to change the surface or interfacial properties. In addition, surfactant micellar catalyses have been used extensively in industry. Studies on the hydrolysis of 5-nitro-2-(trifluoroacetylamino) benzoic acid in water and in the presence of micelles of cetyltrimethylammonium bromide (CTAB) showed that at pH 9 the pseudo first-order rate constant increased by 20 times under the catalysis of micelles of CTAB (Broxton and Cox, 1993). In a separate study, the greatest enhancement on complexation reaction between Ni^{2+} (aq) and pyridine-2-azo-*p*-dimethylaniline was achieved under the catalysis of SDS solution (Favaro and Reinsborough, 1994). The rates of disappearance of dinitrotoluene, dinitrobenzene, and dinitrobenzenesulfonic acid from alkaline borohydride solution, due to reduction and photolysis (>290 nm), were greatly enhanced in the presence of CTAB, both in the presence and in the absence of light (Larson *et al.* 2000). But a nonionic surfactant (Tween 80) had little or no effect on the photoreaction while an anionic surfactant (SDS) slowed the photoreaction slightly (Larson *et al.* 2000).

For a reduction reaction to take place, PCE molecules are sorbed onto ZVI first (Bizzigotti *et al.* 1997; Arnold and Roberts, 2000). The sorbed PCE, after formation of a di-σ-bonded intermediate, may undergo either reductive β-elimination producing dichloroacetylene or hydrogenolysis resulting in TCE formation (Arnold and Roberts, 2000). The sorption of hydrophobic compounds is a function of total organic carbon content of the sorbent. Thus, it is speculated that coating the ZVI with a hydrophobic mosaic will increase the sorption of PCE, so that an enhanced reduction could be achieved.

Cationic surfactants have strong adsorption on solid surfaces, making them ideal for surface modification. Adsolubilization of hydrophobic compounds by adsorbed surfactant micelles (admicelles) can dramatically increase the surface concentration of hydrophobic compounds. Solubilization of toluene in surfactant bilayers formed in the interlayer space of vermiculite was responsible for the uptake of toluene by vermiculite (Becerro *et al.* 1996). Admicelles have also been used as two-dimensional templates for reactions. Admicelle-catalyzed hydrolysis of trimethyl orthobenzoate to methyl benzoate was achieved using SDS sorbed on high surface area alumina (Yu and Lobban, 1995). An increase of six in chromate reduction rate was obtained under the influence of HDTMA admicelle on pelletized ZVI and zeolite surfaces (Li et al. 1999).

Procedures and Methods

The ZVI was obtained from Fisher Scientific (Cat # S71953) with particle sizes less than 100 mesh (< 0.13 mm) and was used without pretreatment. The surfactants used were octyltrimethylammonium (OTMA, from Fluka), dodecyltrimethylammonium (DDTMA, from Acros), and HDTMA (from Aldrich), all in bromide form with critical micelle concentrations (CMC) of 140, 15, and 0.9 mmol/L, respectively (Rosen, 1989). PCE and TCE were also from Aldrich.

In the surfactant sorption study, 2.5 g of ZVI and 10 mL of surfactant solution with initial concentrations from 0.2 to 3 mmol/L at neutral pH with no ionic strength adjustment were put into 40-mL polyallomer centrifuge tubes and the mixtures were shaken for 24 hours at room temperature and 150 rpm on a shaker table. After the mixture centrifuged for 30 min at 4000 rpm, the supernatant was analyzed for equilibrium surfactant concentrations by an HPLC method (Li and Bowman, 1997). The Br^- concentrations were analyzed by a revised bromide electrode method in which only 10 mL instead of 100 mL solution was used (Orion, 1997). The amount of surfactant and Br^- sorbed was calculated from the difference between the initial and the equilibrium concentrations. The solution pH during the surfactant sorption study was about 7-8.

To modify ZVI, 40 g of ZVI and 160 mL of surfactant solution were put into 250-mL centrifuge bottles and shaken at the same conditions as described above. For <CMC treatment with HDTMA, 20 g of ZVI and 200 mL of 0.8 mmol/L HDTMA solution were used. Then the mixture was centrifuged, the supernatant analyzed, and the samples washed twice with distilled water before air-dried. The initial concentrations and final loading of different surfactant treatments can be seen in Table 1.

For batch PCE and TCE degradation kinetics studies, 2.5 g of unmodified or surfactant-modified ZVI and 20 mL of PCE (20 mg/L) or TCE solution (22 mg/L) were put into a 20-mL headspace glass vial and sealed with PTFE-lined septa. The solution pH was between 9-10 at the time when samples were taken. The influence of solution pH was tested with the following initial pH conditions: pH 3.7 (30 mmol/L acetic acid/3 mmol/L sodium acetate), 5.7 (3 mmol/L acetic acid/30 mmol/L sodium acetate), and 11.3 (30 mmol/L Na_2CO_3/3 mmol/L $NaHCO_3$). Separately, the influence of ionic strength was tested with 1, 10, and 100 mmol/L of NaCl as background electrolyte to the PCE solution. The vials were shaken at room temperature and 8 rpm on a tumbling solution mixer for varying amounts of time and then centrifuged at 4000 rpm for 10 minutes to yield a clear supernatant solution. Exactly 20 μL of supernatant was withdrawn from each vial using a 100-μL gas-tight syringe and injected into an HPLC equipped a Regis ODS column. A UV-Vis detector with a wavelength of 195 nm was used for aqueous PCE and TCE concentration analysis. The mobile phase was made of 70% acetonitrile and 30% water. At a flow rate of 2 mL/min, the retention times for PCE and TCE were 3.1 and 2.1 minutes, respectively, and the detection limits were 0.05 mg/L for PCE and TCE. Each vial was sacrificed after being sampled. All batch degradation experiments were run in triplicates.

Table 1. ZVI surfactant treatment levels and apparent rate constants of PCE reduction under each treatment.

Type of Surfactant Treatment	Input Surfactant Concentration (mmol/L)	Surfactant Loading (mmol/kg)	Apparent Rate Constant (h^{-1})^a	$t_{1/2}$ (day)	r^2
Unmodified ZVI	0.0	0.0	0.004±0.003	7.2	0.6
OTMA-High	2.5	1.2	0.015±0.005	1.9	0.92
OTMA-Low	0.5	0.2	0.021±0.004	1.4	0.96
DDTMA-High	2.5	1.9	0.018±0.004	1.6	0.95
DDTMA-Low	0.5	0.8	0.029±0.005	1.0	0.96
HDTMA-High	2.5	8.0	0.048±0.015	0.6	0.90
HDTMA-Low	0.5	2.0	0.076±0.015	0.4	0.97
HDTMA<CMC	0.8	5.0	0.065±0.014	0.4	0.96
HDTMA-ZVI mix	2.5	-	0.012±0.010	2.4	0.83
HDTMA only	2.5	-	0.001±0.001	28.9	0.2

^{a}Uncertainties represent 95 % confidence limits.

Column tests were performed in four glass columns each with 2.54 cm in diameter and 30 cm in length, two of them filled with HDTMA-ZVI and two with raw ZVI. Contaminated water was made in 12 L collapsible Teflon bags and was withdrawn and delivered to each column with a precision syringe pump with four 10-mL gas-tight syringes. The initial PCE concentrations were 6, 12, and 20 mg/L, respectively, while the initial TCE concentrations were 1.7, 6, and 11 mg/L, respectively. The flow rate was 0.25, 0.5, 1.0 and 2.0 mL/min. Input and output PCE and TCE concentrations were measured periodically using the HPLC method.

Results and Discussion

The sorption of cationic surfactants with different hydrophobic chain lengths and counterion bromide on ZVI is plotted in Figure 1. Sorption maxima for OTMA, DDTMA, and HDTMA are 1, 2, and 8 mmol/kg, respectively. The HDTMA sorption on ZVI is comparable to that on a ZVI from another vendor (4 mmol/kg) (Li, 1998). For most cases, counterion bromide sorption was minimal, or even negative, except for higher HDTMA loading. Counterion sorption is an indication of surfactant surface configuration. When sorbed surfactants form a bilayer on solid surface, the ratio of surfactant/bromide sorbed should be close to 2/1 due to surface cation exchange and hydrophobic bonding (Li and Bowman, 1997). The lack of bromide sorption indicates that the sorbed surfactant molecules primarily form a patchy monolayer. Similarly, monolayer sorption of octylsilanes and hexadecylsilanes was found on ZVI (Petrunin *et al.* 1997). When initial HDTMA concentration was less than the CMC, HDTMA sorption maximum was only 2 mmol/kg, while the bromide sorption was negative throughout the concentration range (Fig. 1d). Because the surfactant solution concentrations were lower than the CMC, only surfactant monomers were present in solution; thus, only monolayer sorption is possible. The negative sorption of bromide is probably due to anion exclusion from ZVI surfaces when only cationic surfactants were sorbed.

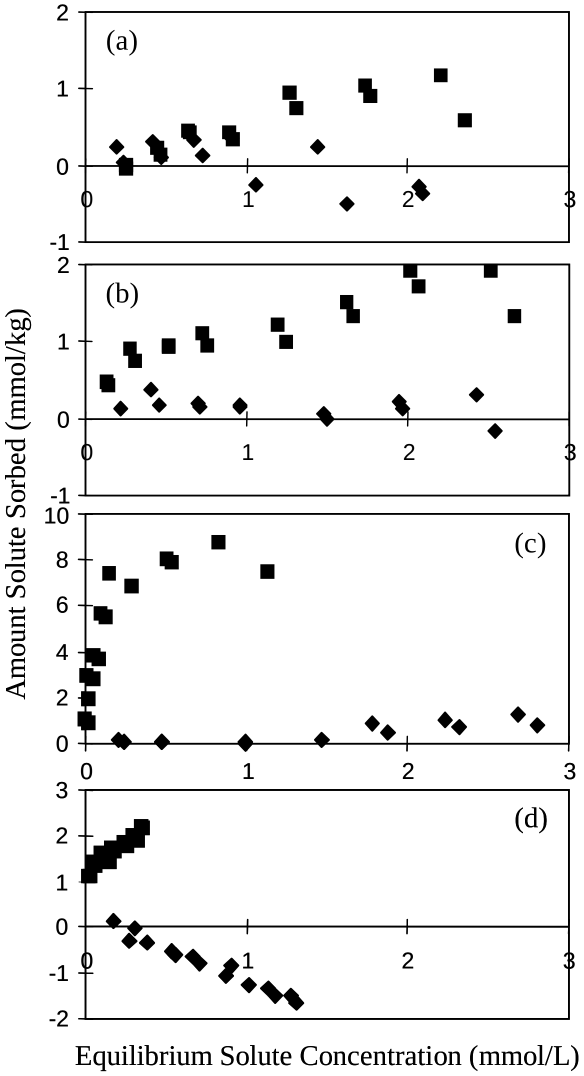

Fig. 1. Sorption of surfactants (•) and counterion bromide (•) on ZVI. (a) OTMA, (b) DDTMA, (c) HDTMA, (d) HDTMA with initial concentrations < CMC.

Fig. 2 shows that degradation of PCE, in the presence of unmodified ZVI and ZVI modified by cationic surfactants with different chain lengths and different surfactant loading, follows a pseudo-first-order reaction kinetics:

$$Ln(C/C_0) = -kt \qquad [1]$$

where C is the PCE solution concentration at time t, C_0 is the initial PCE concentration, and k is the apparent pseudo first-order rate constant. The apparent rate constants calculated from eq. [1] at different surfactant treatments are listed in Table 1. Control samples containing 2.5 mmol/L HDTMA and 20 mg/L PCE showed no PCE loss during the experiment, indicating HDTMA alone will not react with PCE. The unmodified ZVI showed minimal PCE loss throughout the experimental period, resulting an apparent rate constant of 0.004 h^{-1} (Table 1). The rate constants of PCE degradation were 4 to 5 times higher for OTMA-modified ZVI, 5 to 7 times higher for DDTMA-modified ZVI, and 12 to 19 times higher for HDTMA-modified ZVI, compared to the unmodified counterpart. The PCE degradation rates are comparable to those of Bizzigotti *et al.* (1997) and to those by HDTMA modification to a different source of iron (Li, 1998).

Also plotted in Fig. 2 is PCE reduction when ZVI and PCE solution containing 2.5 mmol/L HDTMA were mixed. In this case, the ZVI was not previously modified. The rate constant of PCE degradation was 0.012 h^{-1}, a three-fold increase compared to that when ZVI alone was used. The equilibrium HDTMA concentration was about 1.6-1.8 mmol/L, greater than the CMC of HDTMA. Thus, in the situation when HDTMA and ZVI were mixed, the excess HDTMA form micelles in solution, into which PCE could partition. The excess HDTMA was removed during the rinsing stage for modified ZVI. The comparison indicates that pre-sorbed surfactants may be important in enhancing PCE reduction.

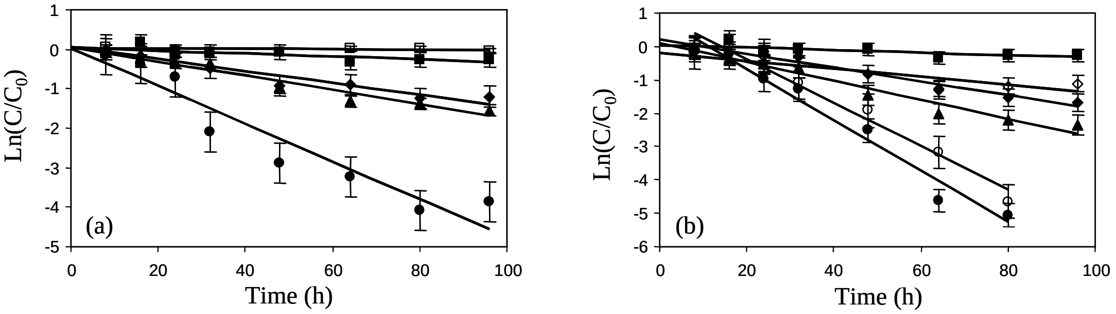

Fig. 2. PCE degradation by ZVI under different surfactant treatments. (a): 2.5 mmol/L HDTMA surfactant solution alone (□), unmodified ZVI (●), ZVI modified to high surfactant loading by OTMA (●), DDTMA (●), and HDTMA (●). (b): 2.5 mmol/L HDTMA and ZVI mixture (◇), unmodified ZVI (●),ZVI modified to low surfactant loading by OTMA (●), DDTMA (●), and HDTMA (●), and by HDTMA with initial concentration < CMC (○).

Reduction by ZVI was surface-mediated as revealed using 4-aminoazobenzene as the probe molecule (Weber, 1996). For dechlorination to occur, PCE is first sorbed to the iron surface, followed by the reaction of sorbed PCE to form degradation products, initially TCE and chloride (Bizzigotti *et al.* 1997) or the reductive-elimination product dichloroacetylene (Arnold and Roberts, 2000). The sorbed HDTMA on ZVI increases the fractional organic carbon content of the iron and serve as hydrophobic mosaics for PCE partitioning, resulting in an elevated PCE surface concentration on reactive sites of iron, thus an increased degradation.

Fig. 2 also shows that ZVIs modified to lower surfactant loading have higher apparent rate constants than that when ZVIs modified to higher surfactant loading. Since reduction of PCE is surface-mediated (Weber, 1996; Bizzigotti *et al.* 1997; Arnold and Roberts, 2000), and the surface contains reactive and non-reactive sites (Burris *et al.* 1995), it is speculated that some of the reduction sites could be blocked with a patchy bilayer, when ZVI was modified to higher surfactant loading. A patchy bilayer formation will change the surface from more hydrophobic to more hydrophilic, resulting in less affinity for PCE. This assumption can be further verified from the PCE degradation by ZVI modified with HDTMA at initial concentration less than the CMC, when only surfactant monomers were present in solution. Thus, when contacted with ZVI, sorption of HDTMA was in monomer form. The surfactant surface configuration would be similar to that by HDTMA-modified to low surfactant loading, resulting in a similar apparent rate constant (Table 1). Studies on direct reduction of TCE showed that preferential reduction of water inhibited TCE reduction, but electrodes coated with a hydrophobic polymer (silicone vacuum grease) increased the direct TCE reduction by inhibiting water reduction (Li and Farrell, 2000). Similar to PCE degradation, the rate constants of TCE degradation was 0.035 h^{-1} and 0.044 h^{-1} by HDTMA-modified ZVI to high and low surfactant loading, respectively, an increase by an order of magnitude compared to 0.003 h^{-1} from unmodified ZVI (Fig. 3).

Using the apparent rate constants obtained from eq. [1] for PCE and TCE and stepwise hydrogenolysis of PCE to TCE, the TCE concentration with time can be determined from (Sivavec *et al.* 1996)

$$[TCE] = \frac{ak_{PCE}}{k_{TCE} - k_{PCE}}(e^{-k_{PCE}t} - e^{-k_{TCE}t})[PCE]_0 \qquad [2]$$

where k_{PCE} and k_{TCE} stand for apparent rate constants for PCE and TCE degradation, $[PCE]_0$ for initial PCE concentration, and a for the fraction of PCE degrading to TCE via hydrogenolysis. The observed PCE and TCE concentrations vs. time are plotted in Fig. 4. Using the apparent rate constants of PCE and TCE degradation obtained by fitting the observed data in Fig. 2 and 3 to eq. [1], the a values can be determined by fitting the observed concentrations for PCE and TCE in Fig. 4 to eq. [2]. The values are 0.15 and 0.88 for unmodified and modified ZVI, respectively. The calculated TCE concentration is then plotted based on the best fitted a values (Fig. 4).

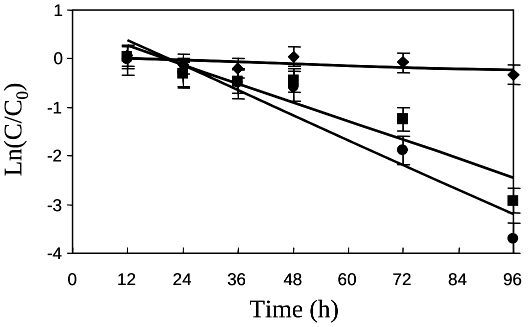

Fig. 3. TCE degradation by unmodified ZVI (●), HDTMA modified ZVI to low (●), and high (●) surfactant loading.

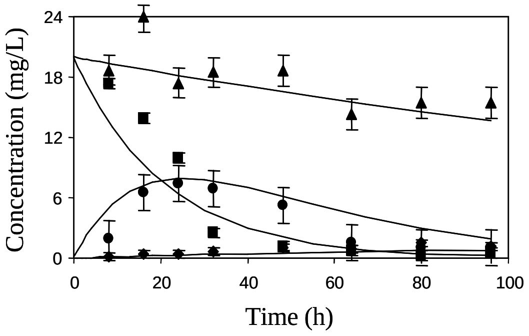

Fig. 4. PCE degradation (●) and TCE production (●) by HDTMA modified ZVI to high surfactant loading. PCE degradation (●) and TCE production (●) by unmodified ZVI. The lines are calculated PCE and TCE concentrations based on eq. [2].

Orth and Gillham (1997) found that, under normal conditions, the amount of daughter products appeared due to TCE degradation accounted for only 3% of the initial TCE concentration, and Schreier and Reinhard (1994) found that the TCE production due to PCE reduction was less than 2% of the initial PCE concentration. In a separate study, it was found that 87 % of initial PCE followed β-elimination and the TCE yield due to hydrogenolysis of PCE accounted for only 10 % of the input PCE (Arnold and Roberts, 2000). The equilibrium TCE concentration of 1 mg/L, corresponding to 5% of the initial PCE concentration for unmodified ZVI is agreeable with these results. However, a significant increase in aqueous TCE concentration (7 mg/L corresponding to 35% of the initial PCE concentration) was observed when HDTMA-modified ZVI was used (Fig. 4). Since the TCE is the product of hydrogenolysis and the product of reductive elimination is dichloroacetylene (Arnold and Roberts, 2000), the significant TCE accumulation when HDTMA-ZVI is used compared to unmodified ZVI again indicates that a relatively larger portion of input PCE undergoes hydrogenolysis compared to reductive elimination. Therefore, there might be a mechanism change under the influence of sorbed surfactants. For PCE degradation to occur, the first step is to form a π-bonded surface species (Arnold and Roberts, 2000). In this sorption step, the alkenes would serve as the Lewis base and partially or fully oxidized metal ions would represent Lewis acid (Arnold and Roberts, 2000). On the surfactant-modified ZVI surface, the sorbed alkylammonium may serve as the Lewis acid, thus promote the interaction. Since TCE is less hydrophobic and much more soluble than PCE, the partitioning of TCE to HDTMA admicelles should be less favorable than PCE. Therefore, the enhancement is slightly less than that of PCE degradation. The slightly lower apparent rate constant for TCE degradation could attribute to the accumulation of TCE during the early stage of the experiment (Fig. 4).

Changes in ionic strength from 1 to 100 mM NaCl had minimal effect on PCE degradation rate constants (data not shown). The result here is different from the observation of carbon tetrachloride degradation by ZVI under the influence of background chloride, in which addition of 60-100 µmol/L NaCl resulted in a four-fold increase in degradation rate constant of carbon tetrachloride (Johnson *et al.* 1998). Compared to low pH conditions (pH 3.7 and 5.7), PCE reduction essentially stopped at pH 11, possibly due to the bicarbonate/carbonate buffer (data not shown). The difference in PCE reduction rate could also result from the difference in composition of the buffer solutions. Significant reduction in vinyl chloride degradation was noticed at high pH (Deng *et al.* 1999). The TCE reduction half-lives at pH 4 and 7 were about the same but increased by a factor of three at pH 10 (Li and Farrell, 2000). The apparent reduction rate constant of CT decreased by a factor of five when pH increased from 5 to 10 (Matheson and Tratnyek, 1994). Thus, the results from this study agree well with the ZVI passivation at higher solution pH, particularly under carbonate/bicarbonate buffer condition.

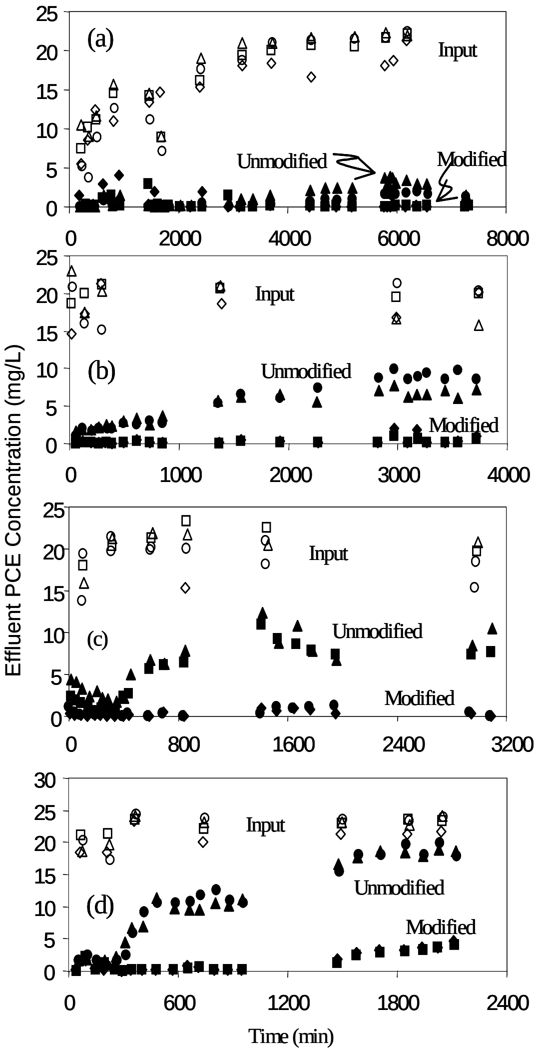

Fig. 5. PCE degradation through packed columns of ZVI and HDTMA-ZVI with flow rate of 0.25 mL/min (a), 0.50 ml/min (b), 1.00 mL/min (c), and 2.00 mL/min (d).

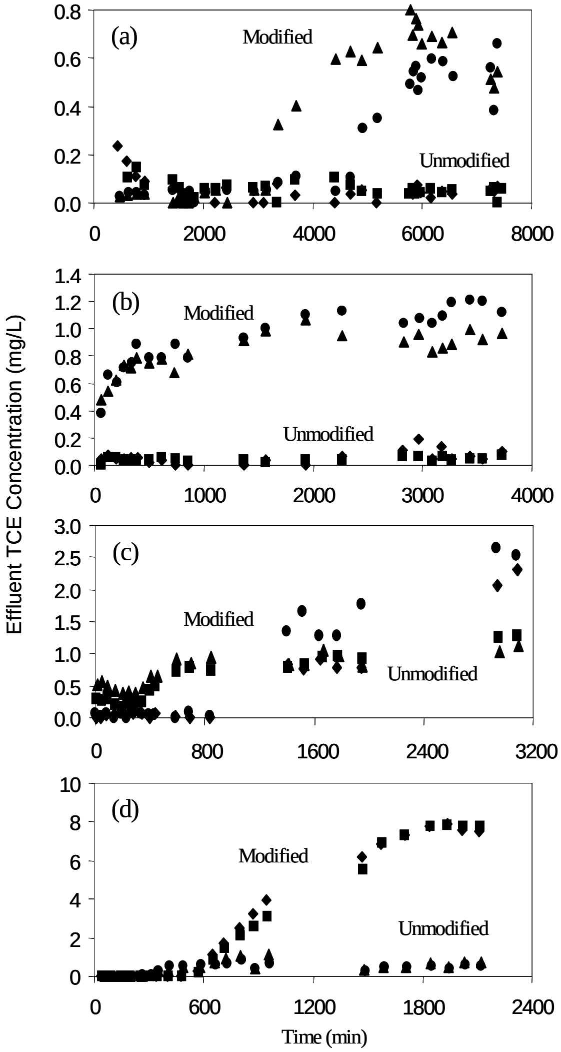

Fig. 6. TCE generation due to PCE degradation through packed columns of ZVI and HDTMA-ZVI with flow rate of 0.25 mL/min (a), 0.50 ml/min (b), 1.00 mL/min (c), and 2.00 mL/min (d).

Column result show that a ten-fold reduction in effluent PCE concentrations was achieved when HDTMA-ZVI was used compared to unmodified ZVI (Fig. 5). When initial PCE concentration was 20 mg/L and the flow rate was 0.25 mL/min, the effluent PCE concentrations were 0.08-0.1 mg/L and 1.1-2.4 mg/L for modified and unmodified columns, respectively. When the flow rate was 0.5 mL/min and 1.0 mL/min, the effluent PCE concentrations increased to 0.3-0.5 ml/L and 6-7 mg/L for modified and unmodified columns, respectively. As the flow rate increased to 2.00 mL/min, the effluent PCE concentrations increased to 1.5-1.7 mg/L and 13-14 mg/L for modified and unmodified columns, respectively (Fig. 5). Also, significant TCE generation was found for HDTMA-ZVI, similar to the observation during batch study (Fig. 6). The effluent TCE concentration increases as the flow rate increases, too. For modified ZVI, the peak TCE concentrations were 0.8, 1.1, 2.5, and 8 mg/L, respectively for flow rates of 0.25, 0.50, 1.00, and 2.00 mL/min, respectively (Fig. 6). At the flow rate of 2 mL/min and the input concentration of 22 mg/L, the effluent PCE concentrations were 1.5-1.7 mg/L and 13-14 mg/L for modified and unmodified columns, respectively. As the input concentration reduced to 12 mg/L, the effluent PCE concentrations were 0.5-0.7 mg/L and 5.6-6.4 mg/L for modified and unmodified columns, respectively. When the input concentration was further reduced to 6 mg/L, the effluent PCE concentrations were 0.1-0.2 mg/L and 3.0-3.3 mg/L for modified and unmodified columns, respectively (Fig. 7). TCE production as a function of initial PCE concentration at the same flow rate can be seen in Fig 8. As the initial PCE concentration decreases, the produced TCE concentration decreases correspondingly. A decrease of input PCE concentration by 50% resulted in 3 times decrease in TCE concentration for the modified ZVI (Fig. 8).

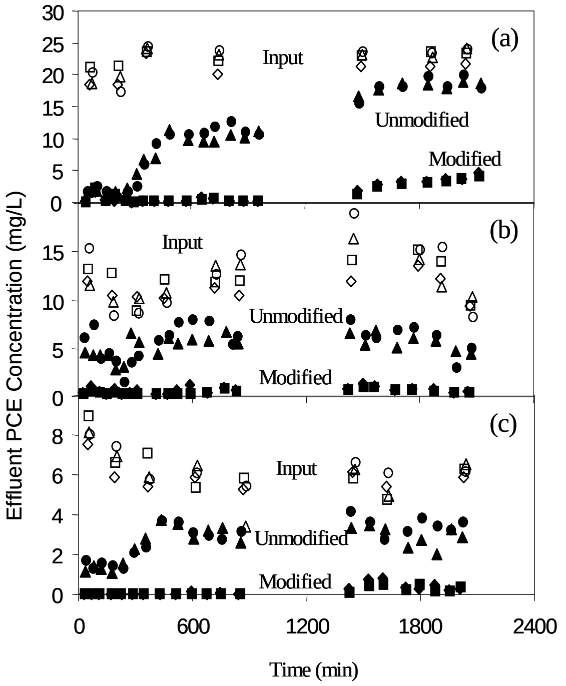

Fig. 7. PCE degradation through packed columns of ZVI and HDTMA-ZVI as a function of initial PCE concentrations. (a) 20 mg/L, (b) 12 mg/L, (c) 6 mg/L.

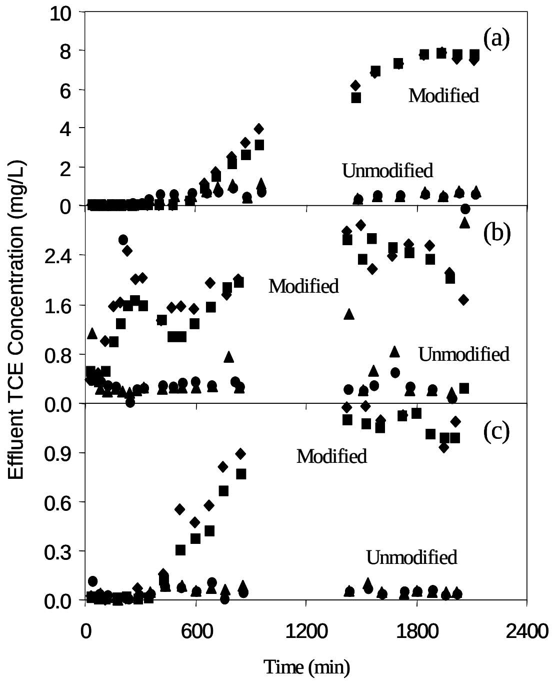

Fig. 8. TCE generation through packed columns of ZVI and HDTMA-ZVI as a function of initial PCE concentrations. (a) 20 mg/L, (b) 12 mg/L, (c) 6 mg/L.

Conclusions and Recommendations

The results from this study suggest that addition of cationic surfactant onto ZVI surfaces could increase the reactant concentration near the reactive ZVI surface. Due to greater affinity of more hydrophobic compound for surfactant-modified ZVI surface, greater enhancement would be expected on dechlorination of more hydrophobic chlorinated compounds. Surfactants sorbed on ZVI surfaces showed synergistic effect on PCE reduction due to sorption or admicellar catalysis. Under these circumstances, the electron transfer from ZVI surface to the chlorinated compound may be enhanced, in contrast to the case where a separate sorbent and ZVI are simply mixed together, such as pelletized mixtures of surfactant-modified zeolite and ZVI (Li *et al.* 1999). For the later case, the enhancement of PCE reduction rate could be attributed to HDTMA-modified ZVI alone, while the surfactant-modified zeolite served as a separate sorbent for PCE sorption only.

Compared to unmodified ZVI, PCE reduction by ZVI under the catalysis of HDTMA increased by an order of magnitude. The significance of the research has two folds. On one hand, if the same maximum concentration level of PCE at the downstream of a permeable barrier needs to be achieved, the barrier thickness, and thus, the material and installation costs could be dramatically reduced. On the other hand, if two barriers with the same thickness were installed, the effluent PCE concentration would be 10 times lower from the ZVI barrier that has surfactant as the synergist. Thus, it is recommended that a pilot scale filed test be conducted in the near future. The PI will request further funding from US DOE for such test. At the same time the PI hopes that the Groundwater Research Council, in conjunction with USGS, would promote the activity by making the influence as far-reaching as possible.

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Appendix A:

Journal Publications:

Alessi, D. S. and Li, Z. (2001) Synergistic Effect of Cationic Surfactants on Perchloroethylene Degradation by Zero Valent Iron, *Environ. Sci. Technol.*, in press.

Li, Z., Willms, C., and Alley, J. (2002) Column Study on Perchloroethylene and Trichloroethylene Degradation Using Zero Valent Iron Under the Catalysis of A Cationic Surfactant, tentative title, in preparation to be submitted to *Ground Water*.

Conference Presentation:

REDUCTIVE DECHLORINATION OF PCE AND TCE USING SURFACTANT MODIFIED ZERO VALENT IRON Daniel S. Alessi, (Dr. Zhaohui Li), Geology Department, University of Wisconsin-Parkside, 900 Wood Road, Kenosha, WI 53141, presented at the annual UW System Undergraduate Symposium at La Crosse, WI in May 2000.

REDUCTIVE DECHLORINATION OF PCE AND TCE USING SURFACTANT MODIFIED ZERO VALENT IRON Daniel S. Alessi and Zhaohui Li*, Geology Department and Chemistry Department, University of Wisconsin-Parkside, 900 Wood Road, Kenosha, WI 53141, presented at the annual meeting of Geologic Society of America at Reno, NV on November 13 2000.