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Enhanced degradation of carbon tetrachloride by surfactant-modified zero-valent iron[*]

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Abstract: Sorption of carbon tetrachloride (CT) by zero-valent iron (ZVI) is the rate-limiting step in the degradation of CT, so the sorption capacity of ZVI is of great importance. This experiment was aimed at enhancing the sorption of CT by ZVI and the degradation rate of CT by modification of surfactants. This study showed that ZVI modified by cationic surfactants has favorable synergistic effect on the degradation of CT. The CT degradation rate of ZVI modified by cetyl pyridinium bromide (CPB) was higher than that of the unmodified ZVI by 130%, and the CT degradation rate of ZVI modified by cetyl trimethyl ammonium bromide (CTAB) was higher than that of the unmodified ZVI by 81%. This study also showed that the best degradation effect is obtained at the near critical micelle concentrations (CMC) and that high loaded cationic surfactant does not have good synergistic effect on the degradation due to its hydrophilicity and the block in surface reduction sites. Furthermore degradation of CT by ZVI modified by nonionic surfactant has not positive effect on the degradation as the ionic surfactant and the ZVI modified by anionic surfactant has hardly any obvious effects on the degradation.

Key words: Enhanced degradation, Sorption, Surfactants, Synergistic effect, Zero-valent iron (ZVI)
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INTRODUCTION

As one of the primary organic solvents and industrial chemicals, chlorinated hydrocarbons are extensively applied in chemical industry, medicine, pesticide and many other fields. However, the application of chlorine for disinfection of drinking water is giving rise to poisonous chlorinated hydrocarbons. Therefore, chlorinated hydrocarbons become the most common organic pollutant in soils and groundwater (Shoemaker, 1995). Many chlorinated hydrocarbons can lead to cancer, monstrosity and mutagenesis. As a result, they are listed as strictly regulated pollutants in many countries.

Degradation of chlorinated hydrocarbons in water by wet oxidation requires high energy (Qin *et al*., 2001) and the degradation product—chloride ion has severe causticity in supercritical water oxidation (SCWO). Particularly, as the Lewis acid (electron acceptor), the multi-chlorine pollutants cannot be treated effectively by advanced oxidation process (AOP). Biological treatment is a potential way, but the microorganism growth should be well controlled. In recent years, as a simple, efficient and low-cost treatment method, the degradation of chlorinated hydrocarbons in industrial wastewater and the groundwater by ZVI (zero-valent iron) at room temperature has been noticed by many researches. As an extensively used metal, iron has favorable dechlorination effect on many chlorinated compounds, such as aliphatics and aromatics and pesticides (Lookman *et al*., 2004; Guan and Meng, 2005; Hara *et al*., 2005; Sayles *et al*., 1997).

In order to accelerate degradation, many researchers tried to modify the ZVI by coating a second catalyst metal such as Pd (Doong and Lai, 2005) on

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the iron surface or increasing the surface area by reducing particle size to enhance the reactivity (Choe *et al.*, 2001).

Many researches show that the use of surfactant could enhance the concentration of organism in solution in soil and in the sediments (Ko *et al.*, 1998; Burris and Antworth, 1992). Ko *et al.*(1998) showed that the use of anionic surfactants enhances the concentration of aromatic compounds on kaolinite particles. The surface concentration depends on the kind and concentration of the surfactant. Cationic surfactant has strong sorption capacity in the surface of solid thus effectively enhancing the degradation rate of chlorinated hydrocarbons (Alessi and Li, 2001; Zhang *et al.*, 2002).

Sayles *et al.*(1997) found that deoxidation of DDT (dichloro-diphenyl-trichloroethane) by ZVI could enhance the degradation rate by 40% in the presence of Triton-114 (a sort of nonionic surfactant). The enhancement of the reaction rate could be attributed to the increase of DDT products dissolubility.

The present study is aimed at finding whether ZVI modified by surfactant has synergistic effect on accelerating the dechlorination. The surfactants involved here are cationic surfactant (cetyl trimethyl ammonium bromide, CTAB; cetyl pyridinium bromide, CPB), nonionic surfactant (Triton-100, Tween 80) and anion surfactant (sodium dodecyl benzene sulfonate, SDBS; sodium dodecyl sulfate, SDS).

MATERIALS AND METHODS

Reagents

ZVI (80 mesh) and surfactants (CTAB, CPB, Triton-100, Tween 80, SDBS and SDS) were all obtained from Shanghai Chemical Co. Carbon tetrachloride (CT) and methanol were purchased from Siyou Chemical Co. All reagents were of AC grade. The critical micelle concentration (CMC) was found in the literature to be 0.9 mmol/L for CTAB (Rosen, 1989), 0.6 mmol/L for CPB (Mukerjee and Mysels, 1971), 0.25 mmol/L for Triton-100 (Partearroyo *et al.*, 1996), 0.185 mmol/L for Tween 80 (Kim *et al.*, 2001), 8.0 mmol/L for SDS (Liu and Roy, 1995), 2.1 mmol/L for SDBS (Bi *et al.*, 1999).

Surfactant modification

In surfactant modifying studies, 10 g iron powder and surfactant CTAB and CPB of different initial concentrations were respectively put into a 50 ml zero headspace conical flask and sealed with Teflon rubber. The pH remained neutral and had no ionic strength. The conical flask was put onto a shaker table kept shaking for 24 h (a period shown to be sufficient to obtain equilibrium) without light and under the conditions of 25 °C and 220 r/min. After modification, the iron powder was filtrated and the concentration of the filtered solution was analyzed by HPLC. The surfactant loaded could be measured from the difference between the initial and equilibrium surfactant (Li *et al.*, 1999).

CT degradation

In CT degradation studies, 2.0 g unmodified or surfactant-modified ZVI and 20 mg/L CT solution were put into 50 ml zero headspace conical flask and sealed with Teflon rubber immediately. The conical flask was put onto a shaker table, and the reaction was conducted without light. The pH remained neutral and the rotating speed was 220 r/min.

Methods of analysis

Cationic surfactant was analyzed by HPLC with ODS column using an aqueous solution of 5 mmol/L ptoluenesul fonate and methanol (45:55, v/v) as the mobile phase. Aliquots of 25 μl were injected into the HPLC (Li and Bowman, 1997).

The CT concentration was measured by GC with ECD detector on a 3 m long and 3 mm diameter glass column. Temperatures of injector, column and detector were set at 180, 80 and 180 °C respectively. The 250 μl samples were put into a 100 ml gas-liquid equilibrium bottle with 50 ml headspace. After a water bath at 38 °C and equilibrium for 40 min, 15 μl zero headspace gas samples were taken and analyzed by GC.

RESULTS AND DISCUSSION

CT degradation with surfactant-modified ZVI

CT degradation by unmodified ZVI or ZVI modified by cationic surfactants followed pseudo first-order reduction (Tamara and Butler, 2004; Tratnyek *et al.*, 2001):

$$C=C_0\mathrm{e}^{-kt}, \tag{1}$$

where C and C_0 are the solute concentrations at time t and t=0, respectively. Table 1 lists the apparent CT rate constants for different surfactant treatment. Control experiment containing different concentrations and 20 mg/L CT showed no CT loss during the experiment, indicating that these surfactants alone would not react with CT.

Table 1 Apparent rate constants of CT degradation under different treatment

Type of surfactant treatment	Input surfactant conc. (mmol/L)	Apparent rate constant (min^{-1})
Only ZVI	0.00	0.0079
CTAB	0.30	0.0120
CTAB	0.90	0.0143
CTAB	2.70	0.0129
CPB	0.20	0.0125
CPB	0.60	0.0182
CPB	1.80	0.0134
Tween 80	0.06	0.0083
Tween 80	0.19	0.0102
Tween 80	0.56	0.0092
Triton-100	0.08	0.0089
Triton-100	0.25	0.0113
Triton-100	0.75	0.0100
SDS	2.70	0.0072
SDS	8.00	0.0069
SDS	24.00	0.0085
SDBS	0.70	0.0069
SDBS	2.10	0.0066
SDBS	6.30	0.0075

The charge of the hydrophilic group has great influence on the nature of the surfactant. The result of degradation of 20 mg/L CT in the presence of unmodified ZVI and ZVI modified by cationic surfactants is presented in Fig.1. Both Fig.1 and Table 1 show that ZVI modified by two kinds of cationic surfactants can effectively accelerate the degradation. The degradation rate of ZVI modified by CPB was higher than that of the unmodified ZVI by 130%, and the degradation rate of ZVI modified by CTAB was higher than that of the unmodified ZVI by 81%.

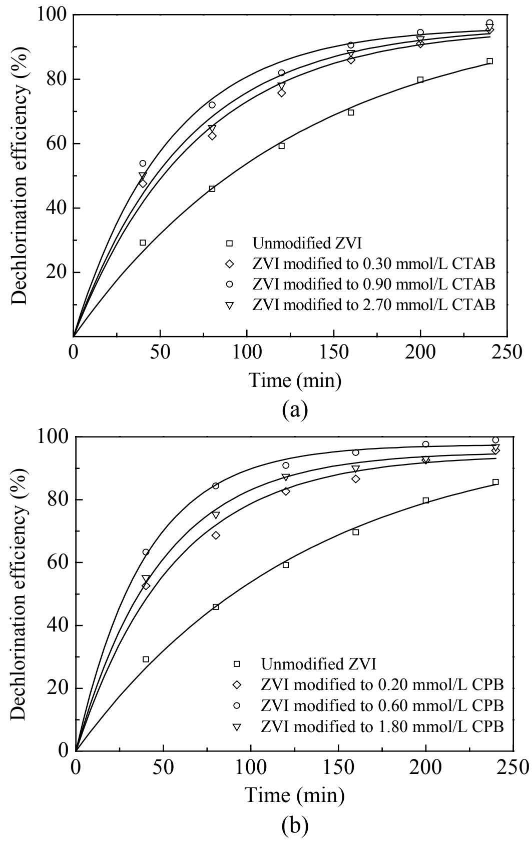


Fig.1 CT (20 mg/L) degradation by ZVI under cationic surfactant (a) CTAB and (b) CPB treatments

In surfactant-iron system, a CT degradation model consists of aqueous phase, surfactant layer on the iron surface, reactive sites on the iron surface, and non-reactive sites on the iron surface. For dechlorination to occur, CT is first sorbed onto the iron surface; then the sorbed CT gives rise to a dechlorination reaction. The cationic modified ZVI can increase sorption of CT onto iron surface, resulting in an elevated CT surface concentration on reactive sites of iron. Therefore both the electron transfer for CT and the reduction of sorbed CT are promoted.

The efficiency of ZVI modified by nonionic surfactants is similar for the ZVI modified by cationic surfactants (Fig.2). The reduction rate on CT of ZVI modified by Tween 80 was 29% higher than the maximum unmodified ZVI and degradation rate on CT of ZVI modified by Triton-100 was 43% higher than that of the unmodified ZVI.

Table 2 lists the surfactant loading on modified ZVI. With increasing of surfactant concentration in solution, the surfactant sorbed onto the ZVI surface increases. However the degradation rate of CT does not necessarily increase with increasing of surfactant capacity (Tables 1 and 2). The iron-water interface bears negative electricity at high pH values (Tratnyek *et al.*, 2001), therefore, as Fig.3 shows, under the

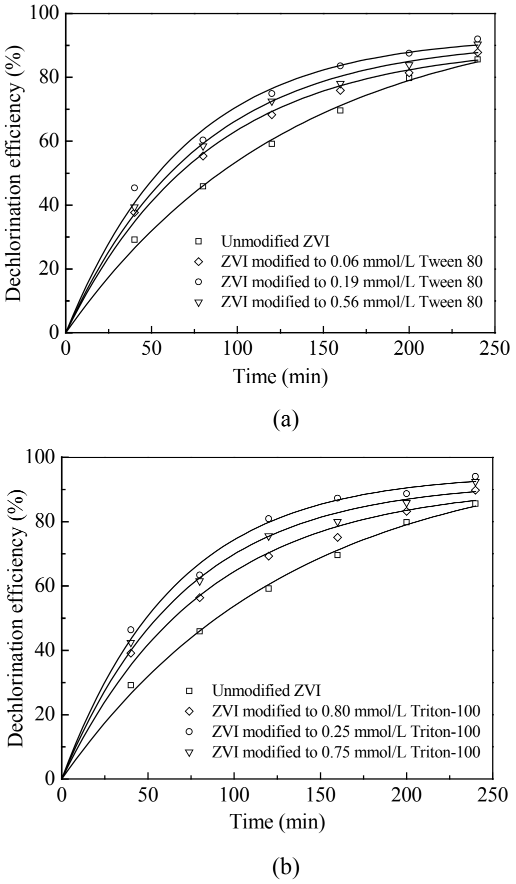


Fig.2 CT (20 mg/L) degradation by ZVI under nonionic surfactant (a) Tween 80 and (b) Triton-100 treatments

Table 2 Surfactant loading under different treatment

Type of surfactant treatment	Input surfactant conc. (mmol/L)	Surfactant loading (mmol/kg)
Only ZVI	0.0	0.0
CTAB	0.3	0.4
CTAB	0.9	1.0
CTAB	2.7	5.9
CPB	0.2	0.4
CPB	0.6	0.7
CPB	1.8	2.8

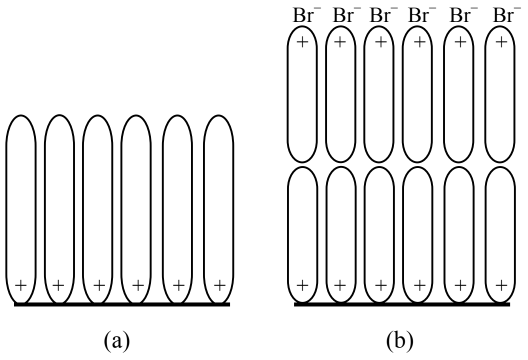


Fig.3 Cationic surfactant (CTAB or CPB) sorption on ZVI. (a) Monolayer sorption; (b) Bilayer sorption

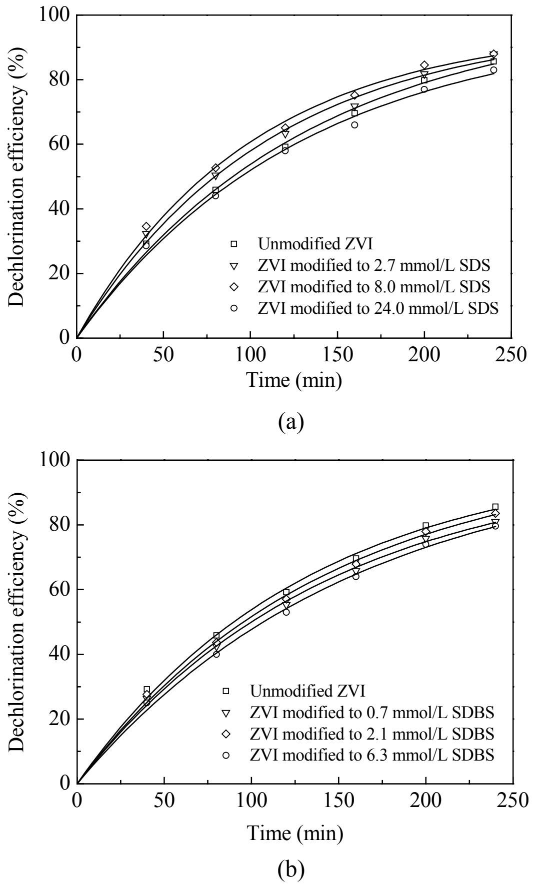
condition of lower concentration of cationic surfactant, the iron surface is sorbed by patchy monolayer and the hydrophobic group points to solution so as to sorb the CT in water. The higher concentration of cationic surfactant forms a patchy bilayer on the iron surface which leads to a hydrophilic group and thus higher concentration unfavorable for sorption of CT. Furthermore, too many surfactants on the iron block the reduction sites, resulting in decreasing the reduction rate of CT decrease with the increasing of the modified surfactant concentration.

Fig.2 shows the reduction of CT by nonionic surfactants modified ZVI. In the case of low concentration of nonionic surfactant, the iron surface is sorbed by patchy monolayer with the modified ZVI having weaker reduction effect on CT when compared to cationic surfactants. In contrast to cationic surfactants modified ZVI, Fig.4 shows that in the case of low concentration of anionic surfactants, the iron surface is sorbed by monolayer and the hydrophilic group points to solution unfavorable for sorption of CT. While in the case of a higher concentration, the anionic surfactant forms a bilayer on the iron surface which leads to a hydrophobic group point to solution. The process is opposite to that in the case when cationic surfactant is used.

Initial rapid decrease in CT solution concentration could be found in Figs.1, 2 and 4. As noted by Burris *et al.*(1995). ZVI can sorb PCE (perchloroethylene), probably due to the presence of carbon in the iron metal. So the initial rapid decrease may be resulted from this effect. The enhanced sorption of CT due to presence of cationic surfactant thus appears to be responsible for the enhanced CT degradation.

Influence of pH

The reduction of CT is greatly influenced by the change of pH in the solution. At lower pH, the reduction rate constant is twice that of the constant at higher pH. The result is shown in Fig.5 and accords with the ZVI corrosion at lower solution pH and passivation at higher solution pH (Chen *et al.*, 2001). The use of phosphate-based buffer solution restrains the reaction, because iron phosphate precipitation results in ZVI coating.



(a)

(b)

Fig.4 CT (20 mg/L) degradation by ZVI under anionic surfactant (a) SDS and (b) SDBS treatment

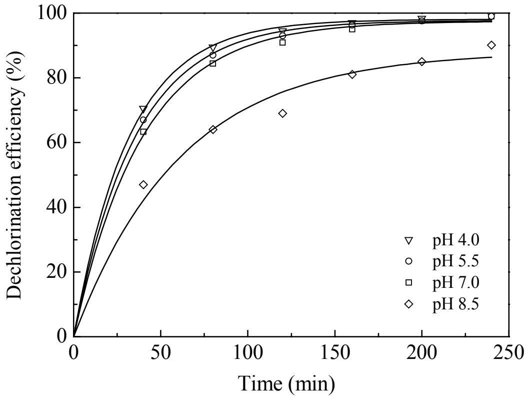


Fig.5 CT degradation by ZVI under 0.6 mmol/L CPB treatment at initial pH 4.0, pH 5.5, pH 7.0, pH 8.5

CONCLUSION

This research showed that the use of cationic surfactants results in the increasing of CT concentration on ZVI and then higher reduction rate. The ZVI modified by cationic surfactant proved to have positive synergistic effect on CT degradation. The best degradation effect was achieved at the near critical micelle concentrations (CMC). High-loaded cationic surfactant did not have good synergistic effect due to its hydrophily and block effect on surface reduction sites. ZVI modified by nonionic surfactant has less positive synergistic effect and ZVI modified by anionic surfactant had hardly any effect.

References

Alessi, D.S., Li, Z., 2001. Synergistic effect of cationic surfactants on perchloroethylene degradation by zero-valent iron. *Environ. Sci. Technol.*, **35**(18):3713-3717. [doi:10.1021/es010564i]

Bi, Z., Zhang, Z., Xu, F., Qian, Y., Yu, J., 1999. Wettability, oil recovery and interfacial tension with an SDBS-dodecane-kaolin system. *Journal of Colloid and Interface Science*, **214**(2):368-372. [doi:10.1006/jcis.1999.6208]

Burris, D.R., Antworth, C.P., 1992. In situ modification of an aquifer material by a cationic surfactant to enhance retardation of organic contaminants. *J. Contam. Hydrol.*, **10**(4):325-337. [doi:10.1016/0169-7722(92)90014-6]

Burris, D.R., Campbell, T.J., Manoranjan, V.S., 1995. Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron-water system. *Environ. Sci. Technol.*, **29**(11):2850-2855. [doi:10.1021/es00011a022]

Chen, J.L., Al-Abed, S.R., Ryan, J.A., Li, Z., 2001. Effects of pH on dechlorination of trichloroethylene by zero-valent iron. *Journal of Hazardous Materials*, **83**(3):243-254. [doi:10.1016/S0304-3894(01)00193-5]

Choe, S., Lee, S.H., Chang, Y.Y., Hwang, K.Y., Khim, J., 2001. Rapid reductive destruction of hazardous organic compounds by nanoscale Fe^0. *Chemosphere*, **42**(4):367-372. [doi:10.1016/S0045-6535(00)00147-8]

Doong, R.A., Lai, Y.J., 2005. Dechlorination of tetrachloroethylene by palladized iron in the presence of humic acid. *Water Research*, **39**(11):2309-2318. [doi:10.1016/j.watres.2005.04.036]

Guan, B.H., Meng, Y.F., 2005. Dechlorination of chloroform in organic fluorine chemical plant wastewater with zero-valent iron. *The American Chemical Society*, **229**:U844.

Hara, J., Ito, H., Suto, K., Inoue, C., Chida, T., 2005. Kinetics of trichloroethene dechlorination with iron powder. *Water Research*, **39**(6):1165-1173. [doi:10.1016/j.watres.2004.12.011]

Kim, I.S., Park, J.S., Kim, K.W., 2001. Enhanced biodegradation of polycyclic aromatic hydrocarbons using nonionic surfactants in soil slurry. *Applied Geochemistry*, **16** (11-12):1419-1428. [doi:10.1016/S0883-2927(01)00043-9]

Ko, S.O., Schlautman, M.A., Carraway, E.R., 1998. Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. Experimental studies. *Environ. Sci. Technol.*, **32**(18):2769-2775. [doi:10.1021/es971075e]

Li, Z., Bowman, R.S., 1997. Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite. *Environ. Sci. Technol.*, **31**(8):2407-2412. [doi:10.1021/es9610693]

Li, Z., Jones, H.K., Bowman, R.S., Helferich, R., 1999. Enhanced reduction of chromate and PCE by pelletized surfactant-modified zeolite/zerovalent iron. *Environ. Sci. Technol.*, **33**(23):4326-4330. [doi:10.1021/es990334s]

Liu, M., Roy, D., 1995. Surfactant-induced interactions and hydraulic conductivity changes in soil. *Waste Management*, **15**(7):463-470. [doi:10.1016/0956-053X(95)00046-3]

Lookman, R., Bastiaens, L., Borremans, B., Maesen, M., Gemoets, J., Diels, L., 2004. Batch-test study on the dechlorination of 1,1,1-trichloroethane in contaminated aquifer material by zero-valent iron. *J. Contam. Hydrol.*, **74**(1-4):133-144. [doi:10.1016/j.jconhyd.2004.02.007]

Mukerjee, P., Mysels, K.J., 1971. Critical Micelle Concentrations of Aqueous Surfactant Systems. US Department of Commerce, US Government Printing Office, Washington, DC.

Partearroyo, M.A., Alonso, A., Goni, F.M., Tribout, M., Paredes, S., 1996. Solubilization of phospholipid bilayers by surfactants belonging to the triton X series: effect of polar group size. *Journal of Colloid and Interface Science*, **178**(1):156-159. [doi:10.1006/jcis.1996.0103]

Qin, J., Zhang, Q., Chuang, K.T., 2001. Catalytic wet oxidation of *p*-chlorophenol over supported noble metal catalysts. *Applied Catalysis B Environmental*, **29**(2):115-123. [doi:10.1016/S0926-3373(00)00200-9]

Rosen, M.J., 1989. Surfactants and Interfacial Phenomena, 2nd Ed. John Wiley & Sons, New York, p.431.

Sayles, G.D., You, G., Wang, M., Kupferle, M.J., 1997. DDT, DDD, and DDE dechlorination by zero-valent iron. *Environ. Sci. Technol.*, **31**(12):3448-3454. [doi:10.1021/es9701669]

Shoemaker, S.H., 1995. Permeable Reactive Barriers. *In*: Rumer, R.R., Mitchell, K. (Eds.), Assessment of Barrier Containment Technologies. International Containment Technology Workshop, Baltimore Maryland, p.301-353.

Tamara, M.L., Butler, E.C., 2004. Effects of Iron Purity and Groundwater Characteristics on Rates and Products in the Degradation of Carbon Tetrachloride by Iron Metal. *Environ. Sci. Technol.*, **38**(6):1866-1876. [doi:10.1021/es0305508]

Tratnyek, P.G., Scherer, M.M., Deng, B., Hu, S., 2001. Effects of natural organic matter, anthropogenic surfactants, and model quinones on the reduction of contaminants by zero-valent iron. *Water Research*, **35**(18):4435-4443. [doi:10.1016/S0043-1354(01)00165-8]

Zhang, P., Tao, X., Li, Z., Bowman, R.S., 2002. Enhanced perchloroethylene reduction in column systems using surfactant-modified zeolite/zero-valent iron pellets. *Environ. Sci. Technol.*, **36**(16):3597-3603. [doi:10.1021/es015816u]