



## Solubilization and degradation of perchloroethylene (PCE) in cationic and nonionic surfactant solutions

Sivaram Harendra<sup>1</sup>, Cumaraswamy Vipulanandan<sup>2,\*</sup>

1. Department of Energy, National Energy Technology Laboratory, 1450 Queens Avenue SW, Albany, OR 97321, USA.

E-mail: [ps.harendra@yahoo.com](mailto:ps.harendra@yahoo.com)

2. Civil and Environmental Engineering, University of Houston, N107 Engineering Bldg. 1, Houston, TX 77204, USA

Received 05 October 2010; revised 28 January 2011; accepted 16 February 2011

### Abstract

Solubilization of perchloroethylene (PCE) in a nonionic (Triton X-100) and a cationic (cetyltrimethylammonium bromide (CTAB)) surfactant solutions and the degradation of surfactant solubilized PCE using fine to nanosize Fe and bi-metallic Fe-Ni particles were investigated. Micelle partition coefficients ( $K_m$ ) and molar solubility ratio (MSR) for PCE in 10 g/L of surfactant solutions have been quantified and the solubility of PCE (100 mg/L in water) in the surfactant solutions increased by about ten fold. Of the two surfactants studied, Triton X-100 solubilized the higher amount of PCE per gram of surfactant. To degrade solubilized PCE, both iron and bi-metallic Fe-Ni particles were used in continuously stirred batch reactors. The iron and bi-metallic particles were synthesized using the solution method and the particles were characterized using the SEM, EDS, TEM and XRD. The PCE solubilized up to 500 mg/L in both surfactant solutions were totally degraded at various rates by 200 g/L of bi-metallic Fe-Ni particles in less than 20 hr, which is the highest concentration of PCE degraded in the shortest time compared to data in the literature. The degradations of PCE solubilized in surfactant solutions were represented by nonlinear kinetic relationships which depended on the type of surfactant used for solubilizing the PCE.

**Key words:** Fe-Ni particles; perchloroethylene (PCE); solubilization; degradation

DOI:10.1016/S1001-0742(10)60576-1

**Citation:** Harendra S, Vipulanandan C, 2011. Solubilization and degradation of perchloroethylene (PCE) in cationic and nonionic surfactant solutions. *Journal of Environmental Sciences*, 23(8): 1240–1248

### Introduction

The chlorinated solvent group is one of the most frequently detected volatile organic carbon (VOC) groups in the groundwater aquifers in the United States (USGS, 2002; Hunkeler et al., 1999). Contamination of groundwater with chlorinated solvents is a common environmental problem and it is a challenge to treat it using the currently available technologies. As a nonaqueous phase, chlorinated solvents spread in complex patterns in heterogeneous aquifers over long time periods. Furthermore, there are often multiple sources of chlorinated solvents in industrial areas (USGS, 2002; Hunkeler et al., 1999). High levels of perchloroethylene (PCE) when inhaled can cause unconsciousness, headache, sleepiness, confusion and adversely affect the liver and kidney (Bengt, 2003). Because of its lower solubility, immiscibility, relatively slower rates of dissolution and high density it is extremely difficult to remedy PCE (Chu, 2003). One important factor that has to be considered in degrading PCE is that it can break down into other hazardous components (Disfento et al., 1992).

PCE can be transformed by reductive dehalogenation to trichloroethylene, dichloroethylene, and vinyl chloride (Arvind and Pradeep, 2008; Burris et al., 1995; Boutonnet et al., 1982; Disfento et al., 1992; Hwang and Batchelor., 2002). The use of zerovalent iron for *in situ* degradation of chlorinated solvent contaminated ground waters has been investigated by many researchers (Gillham and Hannesin, 1994; Kumar and Mittal, 1999; Lee et al., 1999; Wilcoxon and Provencio, 1999; Jovanovic et al., 2005).

Research over the past decade has shown that the use of surface active agents (surfactants) has the potential to increase the rate of remediation of ground water contaminated with nonpolar organic pollutants (Soga et al., 2004; Vipulanandan and Ren, 2000). At concentrations above critical micelle concentration (CMC), surfactants, with the formation of micelles, can increase the apparent water solubility of organic pollutants. Surfactants have long been used to change the surface or interfacial properties to enhance the solubility (Ren et al., 1998; Alessi and Zhaohui, 2001). In a recent study, it was shown the sodium dodecyl sulfate (SDS) and biosurfactant can be used to enhance the solubility of PCE (Harendra and Vipulanandan, 2008; Milton et al., 1999; Nishikido et al., 1991; Srinivas et al.,

\* Corresponding author. E-mail: [cvipulanandan@uh.edu](mailto:cvipulanandan@uh.edu)

2003).

In this study a cationic surfactant (cetyl trimethyl ammonium bromide (CTAB)) and non ionic surfactant (Triton X-100) were selected to solubilize PCE. Triton X-100 has been commonly used in number of field studies (Dipak and James, 1997; Peter and James, 2007). It has been shown that cationic surfactants play a role in PCE reduction. Zerovalent iron (ZVI) has been shown to be effective for degradation of chlorinated compounds in water and has been studied extensively (Zhaohui et al., 1999; Xu and Dibakar, 2007). Iron is capable of degrading a wide range of organic components such as chlorinated aromatics, nitro aromatics, azo dyes and chlorinated aliphatics (Hariharan, 1996; Joos et al., 1990; Li et al., 2003; Li and Vipulanandan, 2006; Linda et al., 2005; Rosane and Monoel, 2004). Although degradation of highly chlorinated methanes is fast, the degradation of chlorinated ethenes is relatively slow. Thus, efforts have been made to increase the reaction rate of chlorinated solvents with ZVI by combining ZVI with other metals such as Ni or Pd. Iron is oxidized more rapidly when it is attached to a less active (noble) metal (Pd, Ag, Cu, Co, Ni) and hence the transformation of environmental contaminants can be enhanced by coupling iron to a noble metal (Harendra and Vipulanandan, 2008). The iron-noble metal couple essentially creates numerous galvanic cells wherein iron serves as the anode and becomes preferably oxidized. Meanwhile, the noble metal (cathode) is protected and remains unchanged. Studies also suggested that noble metals such as palladium and nickel can promote dechlorination through catalytic functions such as hydrogenation (Chen and Wu, 2000; Daniel and Wei, 2001; Kim and Vipulanandan, 2006; Yit-Hong et al., 2005; Zhang et al., 1998, 2002; Zhaohui and Willms, 2002)

The objective of this study was to investigate the solubilization of PCE in two types of surfactants and rapidly degrade it using Fe and Fe/Ni fine metallic particles. The effect of both surfactants (cationic and non ionic) on the rate and total solubilization of PCE in water solution was investigated. The degradation of surfactant solubilized perchloroethylene using fine Fe and Fe/Ni particles produced was quantified by the solution method. The degradation of PCE solubilized in both surfactant solutions was verified.

## 1 Materials and methods

A representative non ionic surfactant (Triton X-100) and a representative cationic surfactant (CTAB) were selected for the solubility study. Surfactants were obtained from Sigma-Aldrich (USA). Sodium borohydride powder (98%) was used for producing the iron nanoparticles using the solution method. Nickel(II) chloride hexa hydrate (Reagent plus), iron(II) sulfate heptahydrate (99%, certified A.C.S) and ferric chloride were used for the preparation of the Fe and Fe-Ni bi-metallic particle using the solution method.

### 1.1 Characterization

A CENCO DuNouy interfacial tensiometer (Central Scientific Co., USA) was used to measure the surface tension of the surfactant solution according to the ASTM

standards D 1331. The surface tension was measured to an accuracy of 0.1 dynes/cm.

pH changes during degradation were measured. Oxidation-reduction potential (ORP) was measured to determine the electron activity in the solutions. The pH/ORP was measured using an Eh/pH (model Orion 290 A) according to ASTM D 1498. The ORP was measured to an accuracy of  $\pm 0.2$  mV or  $\pm 0.05\%$  of reading, whichever was greater.

Dynamic light scattering (DLS) tests were performed using an ALV-5000 (ALV-Laser, Germany) with the green line ( $\lambda = 514.5$  nm) of an argon laser. The correlator (ALV-5000 Multiple Tau Digital Correlator) was equipped with 256 channels. A correlation equation was used to determine the correlation between the measurements of a fluctuating signal (Li and Vipulanandan, 2006). DLS was initially calibrated with nanoparticles of 5 and 60 nm. Based on the DLS measurements, the diameter of the micelles in the 5 g/L surfactant solutions were determined.

### 1.2 Synthesis of metal particles

Fine particles of Fe were prepared using the solution method where freshly prepared 0.4 mol/L solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (50 mL) was reacted with 2.3 g of  $\text{NaBH}_4$  in a flask under an inert atmosphere of nitrogen. After 15 min a homogeneous black color solution was formed. Also a vigorous gas evolution was observed almost instantly with the precipitation of a black jelly like solid. A magnetic stirrer was used to remove the black precipitates from the solution.

To produce the bi-metallic particles 6.15 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1.5 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  were mixed in 50 mL water using magnetic stirrer in 200 mL bottles for 30 min and 1.3 g  $\text{NaBH}_4$  was added into the solution for preparation of Fe-Ni bi-metallic particles. The entire system was kept under nitrogen atmosphere to prevent the oxidation of Fe-Ni bi-metallic particles.

SEM, EDS, TEM and XRD methods were used to verify the production and composition of Fe-Ni particles. The Fe-Ni particles synthesized using the solution method were characterized using the JEOL 2000FX scanning electron microscope (SEM) and Siemens D5000 powder X-ray diffraction (XRD). The bi-metallic particles were deposited on carbon grid for SEM characterization. The SEM micrographs of Fe-Ni bi-metallic particles are shown in Fig. 1. The particles were spherical and the particle size varied from 50 nm to 3  $\mu\text{m}$ . The TEM micrograph of Fe particles are shown in Fig. 2 and the particle size varied from 10 to 100 nm.

### 1.3 Solubility study

The solubility of PCE in surfactant solutions were investigated using up to 10 g/L of surfactant solutions in glass bottles (200 mL) with Teflon-lined screw caps. The magnetic stirrer was used for mixing the solutions at 750 r/min for an hour. The samples were transferred to 40 mL EPA vials for GC analysis. During the experiment bottles and vials were completely filled to ensure no loss due to vaporization of PCE. In the solubility study, the amount of

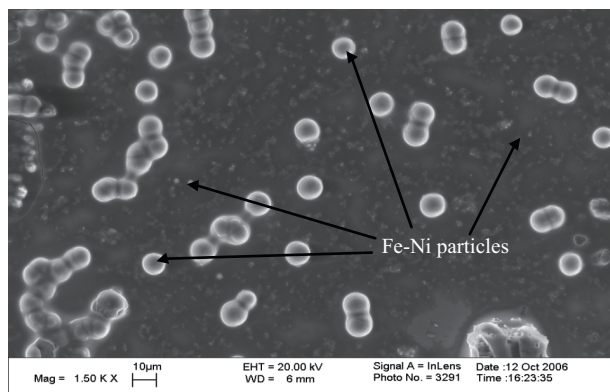


Fig. 1 SEM micrograph of Fe-Ni particles.

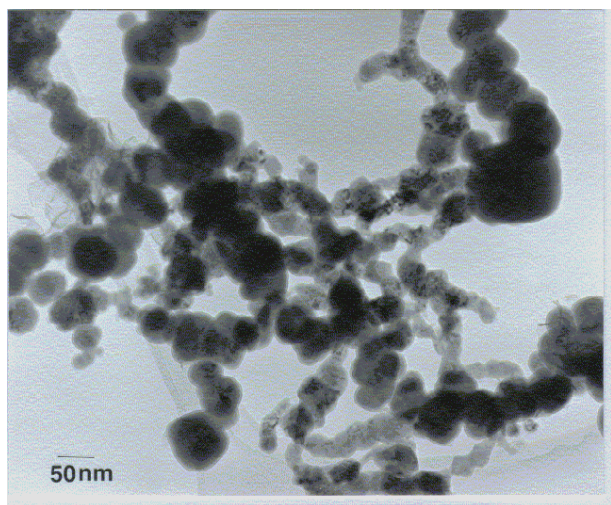


Fig. 2 TEM micrograph of Fe particles.

PCE was varied with surfactant concentrations. Triplicate samples were used for the analysis and average value was used in all the analyses. The PCE was solubilized using surfactant solutions up to 10 g/L.

#### 1.4 Degradation study

The PCE solubility was increased using surfactants for the degradation study. The surfactant solutions with PCE were prepared in 40 mL vials, and Fe and Fe-Ni bi-metallic particles were added. The vials were continuously agitated at 200 r/min. A gas chromatograph (Shimadzu GC-14A, Japan) with a flame ionization detector and a CR501 data processor was used for determining the PCE concentration. The stainless steel column (Alltech) was 6-ft long  $\times$  1/8-in outer diameter  $\times$  0.085-in inner diameter and detection temperature was set at 250°C. The injection volume of sample used for GC analysis was 2  $\mu$ L. The detection limit for PCE was 1 mg/L.

## 2 Results and discussions

The cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension at the liquid-air interface. The variation of surface tension for each surfactant with surfactant concentration is shown in Fig. 3a. The CMC for Triton X-100 and CTAB were 0.13 and 0.40 g/L, respectively. The surface tension at CMC

was 37 dynes/cm (Fig. 3). When two partially miscible liquids are brought into contact the interface thus formed possesses free surface energy which is numerically equal to the interfacial tension (Milton et al., 1999; Nishikido, 1991; Joos et al., 1990). The surface tension and interfacial tension of Triton X-100 and CTAB were observed by varying the concentrations of surfactant with solubilized PCE. The Triton X-100's surface tension and interfacial tension were lower compared to those of CTAB as shown in Fig. 3b. As the Triton X-100 concentration varied from 0 to 10 g/L, the surface tension and interfacial tension of Triton X-100 reduced from 72 to 30 dynes/cm and 13 to 7 dynes/cm, respectively, where as the surface tension and interfacial tension of CTAB reduced from 72 to 32 dynes/cm and 13 to 8 dynes/cm respectively. The average sizes of the Triton X-100 and CTAB surfactant micelle sizes were 4.8 and 7.1 nm, respectively.

### 2.1 Solubilization

Perchloroethylene was solubilized in various surfactants at room temperature. The concentration of PCE solubilized by various amounts of surfactant is shown in Fig. 4.

When a surfactant concentration was 10 g/L, Triton X-100 solubilized up to 1250 mg/L which was the maximum compared to CTAB which solubilized 1210 mg/L of PCE. Also results from the literature for a representative anionic surfactant (sodium dodecyl sulfate SDS) and a biosurfactant are compared in Fig. 4. Clearly Triton X-100 had the highest PCE solubility followed by the UH-biosurfactant, CTAB and SDS. Greater PCE solubility in Triton X-100 could be due to lower interfacial tension, smaller micelles

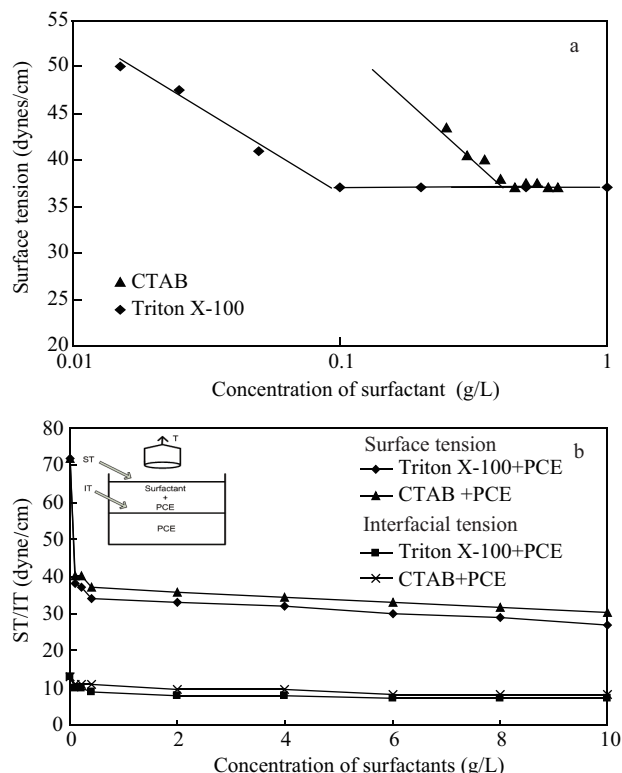


Fig. 3 Variation of surface tension (ST) with surfactant concentration (a), and the variation of surface tension and interfacial tension (IT) (with PCE) for maximum PCE solubilized surfactant solutions (b).

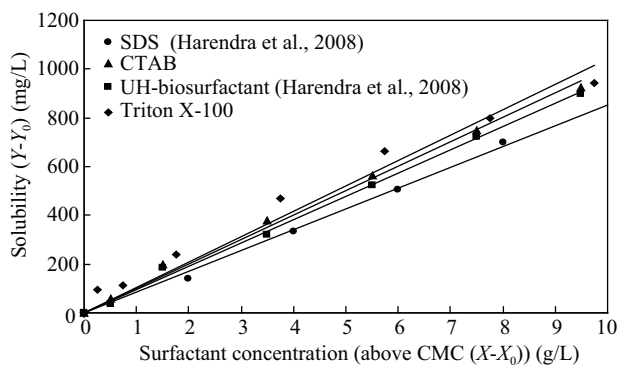


Fig. 4 PCE solubility in various surfactants.

and lower CMC or a combination of these factors.

## 2.2 Partition coefficient ( $K_m$ )

The solubility of PCE increased linearly with the surfactants concentration above CMC. Enhancement in solubility is related to micelles in the solution. The micelle partition coefficient ( $K_m$ ) represents the PCE in the micelles to the PCE in solution and can be defined as (Ren et al., 1998).

$$K_m(x) = \frac{Y - Y_0}{Y_0} \quad \text{for } (X > X_0) \quad (1)$$

where,  $Y$  is the molar concentration of solubilized PCE at a given molar concentration of surfactant ( $X$ ). The solubility of PCE increased linearly with the surfactants concentration above CMC.  $Y_0$  is the molar concentration of solubilized PCE at the CMC of the surfactant ( $X_0$ ). The micelle partition coefficient for Triton X-100 ( $K_m = 120$ ) was 4 times higher compared to CTAB ( $K_m = 30$ ).

## 2.3 Molar solubilization ratio (MSR)

The solubilization capacity of a surfactant can be represented as molar solubilization ratio (MSR) (Ren et al., 1998) (Eq. (2))

$$\text{MSR} = \frac{Y - Y_0}{X - X_0} \quad (2)$$

Hence, MSR is the slope of the solubility relationship above the CMC of the surfactants. Since the relationship between enhanced solubility ( $Y - Y_0$ ) and surfactant concentration above CMC ( $X - X_0$ ) (micelle concentration) was linear (Fig. 5a) and hence MSR was a constant for each surfactant. The maximum solubility ratio of Triton X-100 and CTAB were 0.34 and 0.21, respectively. The relationship between MSR and CMC of PCE is shown in Fig. 5b. As compared to trichloroethylene (TCE) (Srinivas, 2003), MSR values of PCE with the two surfactants were lower but showed similar decreasing trend with increasing CMC (Fig. 5b). Combining Eqs. (1) and (2) will result in the following relationship.

$$K_m = \text{MSR} \times \frac{X - X_0}{Y_0} \quad (3)$$

Since MSR was a constant for each surfactant,  $K_m$  was not a constant but linearly related to the excess surfactant concentration ( $X - X_0$ ) in moles as shown in Fig. 5c for CTAB and Triton X-100.

## 2.4 Degradation kinetics

At the end of PCE degradation, analysis of the nanoparticles showed that there was no PCE sorbed to the particles (in Section 2.5). Also the nanoparticles are highly reactive and hence it is assumed the PCE in the solution or even sorbed to the nanoparticle surface is degraded by the nanoparticles. Hence it was assumed that the initial rate of PCE degradation can be represented as follows:

$$\frac{dC}{dt} = -kC^n \quad (4)$$

where,  $C$  (mg/L) is concentration of PCE in the aqueous phase,  $k$  is dechlorination rate coefficient and  $n$  is the order of reaction. Investigating the test results indicated that some of the degradation kinetic was first order ( $n = 1$ ) and the others are not ( $n \neq 1$ ). Hence the degradation of PCE

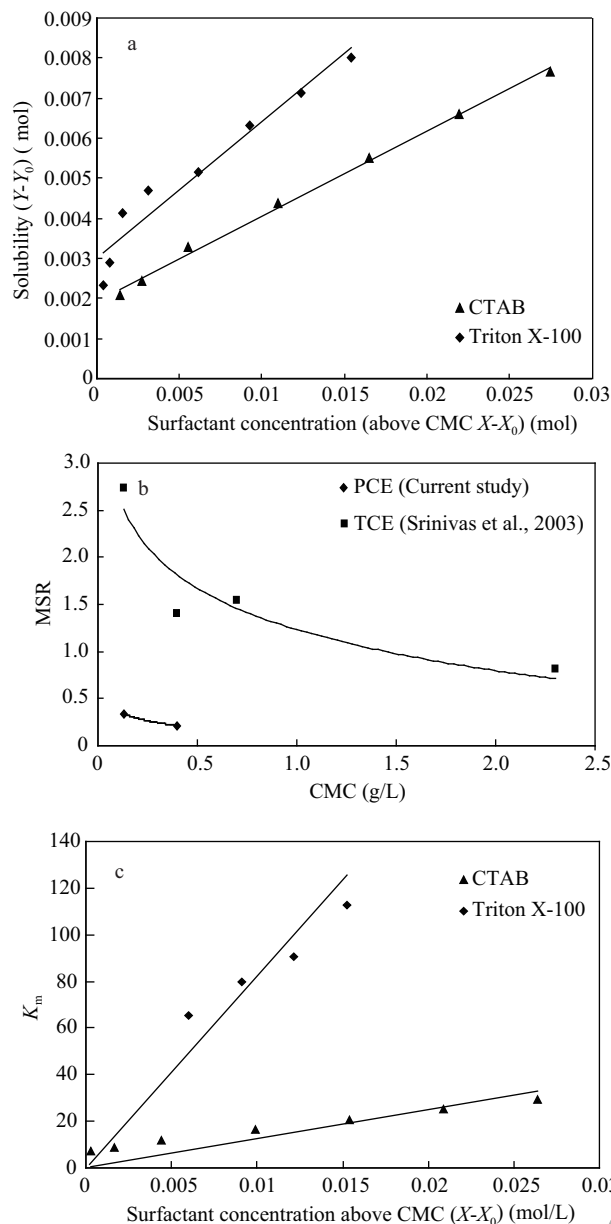


Fig. 5 (a) MSR, (b) relationship between MSR and CMC of various surfactants, and (c) variation of micelle partition coefficient  $K_m$  with surfactant concentration ( $X - X_0$ ).

for the first order ( $n = 1$ ) could be represented as follows:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (5)$$

And when  $n \neq 1$  it could be written as:

$$\ln\left(-\frac{dC}{dT}\right) = n\ln C + \ln k \quad (6)$$

where,  $C_0$  is the initial PCE concentration,  $n$  is the order of degradation. The dechlorination rate coefficient ( $k$ ) also depends upon bi-metallic loading. The degradation of PCE with Fe and Fe/Ni bi-metallic particles for other than first order reactions ( $n \neq 1$ ) is given as follows:

$$C_T = (-k(1-n)t + C_0^{(1-n)})^{(1/(1-n))} \quad (7)$$

#### 2.4.1 Iron particles

Based on preliminary study on rate and total degradation of PCE, 200 g/L of Fe particles was used for detailed investigation. The degradation of PCE solubilized in water (control), CTAB and Triton X-100 by Fe particles is shown in Fig. 6, and the results are summarized in Table 1. The degradation kinetics for three systems were all first order ( $n = 1$  in Eq. (4)). The lowest rate ( $0.003 \text{ hr}^{-1}$ ) for PCE was observed in control, and the highest rate ( $0.018 \text{ hr}^{-1}$ ) was observed in CTAB systems. Also the surfactant solution with higher amount of PCE was far better than the water only control system. This may be due to the micelles present in the surfactant system which could concentrate the PCE in the micelle and interact better with the Fe nanoparticles.

#### 2.4.2 Iron nickel particles

Iron-nickel particles prepared by the solution method showed faster degradation of PCE than the Fe particles

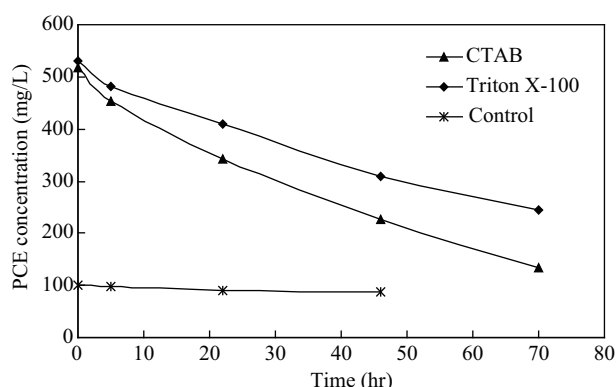


Fig. 6 PCE degradation using Fe metal particles (200 g/L) produced from the solution method.

Table 1 PCE Degradation constants for Fe particles

Surfactant	PCE (mg/L)	PCE degraded	Degradation rate ( $\text{hr}^{-1}$ )	$R^2$
CTAB (2.5 g/L)	517	54% (71 hr)	0.018	0.99
Triton X-100 (1.5 g/L)	531	74% (70 hr)	0.011	0.99
Control	100	27% (71 hr)	0.003	0.89

Fe particle: 200 g/L.

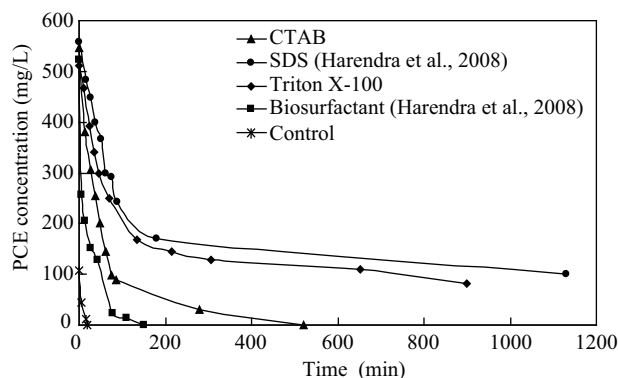


Fig. 7 PCE degradation using Fe-Ni particles (200 g/L) produced from the solution method.

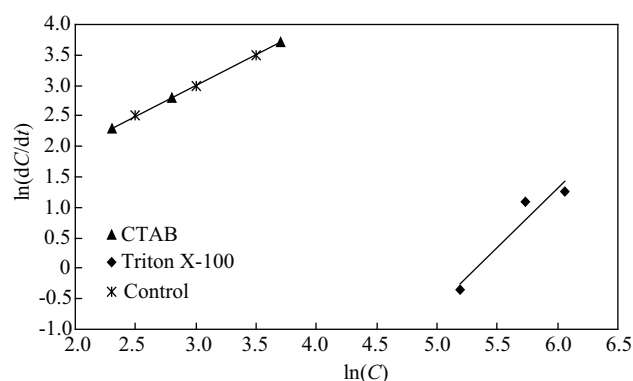


Fig. 8 Verification of order of degradation of PCE solubilized in surfactants.

prepared by the solution method. PCE degradation by Fe-Ni fine to nanoparticles is shown in Fig. 7. The natural logarithm of  $C/C_0$  as a function of time for the PCE degradation relationship was linear with water and CTAB but not with Triton X-100 (Fig. 8), indicating that the reaction was not pseudo first-order. The reaction order with respect to  $C_T$  can be determined using Eq. (7). The reaction orders of PCE degradation with respect to different surfactants are summarized in Table 2. PCE solubilized without surfactant and PCE solubilized in CTAB surfactant showed first order degradation kinetics. PCE solubilized in Triton X-100 surfactant had the reaction order of 1.93 (Table 2). Performance of Triton X-100 was comparable to SDS, while CTAB was better than SDS but was not as good as the UH-biosurfactant (Harendra, 2008). The rate and time for total degradation of PCE with Fe-Ni particles was far better than that with Fe nanoparticles. Compared to Triton X-100 solution, the CTAB solution with PCE was better in the rate and total degradation of solubilized PCE. Hence larger micelles in CTAB solution performed better than the smaller micelles in the Triton X-100 solution, opposite of what was observed with solubility.

#### 2.4.3 Iron nickel particle transformation

The EDS analysis was done for Fe-Ni bi-metallic particle before and after PCE degradation. The elemental composition of Fe and Ni were 68.35% and 27.74% before degradation which was approximately 3:1 ratio as predicted in the Eq. (2). After the PCE degradation the Fe, Ni and O atomic percentage was 25.50%, 13.96% and 53.82% respectively (Table 3). The simplified Fe:Ni:O ratio was



**Table 2** PCE degradation order and reaction constants for Fe-Ni particles

Surfactant	PCE (mg/L)	PCE degraded	Degradation constant (hr <sup>-1</sup> )	Reaction order	R <sup>2</sup>
CTAB (2.8 g/L)	545	100% (8.7 hr)	0.021	1.00	0.99
Triton X-100 (1.5 g/L)	510	85% (15 hr)	0.000034	1.93	0.92
Control	100	100% (20 min)	0.15	1.00	0.99

Fe-Ni particle: 200 g/L

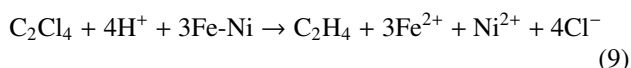
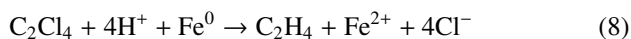
**Table 3** Elemental composition of the Fe-Ni particle (EDX analysis)

	Element composition (%)		Atomic composition (%)	
	Before	After	Before	After
S	2.5	3.37	4.3	3.51
Cl	1.41	3.41	2.19	3.21
Fe	68.35	42.66	67.46	25.50
Ni	27.74	24.54	26.05	13.96
O	0	26.02	0	53.82

2:1:4. This confirms the formation of Fe<sub>2</sub>O<sub>3</sub> and NiO as the degradation products. It also showed that Ni acted as a catalyst in this process where the element compositions of Ni before and after degradation of PCE were 27.74% and 24.54%, respectively. Hence, Ni acted as catalyst and enhanced the surface properties of Fe particles to increase the activation sites. This led to faster degradation of PCE.

## 2.5 Residual analysis

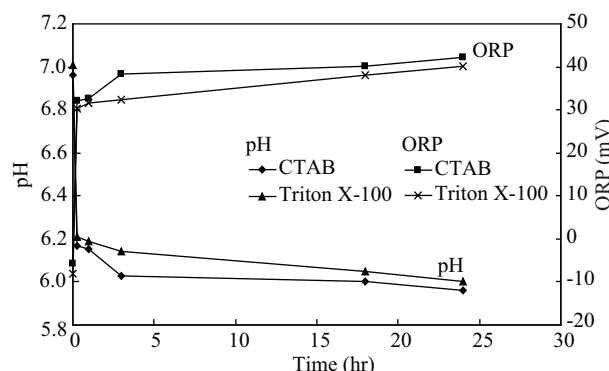
In order to verify the degradation of PCE, few tests were performed (PCE solubilized in CTAB) to evaluate the residual solutions and the transformation of the Fe-Ni particles (Tables 3 and 4). The PCE degradation by Fe and Fe-Ni particles can be represented as follows:



Hence there could be H<sup>+</sup> and Cl<sup>-</sup> present in the residual solution and must be verified.

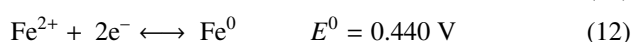
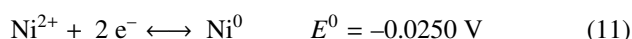
After the degradation of PCE, the solution was centrifuged and Fe-Ni particles were removed from the solution. The centrifuged solution was titrated with AgNO<sub>3</sub> to determine the presence of Cl<sup>-</sup>. Addition of AgNO<sub>3</sub> resulted in a precipitate, which was centrifuged and dried by heating the precipitate to 100°C for 20 min. XRD analysis of the precipitate showed the presence of AgCl. Based on the weight of AgCl, the amount of Cl<sup>-</sup> in the solution was estimated and the amount deviated by less than 5% based on the amount of Cl<sup>-</sup> estimated from Eq. (9). Gas chromatography analysis of the solution before and after the degradation showed that PCE peak was completely reduced indicating that PCE was reduced by Fe-Ni particles. No other peaks were observed.

The pH decreased from 6.96 to 5.96 for CTAB solubilized PCE whereas from 7.01 to 6.00 for Triton X-100 (Fig. 9) which indicates H<sup>+</sup> is produced during dehalogenation, as indicated in Eq. (9). The ORP increased from -5.7 to 42.3 mV for CTAB solubilized PCE whereas from -8.2 to 40.1 mV for Triton X-100 (Fig. 9) which indicated that the electrons are consumed during the reaction and

**Fig. 9** Variation of pH, oxidation-reduction potential (ORP) during surfactant degradation of PCE by 200 g/L of Fe-Ni bimetallic particles.

oxidation of iron takes place during the reaction as indicated by the oxidation of the Fe-Ni particles (Table 3). Other verification methods are shown in Table 4.

Figure 10 shows a schematic image of an emulsion droplet. Since the exterior oil membrane of the emulsion particles has hydrophobic properties similar to that of dense non aqueous phase liquids, the emulsion is miscible with the DNAPL. The partial standard reduction potentials ( $E^0$ ) of aqueous ion at 25°C are listed (Li et al., 2003):

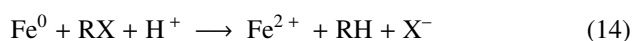


This makes Fe<sup>0</sup> a reducing agent reactive to many redox-labile substances including hydrogen ions, carbonate, sulfate, nitrate, and oxygen. Alkyl halides (RX) can also be reduced by iron. In the presence of a proton donor such as water, they typically undergo reductive dehalogenation



Actually, there are three major reductants in an Fe<sup>0</sup>-H<sub>2</sub>O system: Fe<sup>0</sup>, Fe<sup>2+</sup>, and H<sub>2</sub>. The latter two are intermediate products of corrosion. These reductants suggest three general pathways that may contribute to dehalogenation of alkyl halides.

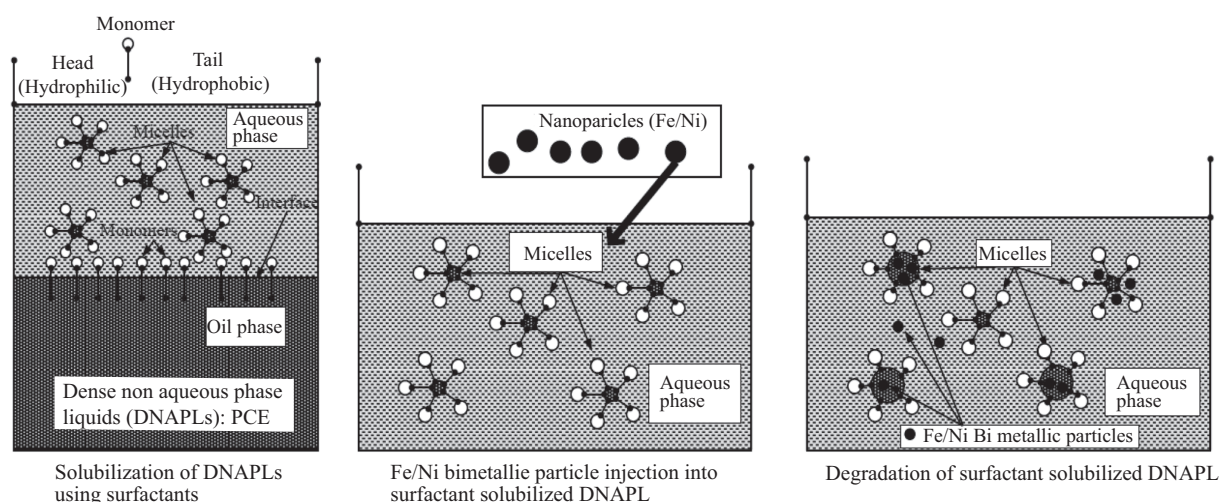
The first pathway (Fig. 11a) involves the Fe<sup>0</sup> directly and implies that reduction occurs by electron transfer from the Fe<sup>0</sup> surface to the adsorbed alkyl halide. Thus, this net reductive dehalogenation by Fe<sup>0</sup> can be represented as



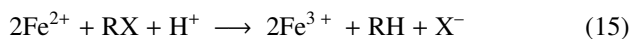
This general reaction represented by Eq. (10) is equivalent to iron corrosion with the alkyl halide serving as the oxidizing agent.

**Table 4** Verification of PCE degradation

Method	Phase examined	Result	Implications
Identify $\text{Cl}^-$ in the residual solution	Liquid	Titration with $\text{AgNO}_3$ solution produced $\text{AgCl}$ precipitate	$\text{Cl}^-$ was produced (over 90% of $\text{Cl}^-$ was accounted for in the precipitates)
ORP	Liquid	ORP increased from $-5.7$ to $42.3$ mV	Oxidation of Fe takes place
Acetone washing of Fe-Ni particles after degradation to determine PCE adsorption to the solid	Solid	PCE was not identified when Fe-Ni particles was washed with acetone	No measurable amount of PCE was adsorbed to the Fe-Ni particle
GC analysis to measure the by products	Liquid	PCE peak was not obtained during the GC analysis	PCE was completely degraded.
Sudan dye	Liquid	No color change	No PCE present

**Fig. 10** Schematic diagram of solubilization of DNAPL and degradation of surfactant solubilized DNAPL.

The second pathway involves the  $\text{Fe}^{2+}$ , which is an intermediate product of corrosion in aqueous systems (Fig. 11b), which can be represented by



Dissolved  $\text{Fe}^{2+}$  is a reductant capable of causing dehalogenation of some alkyl halides, although these reactions are generally quite slow. The importance of this process is probably dictated by the ligands present in the system because speciation of ferrous iron significantly affects its strength as a reductant. Inner-sphere complexation of  $\text{Fe}^{2+}$  to metal oxides can create more reducing species, but it is uncertain whether these species can significantly influence rates of dehalogenation.

A third model for reductive dehalogenation by iron involves the  $\text{H}_2$  produced as a product of corrosion with water (Fig. 11c). In the absence of an effective catalyst,  $\text{H}_2$  is not a facile reductant, and this reaction will not contribute directly to dehalogenation. In fact, excessive  $\text{H}_2$  accumulation at the metal surface is known to inhibit the continuation of corrosion. Rapid dehalogenation by  $\text{H}_2$  is still possible if an effective catalyst is available. The surface of iron, its defects, or other solid phases present in the system could provide this catalysis. Determining the relative importance of these three dehalogenation pathways will be essential for predicting field performance of iron-based materials.

From the above three pathways, it can be seen that the dehalogenation reaction of halogenated contaminants is surface-mediated. Increasing the surface area of the iron (by reducing the size of iron filings) increases the rate of reduction. At the same time, iron also undergoes redox reactions with dissolved oxygen and water, so it is important that these reactions are sufficiently slow during the remediation process (Zhang et al., 1998).

### 3 Conclusions

In this study, solubilization of PCE in cationic and non-ionic surfactant solutions and the degradation of high concentrations of PCE using fine to nanosize Fe and bi-metallic particles were investigated in continuous stirred batch reactors. Based on the experimental study and analyses of the data following can be concluded. (a) Surfactants increased the solubility of PCE in water by reducing the interfacial tension and producing micells on few nanometers. Triton X-100 had better solubilization of PCE compared to CTAB up to 10 g/L of surfactant concentration. As the CMC increased the hydrophobicity of the surfactants decreased and the PCE molar solubility ratio (MSR) decreased. (b) Fine bi-metallic Fe-Ni particles were more effective in degrading PCE as compared to Fe fine particles produced by the solution method. PCE solubilized up to 500 mg/L (5 times the water solubility)

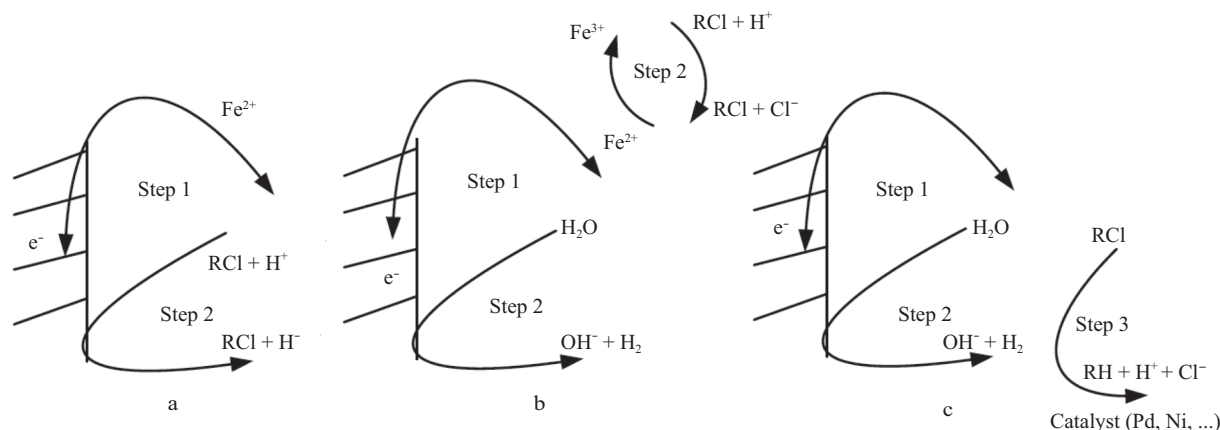


Fig. 11 Three pathways of dehalogenation reactions.

in CTAB was degraded faster by the fine bi-metallic Fe-Ni particles as compared to Triton X-100. This showed that the cationic surfactant enhanced the degradation of PCE. Degradation reaction in CTAB was represented by a first order kinetic relationship. Fe-Ni bi-metallic particles produced by the solution method was far more effective in degrading PCE solubilized in water and surfactant solutions. (c) Degradation of PCE, solubilized in Triton X-100, with Fe-Ni bi-metallic was not of the first order degradation. The rate and total degradation of PCE in the surfactant solution was also influenced by the type of surfactant. (d) The micelle partition coefficient ( $K_m$ ) was not a constant but was linearly related to the excess surfactant concentration (in moles) because MSR was a constant for each of the surfactants investigated in this study.

### Acknowledgments

This study was supported by the Center for Innovative Grouting Materials and Technology (CIGMAT) at the University of Houston with funding from the Texas Hazardous Waste Research Center and Texas Higher Education Coordinating Board (THECB). The contents do not necessarily reflect the views and policies of the funding agencies.

### References

- Alessi S, Zhaohui L, 2001. Synergic effect of cationic surfactants on Perchloroethylene degradation by zerovalent iron. *Environmental Science and Technology*, 35: 3713–3717.
- Arvind K, Pradeep K, 2008. Occurance of anionic surfactants in treated sewage: Risk assessment to aquatic environment. *Journal of Hazardous Materials*, 160: 362–370.
- Bengt E, 2003. Iron materials for the remediation of DNAPL polluted ground water. [www.lwr.kth.se/ Publikationer/PDF/Files/AMOV\\_EX\\_2001\\_10.pdf](http://www.lwr.kth.se/Publikationer/PDF/Files/AMOV_EX_2001_10.pdf).
- Boutonnet M, Kizling J, Stenius P, 1982. The preparation of monodisperse colloidal metal particles from micro emulsions. *Colloids and Surfaces*, 5: 209–225.
- Burris R, Campbell J, Manoranjan S, 1995. Sorption of trichloroethylene and tetra-chloroethylene in a batch reactive metallic iron- water system. *Environmental Science and Technology*, 29: 2850–2855.
- Chen H, Wu H, 2000. Synthesis of nickel nano particles in water in oil micro emulsions. *Chemistry of Materials*, 12: 1354–1360.
- Chu W, 2003. Remediation of contaminated soils by surfactant aided soil washing. *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management*, 7(1): 19–24.
- Daniel W, Wei Z, 2001. Field assessment of nanoscale bimetallic particles for groundwater. *Environmental Science and Technology*, 35: 4922–4926.
- Dipak S, James A, 1997. Enhanced trichloroethylene desorption from long term contaminated soil using Triton X-100 and pH increase. *Environmental Science and Technology*, 1(31): 1910–1915.
- Distefano T, Gossett J, Zinder S, 1992. Hydrogen as an electron donor for dechlorination of tetrachloroethene by an anaerobic mixed culture. *Applied and Environmental Microbiology*, 58: 3622–3629.
- Gillham K, Hannesin O, 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Groundwater*, 32: 958–967.
- Harendra S, Vipulanandan C, 2008. Degradation of high concentrations of PCE solubilized in SDS and biosurfactant with Fe/Ni bi-metallic particles. *Colloids and Surface A: Physicochemical and Engineering Aspects*, 322: 6–13.
- Hariharan S, 1996. Production of biosurfactant from used vegetable oil and use for lead precipitation. Masters Thesis. Department of Civil and Environmental Engineering, University of Houston, Texas.
- Hunkeler D, Arevena R, Butler B, 1999. Monitoring microbial dechlorination of tetrachloroethylene (PCE) in groundwater using compound specific stable carbon isotopes ratios: Microcosm and field studies. *Environmental Science and Technology*, 33: 2733–2738.
- Hwang I, Batchelor B, 2002. Reductive dechlorination of Tetrachloroethylene by Fe(II) in cement slurries. *Environmental Science and Technology*, 34: 5017–5022.
- Joos P, Vollhardt D, Vermeulan M, 1990. Interfacial tension of SDS solutions at the hexane-water interface. *Langmuir*, 6: 524–529.
- Jovanovic G, Plazl P, Sakrithichai P, Al-Khaldi K, 2005. Dechlorination of p-chlorophenol in a microreactor with bimetallic Pd/Fe catalyst. *Industrial & Engineering Chemistry Research*, 44: 5099–5106.
- Kim J, Vipulanandan C, 2006. Removal of lead from contaminated water and clay soil using a biosurfactant. *Journal of Environmental Engineering*, 132(7): 857–865.
- Kumar P, Mittal K, 1999. Hand Book of Micro Emulsion Science and Technology. Marcel-Dekker, New York.



- Lee H, Lee W, Furubayashi T, 1999. A comparison of coprecipitation with microemulsion methods in the preparation of magnetite. *Journal of Applied Physics*, 85: 5231–5233.
- Li F, Vipulanandan C, Mohanty K, 2003. Microemulsion solution approaches to nanoscale iron production for degradation of TCE. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 223: 103–112.
- Li F, Vipulanandan C, 2006. Characterization of  $\text{Y}_2\text{BaCuO}_5$  nanoparticles synthesized by nano-emulsion method. *Journal of Nanoparticle Research*, 10: 1007–1016.
- Linda M A, Chad D D, Ernest H J, Kim H F, Tohren K C G, Lawrence L D et al., 2005. Pilot scale demonstration of surfactant enhanced PCE solubilization at the Bachman road site 1, site characterization and test design. *Environmental Science and Technology*, 39: 1778–1790.
- Milton J, Joann H, Lesley D, 1999. Aberrant aggregation behaviour in cationic Gemini surfactants investigated by surface tension, interfacial tension and fluorescence methods. *Langmuir*, 15: 7340–7346.
- Nishikido N, 1991. Thermodynamic equations expressing the synergistic solubilization effect by surfactant mixtures. *Langmuir*, 7: 2076–2082.
- Peter R, James A, 2007. Fourier Transform Infrared Spectroscopy. Wiley-Interscience. ISBN No: 9780471194040.
- Ren X, 1998. Application of a biosurfactant in naphthalene, phenanthrene and TCE remediation, Ph.D Thesis. University of Houston, TX.
- Rosane C, Manoel M, 2004. Natural attenuation of chlorinated organics in a shallow sand aquifer. *Journal of Hazardous Materials*, 110: 129–137.
- Soga K, Page J, Illangasekare T, 2004. A review of NAPL source zone remediation efficiency and the mass flux approach. *Journal of Hazardous Materials*, 110: 13–27.
- Srinivas B, 2003. Surfactant enhanced solubilization and degradation of TCE using bimetallic iron-nickel particles produced by solution method and foaming method. Masters Thesis. University of Houston, Dept of Civil and Environmental Engineering.
- USGS, 2002. Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells, Circular 1292. National Water-Quality Assessment Program. U.S. Department of Interior and U.S. Geological Survey.
- Vipulanandan C, Ren X, 2000. Enhanced solubility and biodegradation of naphthalene with biosurfactant. *Journal of Environmental Engineering*, 126(7): 629–634.
- Wilcoxon P, Provencio P, 1999. Use of surfactant micelles to control the structural phase of nanosized iron clusters. *The Journal of Physical Chemistry B*, 103: 9809–9812.
- Xu J, Dibakar B, 2007. Fe/Pd Nanoparticle immobilization in microfiltration membrane pores: Synthesis, characterization and application in the dechlorination of polychlorinated biphenyls. *Industrial & Engineering Chemistry Research*, 46: 2348–2359.
- Yit-Hong T, Eric G, Dibakar B, 2005. Role of Ni/Fe nanoparticle composition on the degradation of trichloroethylene from water. *Industrial & Engineering Chemistry Research*, 44: 7062–7070.
- Zhaohui L, Kirk J, Robert S, Richard H, 1999. Enhanced reduction of chromate and PCE by palletized surfactant-modified zeolite/zerovalent iron. *Environmental Science and Technology*, 33: 4326–4330.
- Zhang P F, Tao X, Li Z H, Bowman S, 2002. Enhanced perchloroethylene reduction in column systems using surfactant modified zeolite/zerovalent iron pellets. *Environmental Science and Technology*, 36: 3597–3603.
- Zhang W, Wang C, Lien H, 1998. Treatment of chlorinated organic contaminants with nanoscale bi-metallic particles. *Catalysis Today*, 40: 387–395.
- Zhaohui L, Willms C, 2002. Rate and pathway changes in PCE dechlorination by zerovalent iron in the presence of cationic surfactant. *Proceedings of Remediation of Chlorinated and Recalcitrant Compounds*, 2C-35.