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Dechlorination of tetrachloroethylene in water using stabilized nanoscale iron and palladized iron particles

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ABSTRACT

Chlorinated solvents such as tetrachloroethylene (PCE) in aquifers should be remediated due to their toxicity that limited the use of groundwater resources. Nanoscale zero-valent iron (NZVI) and palladized/iron (Pd/Fe) bimetallic particles were synthesized and employed to react with PCE in water to investigate its degradation behaviors. Batch tests were conducted in a 1 L serum bottle under airtight and anaerobic conditions with parameters of Pd mass contents, temperature, pH, and dispersant. The results showed that specific reaction rate constants (k_{SA}) of $5\,\mathrm{mg\,L^{-1}}$ PCE degraded by metal particles at 30˚C in the absence of dispersant enhanced with higher Pd mass contents on the Pd/Fe particles. Degradation rates of PCE increased as the reaction temperature was raised from 20 to 40˚C. Carboxymethyl cellulose (CMC), a dispersant, enhanced the k_{SA} values of NZVI and 1:100 Pd/Fe particles by a factor of about 33 and 4 at 30˚C, respectively. The tests of pH control with buffer solution indicated that PCE degradation rates were promoted under acid and neutral conditions. Additionally, no chlorinated by-products were observed during the experimental period in each test. This study shows that effective dechlorination of PCE in water could be achieved by synthesized Pd/Fe and NZVI particles coupled with CMC dispersant.

Keywords: Reaction kinetics; Bimetallic; Dispersant; Dechlorination; Chlorinated solvent

1. Introduction

Hazardous organic compounds used in the industry possibly leak into the environment and further pollute the aquifers. Among many contaminated sites, chlorinated solvents, such as tetrachloroethylene (PCE) and trichloroethylene (TCE), were frequently detected in aquifers that limited the use of groundwater resources. Those solvents have been identified as the prior pollutants that should be remediated due to their toxicity and bioaccumulation. Therefore, it is necessary to develop an efficacious technology for the remediation of groundwater contaminated by chlorinated solvents.

Several researchers employed zero-valent iron (ZVI) for reductive dechlorination of chlorinated contaminants such as TCE [1–5], PCE [2,3],

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chlorinated ethylenes [6], and chlorinated methanes [7] in aquifer. Matheson and Tratnyek [7] reported in the Fe^0–H_2O system, among the major reductants of Fe^0, Fe^{2+}, and H_2, Fe^0 was dominant based on the dechlorination tests of $CC1_4$. Reduction of chlorinated compounds by Fe^0 occurs according to Eq. (1), two electrons transfer from Fe^0 to chlorinated contaminant [7].

$$Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \quad (1)$$

Chlorinated compounds are reduced by Fe^0 through two pathways: hydrogenolysis (a Cl^- replaced by an H^+) and reductive β-elimination (two Cl^- released) [3,6]. One of the major defects limiting the application of ZVI technology to chlorinated contaminants degradation is the formation and accumulation of lightly chlorinated by-products, such as vinyl chloride (VC), that may be more toxic than their parent compounds [8,9]. Therefore, many studies focusing on the improvement of ZVI capacity to degrade the chlorinated solvents have been developed [8–11]. Nanoscale ZVI (NZVI) particles with smaller particle sizes and larger specific surface area than commercial ZVI were synthesized to enhance the reactivity of Fe particles [12–17]. Wang and Zhang [17] prepared NZVI particles with a BET specific area of $33.5\,m^2\,g^{-1}$ to react with TCE and polychlorinated biphenyls (PCBs). Their results indicated that NZVI was more active than commercial ZVI. Besides another way to meliorate the reactivity of Fe particles is to synthesize the bimetallic complexes.

Bimetallic materials for the remediation of chlorinated contaminants have been newly developed. Studies were implemented with reduction of chlorinated solvents such as chlorinated methanes [18,19], chlorinated ethylenes [9,20–23], and chlorinated aromatics [9,24–26]. Muftikian et al. [19] carried out a series of batch experiments of palladized/iron (Pd/Fe) bimetallic particles reacted with some chlorinated methanes and ethylenes. The results showed that PCE was rapidly and effectively degraded by Pd/Fe particles. Similar conclusions were also drawn in other studies [18]. Therefore, application of bimetallic technology for the remediation of chlorinated contaminants is quite promising owing to their rapid and complete dechlorination potentials. However, due to the van der waals force and magnetic attraction, the nano metal particles bring together rapidly to form larger aggregates in water and lose their reactivity gradually. Recently, researchers utilized the polysaccharides, such as starch or carboxymethyl cellulose (CMC), as stabilizers to inhibit the aggregation of metal particles in solution. The results of their studies indicated that the stabilized Fe and Pd/Fe particles displayed greater reactivity than the nonstabilized ones for the degradation of chlorinated contaminants [27–31]. To evaluate the feasibility of dispersed technology integrated with commercial metal particles, the suspensions in this study were prepared by mixing CMC solution with already synthesized NZVI and nano Pd/Fe particles. The technology to prepare the metal suspensions in this study is different from that proposed by He and Zhao [28–30].

In this study, NZVI and nano Pd/Fe particles were synthesized and used to react with PCE in solution to investigate its degradation behaviors and reduction kinetics. The effects of several experimental parameters such as Pd mass content, temperature, dispersant, mass concentration of metal particles, and pH on PCE degradation were also evaluated. The results may provide some valuable information for further studies to develop an effective bimetallic permeable reactive barrier system for the remediation of aquifer contaminated by chlorinated solvents.

2. Materials and methods

2.1. NZVI and Pd/Fe preparations

NZVI particles were prepared by mixing 1:1 volume ratio of 0.50 M $NaBH_4$ and 0.28 M $FeSO_4{\cdot}7H_2O$ under intensive agitation: Fe particles formed according to Eq. (2) were filtered out [14]. The preparation process must be prompt and continuous to keep the NZVI particles fresh.

$$\begin{aligned} &2Fe^{2+}_{aq} + BH^-_{4(aq)} + 3H_2O_{(1)} \\ &\quad \rightarrow 2Fe^0_{(s)} + H_2BO^-_{3(aq)} + 4H^+_{(aq)} + 2H_{2(g)} \end{aligned} \quad (2)$$

Three types of Pd/Fe particles with various Pd loadings were synthesized by mixing the freshly prepared NZVI solution with $Pd(C_2H_3O_2)_2$ in ethanol solution to form 1:100, 1:250, and 1:500 mass ratio of Pd/Fe, that is, 10, 4, and 2 mg Pd/g Fe, respectively. Pd^{2+} was converted to Pd^0 and then deposited on the surface of Fe particles through the Eq. (3). The Pd/Fe particles were also filtered out [16].

$$Pd^{2+}_{(aq)} + Fe^0_{(s)} \rightarrow Pd^0_{(s)} + Fe^{2+}_{(aq)} \quad (3)$$

Suspensions of NZVI and nano Pd/Fe particles were prepared by utilizing CMC as a dispersant to compare their PCE degradation efficiency with the nonstabilized ones. The Milli-Q deionized water used for metal preparation and solution dilution was boiled to strip dissolved oxygen (DO). First, 1.5 g CMC was added into 200 mL boiled water and then stirred the mixture until the CMC completely dissolved (about 20 min). Then, 5 g freshly prepared metal (Fe or Pd/Fe) particles was mixed with CMC solution to form a suspension of 30% mass ratio of CMC to metal. Afterward, the suspension was vibrated with ultrasonics for 30 min under airtight condition. The metal particles and suspensions were prepared just before each batch test to keep them fresh and to maintain their reactivity.

2.2. Particle characterization

The metal particles prepared were dried in vacuum for 24 h via an Eyela FDU-1200 freeze dryer at room temperature and then sealed in brown bottle filled with nitrogen gas to avoid further oxidation of particles for particle characterization. Particle sizes of prepared NZVI and nano Pd/Fe were measured by a Beckman Coulter N5 particle diameter analyzer, and their BET specific surface area was determined by a Beckman Coulter SA3100 surface area analyzer using the nitrogen adsorption method at 77 K. Surface morphology and elements of the particles were examined through a Hitachi S-3000 N scanning electronic microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). SEM images were observed at beam energies of 15 kV and magnification of 18,000 times.

2.3. Batch experiments

Batch tests were conducted to investigate the capacity of laboratory-synthesized NZVI and Pd/Fe particles on dechlorination of PCE in solution. The water used for dilution was also boiled to strip away DO. Next, 1,000 mL of PCE solution was prepared in the reactor by diluting the stock solution to 5 mg L^{-1} and then NZVI (1, 2.5, and 5 g L^{-1}) or various mass ratio of Pd/Fe (1, 2.5, and 5 g L^{-1}) powders were added into solution with continuous stirring. Experiments were performed in a 1-L serum bottle under airtight and anaerobic conditions. The openings of serum bottle were sealed with screw-topped caps and parafilm during the test. Control tests (without addition of nanoparticles) were also carried out for comparisons. The suspensions of NZVI and nano Pd/Fe particles were also prepared by using CMC as a dispersant to compare their degradation efficiency with the nonstabilized ones. Samples were periodically collected by a polypropylene syringes attached with a stainless needle and then filtered through a 0.22-μm filters for further analysis. The total reaction time was set at 300 min for each test. The reaction temperature was maintained at 20 ± 1, 30 ± 1, or 40 ± 1℃ for each preset batch test. PCE and its potential chlorinated byproducts formed from PCE dechlorination processes including TCE, 1,1-dichloroethylene (1,1-DCE), cis-1,2-dichloroethylene (cis-1,2-DCE), tran-1,2-dichloroethylene (tran-1,2-DCE), and VC were monitored at various reaction time. Electric conductivity, pH, redox potential (ORP), and concentrations of Fe^{2+}, total Fe, Cl^{-} were also monitored during the experimental period. DO was also measured at the beginning and the end of the test.

2.4. Analysis methods

PCE, TCE, 1,1-DCE, cis-1,2-DCE, tran-1,2-DCE, and VC were detected via a HPLC (Hitachi L-7100) equipped with a RP-18 column (Mightsil) and a UV-vis detector (Hitachi L-7420). The UV wavelength was set at 245 nm for the detection of PCE and TCE, and 210 nm for 1,1-DCE, cis-1,2-DCE, tran-1,2-DCE, and VC. The mobile phase was 80% methanol and 20% water (v/v) for PCE and TCE, and 70% methanol and 30% water (v/v) for other compounds to separate them under various retention times. The flow rate was set at 1 mL min^{-1} for PCE and TCE, and 0.7 mL min^{-1} for other compounds. The detection limits of PCE, TCE, 1,1-DCE, cis-1,2-DCE, tran-1,2-DCE, and VC were 0.005, 0.020, 0.004, 0.028, 0.005, and 0.021 mg L^{-1}, respectively. Cl^{-} was also detected by a Dionex-120 ion chromatography equipped with a Dionex AS-12A column. The flow rate of the mobile phase containing 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$ was maintained at 1.5 mL min^{-1}. Concentrations of Fe^{2+} and total Fe were measured by a HACH DR-2400 spectrophotometer.

3. Results and discussion

3.1. Characteristics of synthesized NZVI and nano Pd/Fe particles

The average diameters of laboratory-synthesized NZVI and nano Pd/Fe particles measured by a particle diameter counter were between 102 and 111 nm that were larger than those ranged from 2.4 to 100 nm in the literature estimated by the images of SEM and transmission electron microscope [16,24,27–30]. However, in this study, the particle sizes measured by a particle diameter counter were much closer to the real sizes of metal particles present in the solution of batch reactor. Table 1 displayed that the BET-specific surface area increased with higher Pd mass loadings and

Table 1
Summary for the tests of 5 mg L^{-1} PCE degraded by NZVI and Pd/Fe particles

Particles (mass concentration)	Reaction temp. (℃)	CMC dispersant (%)	Specific surface area (m^2 g^{-1})	PCE removal ratio (%)	k_{obs} (h^{-1})	k_{SA} (L h^{-1} m^{-2})	r^2
1:100 Pd/Fe (5 g L^{-1})	30 ± 1	–	56	>99.9[a]	2.6	9.3×10^{-3}	0.94
1:250 Pd/Fe (5 g L^{-1})	30 ± 1	–	52	>99.9	1.6	6.2×10^{-3}	0.95
1:500 Pd/Fe (5 g L^{-1})	30 ± 1	–	46	>99.9	1.6	6.9×10^{-3}	0.97
1:100 Pd/Fe (2.5 g L^{-1})	30 ± 1	–	56	>99.9	1.5	10.7×10^{-3}	0.94
1:100 Pd/Fe (1 g L^{-1})	30 ± 1	–	56	93.9	0.6	10.7×10^{-3}	0.86
1:100 Pd/Fe (5 g L^{-1})	40 ± 1	–	56	>99.9	4.4	15.7×10^{-3}	0.96
1:100 Pd/Fe (5 g L^{-1})	20 ± 1	–	56	>99.9	1.9	6.8×10^{-3}	0.99
1:100 Pd/Fe (5 g L^{-1})	30 ± 1	30	56	>99.9	10.5	37.5×10^{-3}	0.90
1:100 Pd/Fe (1 g L^{-1})	30 ± 1	30	56	>99.9	2.0	35.7×10^{-3}	0.95
NZVI (5 g L^{-1})	30 ± 1	–	38	65.5	0.1	0.5×10^{-3}	0.69
NZVI (5 g L^{-1})	30 ± 1	30	38	>99.9	2.9	15.3×10^{-3}	0.95
NZVI (2.5 g L^{-1})	30 ± 1	30	38	>99.9	1.7	17.9×10^{-3}	0.95
NZVI (1 g L^{-1})	30 ± 1	30	38	94.3	0.6	15.8×10^{-3}	0.83

[a] The method detection limit and initial concentration of PCE were 0.005 and 5 mg L^{-1}, respectively. Therefore, the PCE removal ratio should be greater than 99.9% for the experiments that PCE was not detected at the end of test.

ranged between 38 and 56 m^2 g^{-1} that were close to the reported values (35–55 m^2 g^{-1}) [16,28]. From the SEM images, the surface of NZVI and Pd/Fe particles was chain-linked and rough (Fig. 1). Pd was identified on the bimetallic particles, and Fe was the primary element from the analysis of SEM-EDS.

3.2. Kinetics of PCE degradation

Assuming that the data in Fig. 2 follows the pseudo-first-order reaction kinetics, the observed pseudo-first-order reaction coefficient (k_{obs}) can be obtained by fitting the test data to Eq. (4) [15,27,28,30,32].

$$-\frac{dC}{dt} = k_{obs}C = k_{SA}a_s\rho_m C \tag{4}$$

where C is the PCE concentration in water (mg L^{-1}) at time t (h), k_{obs} is the observed pseudo-first-order reaction coefficient, k_{SA} is the specific reaction rate constant (L h^{-1} m^{-2}), a_s is the BET-specific surface area of metal particles (m^2 g^{-1}), and ρ_m is the mass concentration of the metal particles in the reactor (g L^{-1}).

As shown in Table 1, the k_{obs} values at 30℃ for the tests of 5 mg L^{-1} PCE with 5 g L^{-1} NZVI and 5 g L^{-1} nano Pd/Fe particles ranged 0.1–2.9 and 1.6–10.5 h^{-1}, respectively. The k_{obs} values at 30℃ of the tests for 5 mg L^{-1} PCE with 1 g L^{-1} dispersed NZVI and 1 g L^{-1} dispersed 1:100 Pd/Fe particles were 0.6 and 2.0 h^{-1}, respectively. Obviously, the Pd/Fe particles were more active than NZVI for the degradation

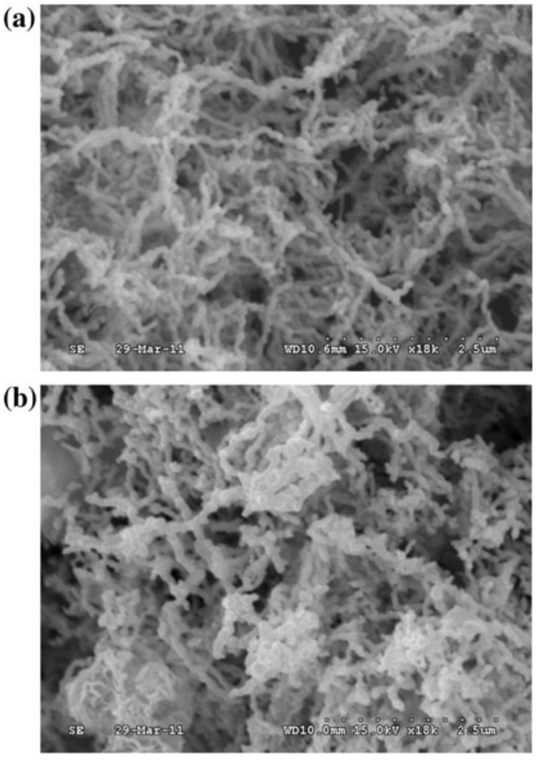

Fig. 1. Surface morphology of (a) NZVI; (b) 1:100 nano Pd/Fe particles (15 kV, 18000X).

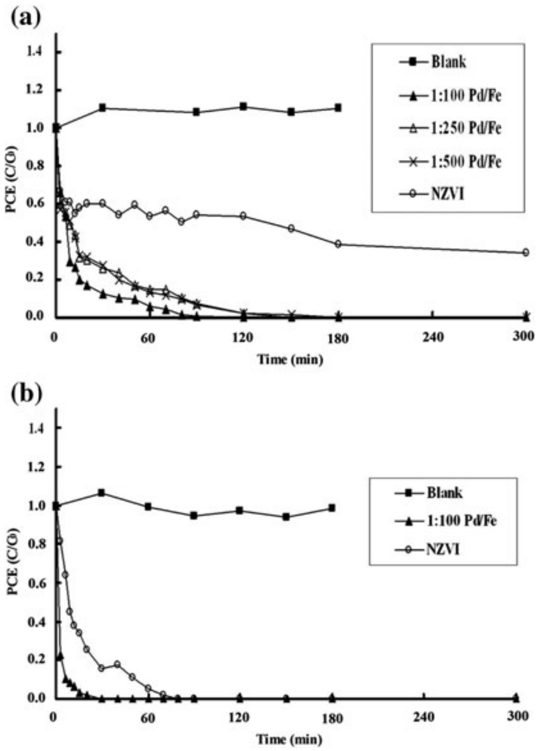

Fig. 2. Variations of PCE concentrations ($C_0 = 5\,mg\,L^{-1}$) with $5\,g\,L^{-1}$ (a) nondispersed; (b) CMC-dispersed NZVI or Pd/Fe at 30℃.

of PCE. Almost all k_{obs} values were well fitted to the pseudo-first-order model ($r^2 = 0.83$–0.99) except for the test of $5\,g\,L^{-1}$ NZVI without a dispersant ($r^2 = 0.69$). Fig. 2 shows that the tests using nano Pd/Fe particles yielded quicker and more complete PCE degradation than using NZVI. In the absence of dispersant (Fig. 2 (a)), PCE was completely removed after 180-min reaction in the tests with various Pd mass contents of $5\,g\,L^{-1}$ Pd/Fe, but only 65.5% PCE removal for NZVI test after 300-min reaction time. While in the presence of dispersant (Fig. 2(b)), PCE was completely removed by 1:100 Pd/Fe and NZVI, but the degradation rate of the former was higher than that of the latter. The k_{obs} value of PCE degradation with $5\,g\,L^{-1}$ dispersed 1:100 Pd-Fe bimetallic nanoparticles ($10.5\,h^{-1}$) was significantly higher than that with $5\,g\,L^{-1}$ nondispersed one ($2.6\,h^{-1}$) at 30℃. The results are similar to those using CMC as stabilizer to degrade para-nitrochlorobenzene (PNCB) [27] and to degrade TCE [30] with Pd-Fe bimetallic nanoparticles reported in the literatures. As shown in Table 1, the k_{obs} value of $10.5\,h^{-1}$ was observed the highest for the test of $5\,g\,L^{-1}$ 1:100 Pd/Fe with CMC dispersant resulting in a complete PCE degradation within 30 min.

3.3. Effect of Pd mass contents

For the purpose to further compare the dechlorination capacity of various metal particles to PCE, the k_{obs} values can be normalized to the specific surface area (a_s) and the mass concentration (ρ_m) of metal particles according to Eq. (5), where they then become no longer a_s and ρ_m specific.

$$k_{SA} = \frac{k_{obs}}{a_s \rho_m} \tag{5}$$

As shown in Table 1, PCE degradation capacity per unit surface area, k_{SA}, of 1:100 Pd/Fe (10 mg Pd/g Fe) was slightly greater than those of 1:250 (4 mg Pd/g Fe) and 1:500 Pd/Fe (2 mg Pd/g Fe) but much higher than that of NZVI at reaction temperature of 30℃ without addition of CMC. As shown in Fig. 2, the variations of residual PCE of 1:250 Pd/Fe mass contents were similar to those of 1:500 ones. Therefore, their k_{SA} values were close to each other. In the absence of dispersant, the k_{SA} values of $5\,g\,L^{-1}$ 1:100 and 1:250 Pd/Fe particles were 18.6 and 12.4 times higher than this of $5\,g\,L^{-1}$ NZVI. He and Zhao indicated that as Pd/Fe loadings were higher than 1:1,000, respectively. k_{SA} values on TCE degradation remained nearly unchanged [29]. Similar results were also observed that the increase in k_{obs} values became much less considerable as the Pd loading was raised more than 1 mg Pd/g Fe for microsacle Pd/Fe [33] and stabilized nanoscale Pd/Fe particles [27]. For the case of addition of dispersant, the k_{SA} values of 5 g and 1 g 1:100 Pd/Fe nanoparticles were nearly the same that were about 3.9 and 73 times higher than those of nondispersed and NZVI ones, respectively. In other words, the Pd-modified technology actually enhanced the degradation capacity of Fe particles to PCE in solution. He and Zhao [29] reported that the k_{obs} values of TCE degradation increased with higher Pd loadings (0, 1:2000, and 1:1,000 Pd/Fe) with 0.2 wt.% CMC dispersant. Dong et al. [27] also presented that the k_{obs} values of PNCB degradation also increased with higher Pd loadings with 0.8 wt.% CMC dispersant.

3.4. Effect of temperature

The experiments of PCE dechlorination with 1:100 Pd/Fe particles were conducted at temperatures of 20, 30, and 40℃. As shown in Fig. 3, $5\,mg\,L^{-1}$ PCE was effectively degraded by $5\,g\,L^{-1}$ 1:100 Pd/Fe particles. Complete removal of PCE was faster at 40℃ (within 60 min) than at 30℃ (within 120 min) and 20℃ (within 150 min). As shown in Table 1, the higher the reaction temperature, the larger the k_{SA} values were, that is, the faster the PCE was degraded by 1:100 Pd/Fe particles. Therefore, the remediation of PCE with Pd/Fe particles may be restrained in the cold area. Similarly, the k_{obs} values on degradation of 2,4-dichlorophenol [24] and PNCB [27] with respective nondispersed and dispersed Pd/Fe nanoparticles also increased with higher temperatures.

3.5. Effect of dispersant

As reported in literatures, the metal nanoparticles bring together rapidly to form larger aggregates in water [27,28]. Therefore, CMC was employed as a dispersant to prepare the suspensions of NZVI and nano Pd/Fe to prevent the metal particles from agglomeration and precipitation and to preserve their high specific surface area. NZVI and Pd/Fe particles were observed to maintain suspended over 24 h of the dispersed metal tests, but they quickly precipitated within a few min of the nondispersed ones after the experiments had finished and stopped stirring. As shown in Table 1 and Fig. 2, 30% of CMC-to-metal mass ratio effectively dispersed the NZVI and 1:100 Pd/Fe particles in water and enhanced their k_{SA} values of $5\,mg\,L^{-1}$ PCE degradation tests by a factor of about 33 and 4 or the k_{obs} values around 29 and 4 times, respectively (i.e. CMC was increased from 0 to 30% mass ratio with a fixed NZVI and Pd/Fe concentration of $5\,g\,L^{-1}$). He and Zhao [29] obtained the similar results and the k_{obs} values of $20\,mg\,L^{-1}$ TCE degradation increased from 0.86 to $6.8\,h^{-1}$, around 7.9 times, as the CMC-to-Fe molar ratio increased from 0 to 0.0124. Degradation of PNCB [27] and chlorinated hydrocarbon (TCE and PCBs) [28] were also ameliorated by the CMC dispersed Pd/Fe particles. Besides, the method for suspensions prepared in this study was different from those proposed in the literatures by mixing the CMC solution with already prepared NZVI and nano Pd/Fe particles [27–30]. The results showed that the CMC-dispersed technology could be integrated with commercial metal particles that were already synthesized in advance.

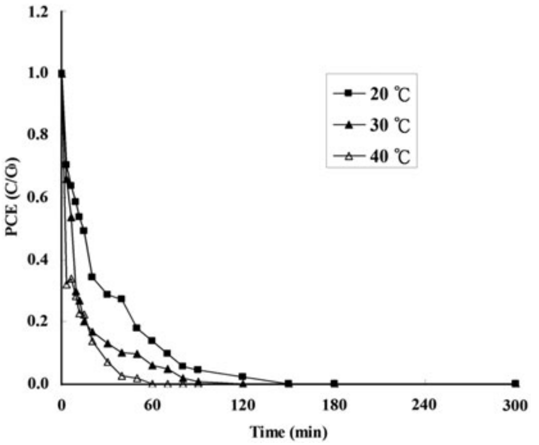

Fig. 3. Variations of PVariations of PCE concentrations with reactor temperatures, $5\,mg\,L^{-1}$ PCE with $5\,g\,L^{-1}$ nondispersive 1:100 Pd/Fe.

3.6. Effect of mass concentration of metal particles

Experiments were also performed by employing various mass concentrations (5, 2.5, and $1\,g\,L^{-1}$) of 1:100 Pd/Fe nanoparticles without a dispersant at 30℃ (Fig. 4(a)). For $1\,g\,L^{-1}$ particles, 94% of PCE was removed at the end of test with k_{obs} value of $0.6\,h^{-1}$. The k_{obs} values increased to 1.5 and $2.6\,h^{-1}$ as the mass concentrations were raised to 2.5 and $5\,g\,L^{-1}$, and PCE was completely removed within 150 and 120 min, respectively. Dong et al. [27] also presented that the k_{obs} values of PNCB degradation also raised with higher CMC-dispersed Pd/Fe mass concentration [27].

The respective k_{SA} values of 5 g 1:100 Pd/Fe nanoparticles at 30℃ were very close to each other that ranged between 9.3×10^{-3} and $10.7 \times 10^{-3}\,L\,h^{-1}\,m^{-2}$. The results of various mass concentrations of dispersed 1:100 Pd/Fe shown in Table 1 and dispersed NZVI tests shown in Fig. 4b were similar to those of nondispersed 1:100 Pd/Fe particles. The k_{SA} values ($10.2 \pm 0.81 \times 10^{-3}\,L\,h^{-1}\,m^{-2}$) at 30℃ obtained in this study were close to the reported values ($12.2 \pm 0.36 \times 10^{-3}\,L\,h^{-1}\,m^{-2}$) at 22℃ [16].

3.7. Effect of pH

He and Zhao [29] presented that pH affected the reaction rates of Fe corrosion and TCE degradation with stabilized Pd/Fe nanoparticles in water. To master the influence of pH on the degradation efficiency of PCE by Pd/Fe particles, three experiments were performed with $5\,g\,L^{-1}$ 1:100 Pd/Fe particles without CMC at 30℃. Those tests were conducted at pH 4 and 7 with buffer solution of Na_2HPO_4 and $C_8H_6O_7{\cdot}H_2O$ as well as at pH 9 with $NaHCO_3$ and $Na_2CO_3{\cdot}9H_2O$. The results indicated that $5\,mg\,L^{-1}$ PCE was completely removed within 3 min (the first sampling time) at pH 4 and 7, but only 11% PCE degraded at the end of test (300 min) at pH 9. This may be due to the sufficient H^+ in solution which promoted the degradation rate of PCE by Pd/Fe under the acid and neutral condition. This result is

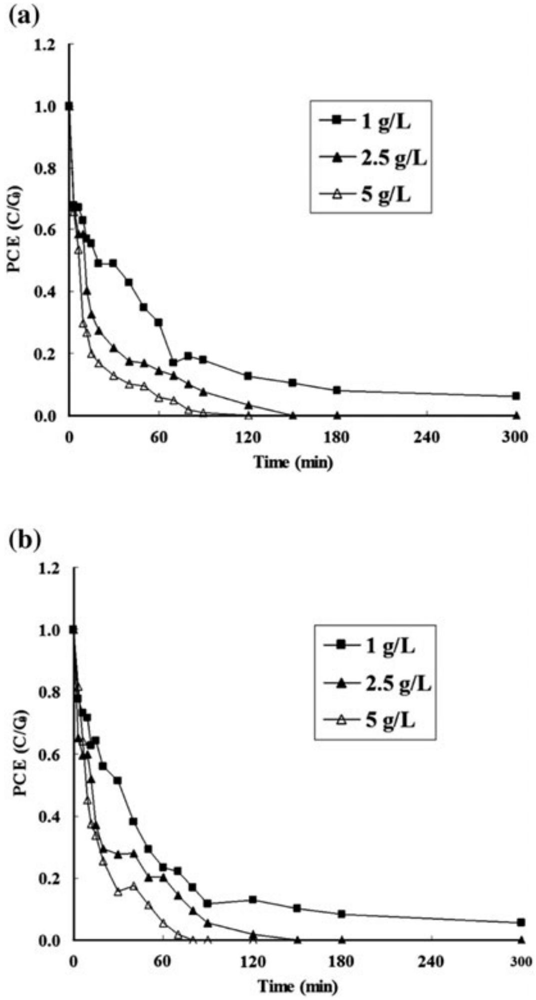

Fig. 4. Variations of PCE concentrations ($C_0 = 5$ mg L^{-1}) with mass concentrations of (a) nondispersed 1:100 Pd/Fe; (b) CMC-dispersed NZVI at 30℃.

consistent with the previous reports that the trend of dechlorination rate of TCE or PNCB by CMC-stabilized nanoparticles [27,29] and 2,4-dichlorophenol by Pd/Fe nanoparticles [24] decreased with increasing pH. Further study will be conducted with higher temperature, lower Pd/Fe mass concentration, and smaller pH range buffer to investigate the effect of pH between 7 and 9 on PCE dechlorination.

3.8. Variations of Cl^-, Fe^{2+}, redox, and pH

As shown in Fig. 5(a) and (b), Cl^- and Fe^{2+} continuously released and accumulated in solution as PCE was dechlorinated by various loadings of Pd/Fe. Fe^{2+} concentrations were not greater than 4 mg L^{-1} during the tests without CMC as shown in Fig. 5(b), but over 14 mg L^{-1} with CMC. Obviously, CMC enhanced the reactivity of Pd/Fe particles resulting in more Fe^{2+} released from Fe corrosion. In the experiments of PCE degradation using NZVI also released more Fe^{2+} when CMC was employed (not shown).

Fig. 5(c) shows that the ORP in solutions descended to reductive condition immediately at the beginning of experiments and kept in the range between around −700 and −850 mV to the end of tests. In the absence of CMC, the ORP of nondispersed 1:100 Pd/Fe particles test at 30℃ was not lower than −800 mV during the test. But it was observed to reach about −860 mV for the test of dispersed 1:100 Pd/Fe at 30℃. This might be attributed to the effect of CMC dispersant that improved the reduction capacity of Pd/Fe particles to PCE [12]. Because H^+ was continuously consumed, while PCE was degraded by NZVI and Pd/Fe according to Eq. (1), pH quickly increased from about 5–6 to 8–9 at the beginning of tests and then maintained at about 8–9 to the end of tests as shown in Fig. 5(d). Similar results were observed in previous studies for TCE, 2,4-dichlorophenol, and PNCB degraded by NZVI [34], Pd/Fe [24], and CMC-stabilized Pd/Fe [27] nanoparticles, respectively. The variations of ORP and pH for the other tests listed in Table 1 were similar to those shown in Fig. 5(c) and (d).

3.9. Mass balance of dechlorination products

The preceding studies showed that PCE could be completely dechlorinated by Pd/Fe particles to form ethane as a final product [16,21]. In this study, the concentrations of residual PCE and its potential chlorinated by-products derived from PCE dechlorination such as TCE, 1,1-DCE, cis-1,2-DCE, tran-1,2-DCE, and VC in solutions were monitored at various reaction times to identify the degradation levels of PCE. Potential chlorinated by-products were not detected in each test. This is similar to the earlier findings of Lien and Zhang [16] that only trace amount of TCE (around 10 μg L^{-1}) was detected. The slight variations may be due to the experimental conditions in both studies. As the results revealed, Pd/Fe particles showed a fast and complete dechlorination capacity to 5 mg L^{-1} PCE in solution.

Fig. 6(a)–(d) presented the variations of PCE and Cl^- concentration along the tests with 5 g L^{-1} Pd/Fe of various mass ratios and NZVI at 30℃. In the control tests of NZVI and Pd/Fe without addition of PCE, Cl^- was detected around 0.78 mg L^{-1} on average. The measured Cl^- concentrations were deducted by 0.78 mg L^{-1} first for the following mass balance

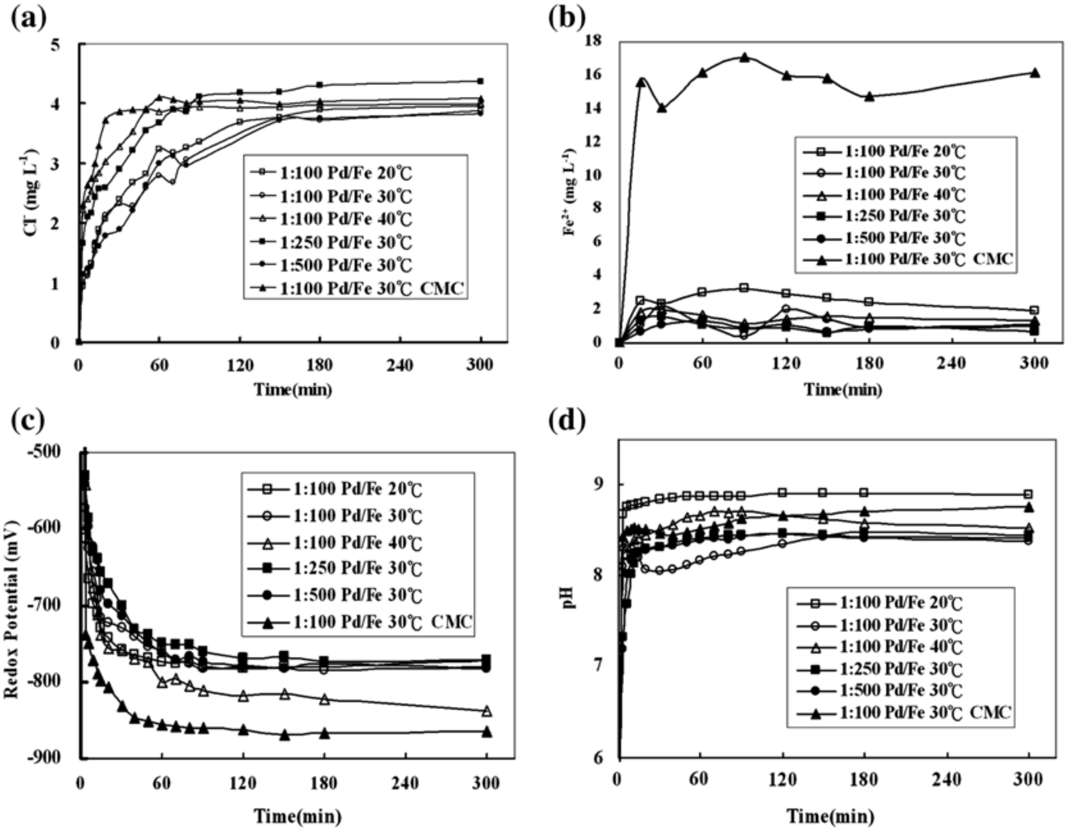

Fig. 5. Variations of (a) Cl^- concentrations; (b) Fe^{2+} concentrations; (c) ORP; (d) pH along the tests of 5 mg L^{-1} PCE with 5g L^{-1} Pd/Fe at 30℃.

calculation. Hence, the concentration curve of the sum of PCE and Cl^- started from the initial PCE concentration and tended to reach the theoretical Cl^- concentration at the end of tests. The theoretical Cl^- concentration calculated from the measured initial PCE concentration of each test is the prospective amount of Cl^- released into solution, when the parent PCE is completely dechlorinated. The NZVI and nano Pd/Fe particles used in this study were synthesized by sulfate method instead of chloride method. Therefore, theoretically, no Cl^- would be released from the particles matrix through the tests that should not interfere with the mass balance calculation. The variations between the theoretical and measured Cl^- concentration at the end of tests indicated that PCE was almost completely degraded by Pd/Fe particles. The results obtained in this study were consistent with the previous findings on the TCE degraded by Pd/Fe particles [28,30]. The mass balances for the other tests listed in Table 1 were similar to those shown in Fig. 6.

4. Conclusion

PCE in solution is effectively dechlorinated by dispersed NZVI and nondispersed or dispersed nano Pd/Fe bimetallic particles. Pd/Fe nanoparticles showed higher degradation capacity per unit surface area (k_{SA}) than NZVI, and yielded a quicker and more complete PCE degradation. The Pd-modified technology really promoted the reactivity of Fe particles to PCE degradation. The observed reaction rates (k_{obs}) of PCE dechlorination were obviously influenced by the system temperatures. The results indicated that the higher the reaction temperature, the faster the PCE degraded by metal particles. CMC successfully dispersed NZVI and nano Pd/Fe particles in water and enhanced their reactivity of unit surface area. PCE degradation rates were raised under acid and neutral conditions. The dispersed Pd/Fe bimetallic technology for the removal of PCE contaminants are quite promising and may provide some valuable information to develop an efficacious system for the remediation of

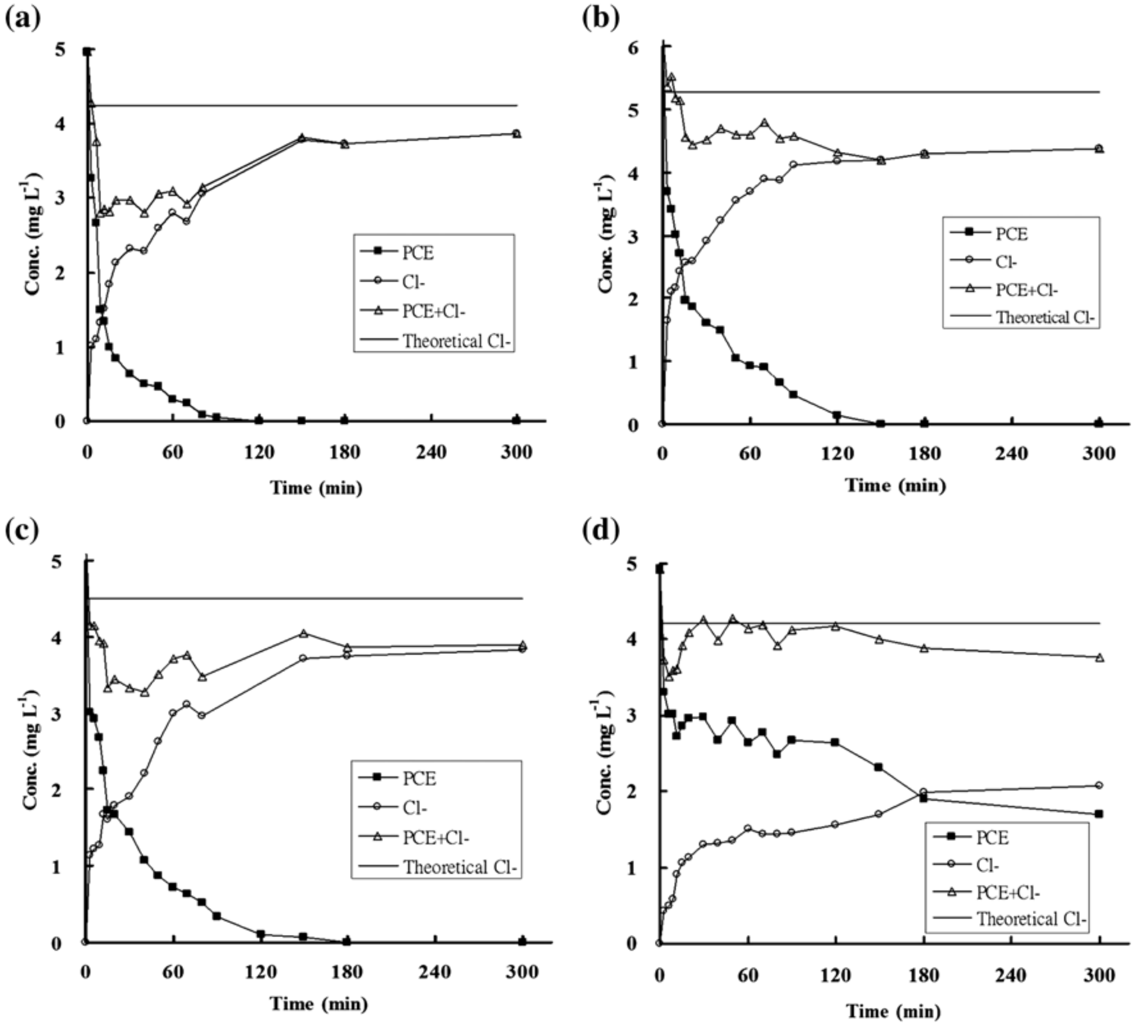

Fig. 6. Variations of PCE and Cl^- concentrations along the tests at 30°C of 5 mg L^{-1} PCE with 5 g L^{-1} nondispersed (a) 1:100 Pd/Fe; (b) 1:250 Pd/Fe; (c) 1:500 Pd/Fe; and (d) NZVI.

aquifer contaminated by chlorinated solvents. However, the possibilities or the levels of Fe or Pd/Fe leached out to the solution during the dechlorination process will be worthwhile for further study.

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References

[1] J.L. Chen, S.R. Al-Abed, J.A. Ryan, Z. Li, Effects of pH on dechlorination of trichloroethylene by zero-valent iron, J. Hazard. Mater. B 83 (2001) 243–254.

[2] J. Farrell, N. Melitas, M. Kason, T. Li, Electrochemical and column investigation of iron-mediated reductive dechlorination of trichloroethylene and perchloroethylene, Environ. Sci. Technol. 34 (2000) 2549–2556.

[3] G.A. Loraine, Effects of alcohols, anionic and nonionic surfactants on the reduction of PCE and TCE by zero-valent iron, Water Res. 35 (2001) 1453–1460.

[4] M.C. Shin, H.D. Choi, D.H. Kim, K. Baek, Effect of surfactant on reductive dechlorination of trichloroethylene by zero-valent iron, Desalination 223 (2008) 299–307.

[5] Y. Bae, J.W. Park, TCE reduction modeling in soil column: Effect of zero-valent iron, ferrous iron, and iron-reducing bacteria, Desalin. Water Treat. 4 (2009) 229–232.

[6] A.L. Roberts, L.A. Totten, W.A. Arnold, D.R. Burris, T.J. Campbell, Reductive elimination of chlorinated ethylenes by zero-valent metals, Environ. Sci. Technol. 30 (1996) 2654–2659.

[7] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, Environ. Sci. Technol. 28 (1994) 2045–2053.

[8] A.D. Gusmao, T.M.P. Campos, M.M.M. Nobre, E.A. Vargas, Jr., Laboratory test for reactive barrier design, J. Hazard. Mater. 110 (2004) 105–112.

[9] W.X. Zhang, C.B. Wang, H.L. Lien, Treatment of chlorinated organic contaminants with nanoscale bimetallic particles, Catal. Today 40 (1998) 387–395.

[10] J.H. Chang, S.F. Cheng, The remediation performance of a specific electrokinetics integrated with zero-valent metals for perchloroethylene contaminated soils, J. Hazard. Mater. B 131 (2006) 153–162.

[11] L.J. Graham, G. Jovanovic, Dechlorination of p-chlorophenol on a Pd/Fe catalyst in a magnetically stabilized fluidized bed; implications for sludge and liquid remediation, Chem. Eng. Sci. 54 (1999) 3085–3093.

[12] S.S. Chen, Y.C. Huang, T.Y. Kuo, The remediation of perchloroethylene contaminated groundwater by nanoscale iron reactive barrier integrated with surfactant and electrokinetics, Ground Water Monit. Rem. 30 (2010) 90–98.

[13] Y.C. Huang, T.Y. Chen, J.S. Huang, Y.T. Chen, Effects of size and surface area of iron on reduction of hexavalent chromium, J. Univ. Sci. Technol. Beijing 30 (2008) 53–57.

[14] H.L. Lien, D.W. Elliott, Y.P. Sun, W.X. Zhang, Recent progress in zero-valent iron nanoparticles for groundwater remediation, J. Environ. Eng. Manage. 16 (2006) 371–380.

[15] C.J. Clark, II, P.S.C. Rao, M.D. Annable, Degradation of perchloroethylene in cosolvent solutions by zero-valent iron, J. Hazard. Mater. B 96 (2003) 65–78.

[16] H.L. Lien, W.X. Zhang, Nanoscale iron particles for complete reduction of chlorinated ethenes, Colloids Surf. A 191 (2001) 97–105.

[17] C.B. Wang, W.X. Zhang, Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs, Environ. Sci. Technol. 31 (1997) 2154–2156.

[18] H.L. Lien, W.X. Zhang, Enhanced dehalogenation of halogenated methanes by bimetallic Cu/Al, Chemosphere 49 (2002) 371–378.

[19] R. Muftikian, Q. Fernando, N. Korte, A method for the rapid dechlorination of low molecular weight chlorinated hydrocarbons in water, Water Res. 29 (1995) 2434–2439.

[20] S.F. Cheng, S.C. Wu, The enhancement methods for the degradation of TCE by zero-valent metals, Chemosphere 41 (2000) 1263–1270.

[21] S.F. Cheng, S.C. Wu, Feasibility of using metals to remediate water containing TCE, Chemosphere 43 (2001) 1023–1028.

[22] C.J. Lin, S.L. Lo, Y.H. Liou, Dechlorination of trichloroethylene in aqueous solution by noble metal-modified iron, J. Hazard. Mater. B 116 (2004) 219–228.

[23] B. Schrick, J.L. Blough, A.D. Jones, T.E. Mallouk, Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoparticles, Chem. Mater. 14 (2002) 5140–5147.

[24] J. Wei, X. Xu, Y. Liu, D. Wang, Catalytic hydrodechlorination of 2,4-dichlorophenol over nanoscale Pd/Fe: Reaction pathway and some experimental parameters, Water Res. 40 (2006) 348–354.

[25] X. Xu, M. Zhou, P. He, Z. Hao, Catalytic reduction of chlorinated and recalcitrant compounds in contaminated water, J. Hazard. Mater. B 123 (2005) 89–93.

[26] Y. Xu, W.X. Zhang, Subcolloidal Fe/Ag particles for reductive dehalogenation of chlorinated benzenes, Ind. Eng. Chem. Res. 39 (2000) 2238–2244.

[27] T. Dong, H. Luo, Y. Wang, B. Hu, H. Chen, Stabilization of Fe-Pd bimetallic nanoparticles with sodium carboxymethyl cellulose for catalytic reduction of para-nitrochlorobenzene in water, Desalination 271 (2011) 11–19.

[28] F. He, D. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water, Environ. Sci. Technol. 39 (2005) 3314–3320.

[29] F. He, D. Zhao, Hydrodechlorination of trichloroethene using stabilized Fe-Pd nanoparticles: Reaction mechanism and effects of stabilizers, catalysts and reaction conditions, Appl. Catal. B B84 (2008) 533–540.

[30] F. He, D. Zhao, J. Liu, C.B. Roberts, Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater, Ind. Eng. Chem. Res. 46 (2007) 29–34.

[31] L.F. Greenlee, S.A. Hooker, Development of stabilized zero valent iron nanoparticles, Desalin. Water Treat. 37 (2012) 114–121.

[32] T.L. Johnson, M.M. Scherer, P.G. Tratnyek, Kinetics of halogenated organic compound degradation by iron metal, Environ. Sci. Technol. 30 (1996) 2634–2640.

[33] Y.H. Kim, E.R. Carraway, Dechlorination of chlorinated ethenes and acetylenes by palladized iron, Environ. Technol. 24 (2003) 809–819.

[34] Y.C. Huang, Y.W. Cheng, Electrokinetic-enhanced nanoscale iron reactive barrier of trichloroethylene solubilized by Triton X-100 from groundwater, Electrochim. Acta 86 (2012) 177–184.