Influence of nanoscale zero-valent iron on geochemical properties of groundwater and vinyl chloride degradation: A field case study

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ABSTRACT

A 200 m^2 pilot-scale field test successfully demonstrated the use of nanoscale zero-valent iron (NZVI) for effective remediation of groundwater contaminated with chlorinated organic compounds in Taiwan within six months. Both commercially available and on-site synthesized NZVI were used. A well-defined monitoring program allowing to collect three-dimensional spatial data from 13 nested multi-level monitoring wells was conducted to monitor geochemical parameters in groundwater. The degradation efficiency of vinyl chloride (VC) determined at most of monitoring wells was 50–99%. It was found that the injection of NZVI caused a significant change in total iron, total solid (TS) and suspended solid (SS) concentrations in groundwater. Total iron concentration showed a moderate and weak correlation with SS and TS, respectively, suggesting that SS may be used to indicate the NZVI distribution in groundwater. A decrease in oxidation–reduction potential (ORP) values from about −100 to −400 mV after NZVI injection was observed. This revealed that NZVI is an effective means of achieving highly reducing conditions in the subsurface environment. Both VC degradation efficiency and ORP showed a correlative tendency as an increase in VC degradation efficiency corresponded to a decrease of ORP. This is in agreement with the previous studies suggesting that ORP can serve as an indicator for the NZVI reactivity.

1. Introduction

Using nanoscale zero-valent iron (NZVI) for groundwater remediation is one of the most promising environmental nanotechnologies up to date. It has been demonstrated that, with its high specific surface area and special molecular conformation (Zhang, 2003), NZVI is a reactive reagent for the treatment of various contaminants in aqueous systems including chlorinated organics, heavy metals, perchlorate and nitrate (Cao et al., 2005; Elliott et al., 2008; Giasuddin et al., 2007; Lien et al., 2007; Liu et al., 2007; Ponder et al., 2000; Sohn et al., 2006; Wang and Zhang, 1997; Yuan and Lien, 2006). Additionally, bimetallic iron nanoparticles prepared by coating catalytic metals such as palladium or nickel on NZVI exhibited an enhancing effect to accelerate the reactivity and reduce the formation of toxic byproduct during the dechlorination
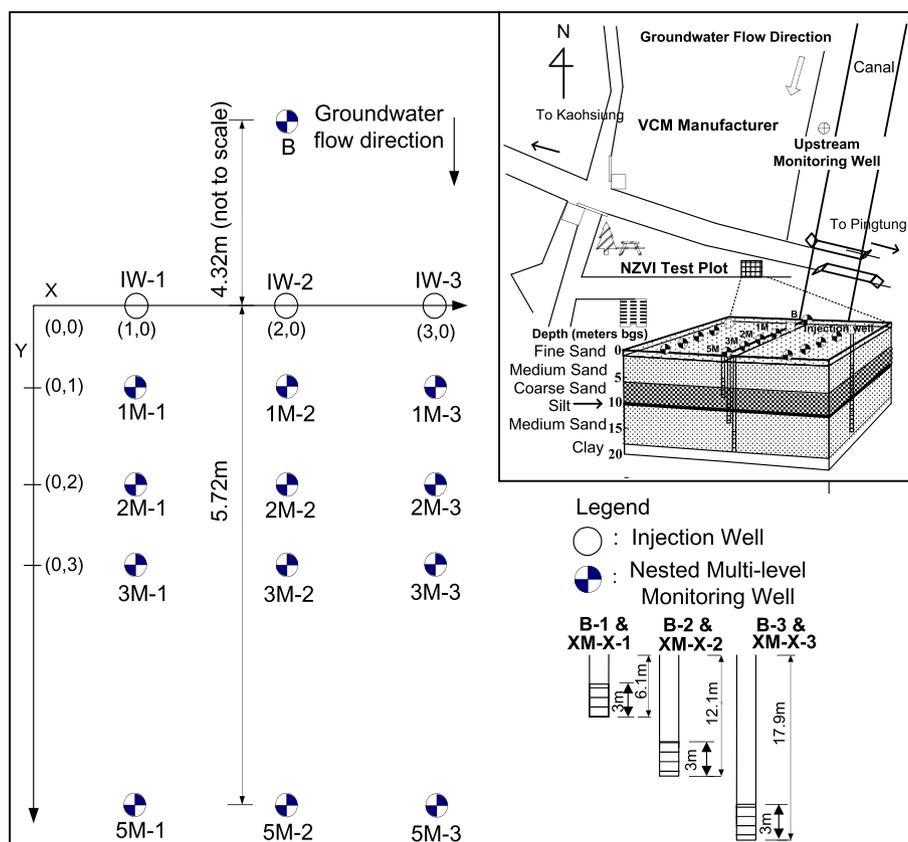
Fig. 1 – Layout of the pilot study area and injection and monitoring wells.

reaction (Choi et al., 2009; Feng and Lim, 2005; He and Zhao, 2005; Lien and Zhang, 2001, 2005, 2007; Nutt et al., 2005, 2006; Zhang et al., 1998).

While laboratory studies have indicated the superior capability of NZVI, the feasibility for implementation and application of NZVI in groundwater remediation needs to be further tested in the field. An increasing number of field tests including pilot- and full-scale remediation sites have been implemented using NZVI (Glazier et al., 2003; Lien et al., 2006; Macé et al., 2006). The United States Environmental Protection Agency (USEPA) has reported a summary of a total of 26 sites using or testing nanoparticles for remediation in the U.S. and Canada (USEPA, 2008). Several pilot tests have been conducted in other countries including Czech Republic, Germany, Italy and Slovakia (Macé et al., 2006). The cost of NZVI was on the order of 50 USD/kg as of mid-2004 and is expected to decrease as supply increases (Elliott et al., 2009). Though NZVI is considered the most widely used nanoparticle in groundwater remediation, our current understanding of its risk to human or ecological health is still limited (Tratnyek and Johnson, 2006; USEPA, 2008). The assessment of the impact of nano-materials on the environment and human health has attrac-ted worldwide attention (e.g., Nel et al., 2006).

Taiwan has long been known as an island with dynamic and flexible industries. The manufacturing industry including the production of chemicals, petrochemicals, advanced electrical equipment, and electronics accounted for 27.5% of the gross domestic product (GDP) in 2007 (Government Information Office, 2008). To protect the groundwater resource, Taiwanese government promulgated The Soil and Groundwater Pollution Remediation Act in 2000. The groundwater pollution control standards of chlorinated hydrocarbons vary from 0.02 to 8.5 mg/L for non-drinking water source protection areas. The acceptable level of vinyl chloride in groundwater is regulated at 0.02 mg/L (Environmental Protection Administration, Taiwan, 2006). However, limited technologies such as pump-and-treat and chemical oxidation are currently available for ground-water remediation in Taiwan. As a result, the development of suitable remedial technologies is certainly a need.

In this paper, we report the first field test for groundwater remediation using the NZVI technology in Taiwan. The study focuses on a pilot-scale field demonstration of injecting NZVI, either on-site synthesized or commercially available, to degrade a variety of chlorinated organic contaminants in the groundwater. A well-defined monitoring program was estab-lished by measuring the iron concentration and groundwater geochemical parameters including dissolved oxygen (DO), oxidation–reduction potential (ORP), pH and electric conduc-tivity (EC) from 13 nested multi-level monitoring wells installed on a 200 m^2 plot. Total solid (TS), suspended solid (SS), chloride and chlorinated organic compound concentra-tions in the groundwater were also determined. The moni-toring program allows this study to collect three-dimensional spatial data that offer a systematic analysis to better under-stand the influence of NZVI on the groundwater geochemistry and the impact of geochemical properties on the effectiveness
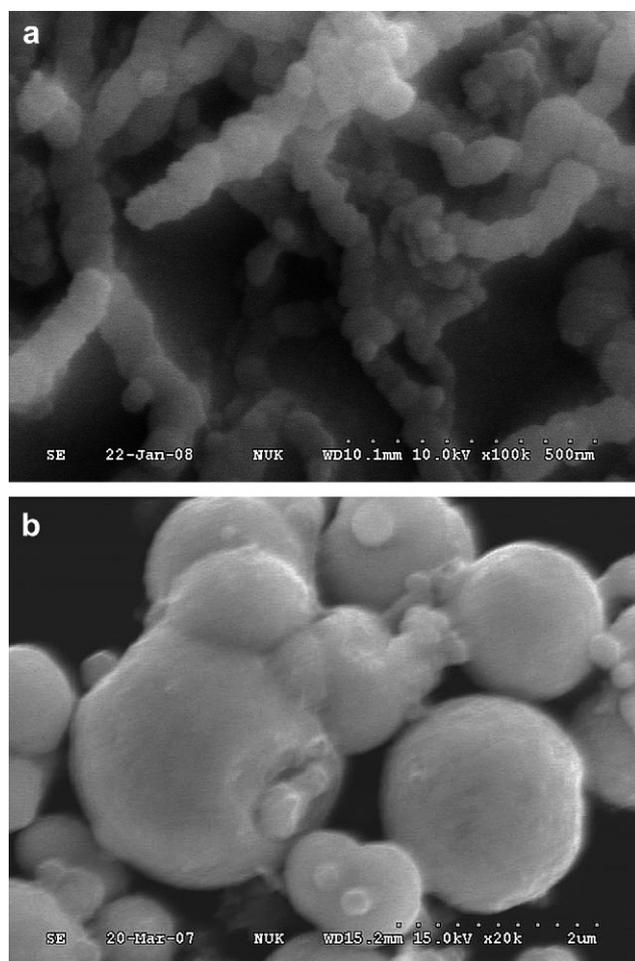
Fig. 2 – SEM images of (a) on-site synthesized NZVI and (b) commercial NZVI.

of NZVI. To the best of our knowledge, this study presents the first three-dimensional spatial data for the *in situ* field test using the NZVI technology.

2.   Experimental methods

2.1.   Site selection and test area description

The testing site was selected at an active industrial complex including petrochemical plants and vinyl chloride monomer (VCM) manufacturing plants in Kaohsiung, Taiwan. The NZVI pilot test was conducted in a 10 m × 20 m area located south of the VCM plant in the downstream groundwater direction (Fig. 1 inset) where the groundwater was contaminated with high concentrations of chlorinated organic compounds. The contaminated plume containing vinyl chloride (VC, 620–4562 μg/L), trichloroethylene (TCE, 53–682 μg/L), 1,1-dichloroethylene (42–134 μg/L), *cis*-1,2-dichloroethylene (27–1151 μg/L), and dichloroethanes (55–270 μg/L) was measured from an upgradient monitoring well near the plant. In this paper, VC was selected as a target compound because of its high concentration. At the testing site, an unconfined aquifer, composed of medium to coarse sand and few silt, lies approximately 4–18 m

below ground surface (m bgs) (Fig. 1 inset). The pumping test indicated that the hydraulic conductivity is 0.275 cm/sec, the transmissivity is 4349 m^2/day, specific yield is 0.18 and the anisotropy is 14.3. The linear velocity of the groundwater is 28.5 cm/day. The natural gradient at the site is approximately 0.0012 m/m.

Three injection wells and 13 nested multi-level monitoring wells were installed within the 200 m^2 plot (Fig. 1). A background well was located upgradient of the injection wells while four multi-level monitoring wells were installed in the downstream direction of each injection well. The positions of the four nested monitoring wells are approximately one, two, three, and five meters away from the injection well. The injection wells are all eighteen-meter deep with fifteen-meter screens. The nested monitoring wells are consisted of three separate wells approximately six, twelve and eighteen-meter deep with three-meter screens (Fig. 1). Groundwater samples can therefore be collected from three different depths: upper, middle and bottom layers.

2.2.   Preparation of NZVI

Two types of NZVI were used in this study. A commercially available nanoiron solution was purchased from Lehigh Nanotech, LLC and an on-site synthesized NZVI was prepared using a borohydride reduction. Prior to the field test, laboratory feasibility experiments for two kinds of NZVI were conducted to treat contaminated groundwater obtained from the testing site. Bench-scale batch tests indicated that both NZVI showed a better performance for TCE degradation in the TCE-spiked deionized water than in the TCE-contaminated groundwater (Fig. S-1). Nevertheless, palladized NZVI (0.5–1 wt%) exhibited a rapid and effective degradation of TCE regardless of the types of iron and water samples (Figs. S-2 and S-3).

The on-site synthesized NZVI was prepared by slowly adding ferrous sulfate solution into sodium borohydride solution (>98.5%, Beckman Coulter, Inc.) containing a nonionic surfactant (Taiwan NJC Corp., industrial grade) in a 1000-L tank. After the reaction was complete, palladium acetate dissolved in methanol was mixed with the NZVI suspension to
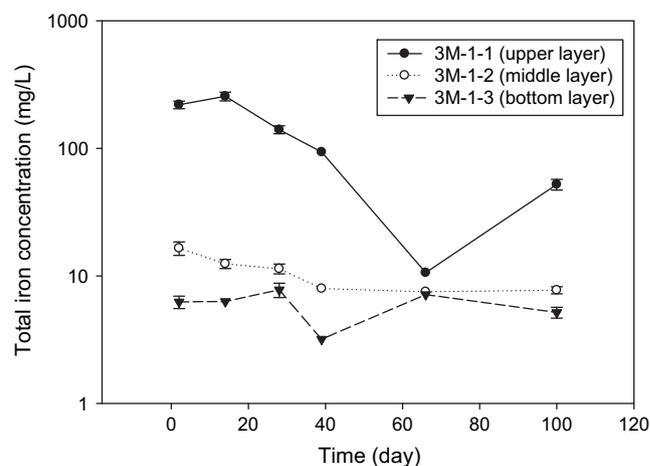

Fig. 3 – Total iron concentration measured at different depths in the monitoring well (3M-1) during the period of on-site synthesized NZVI injection.
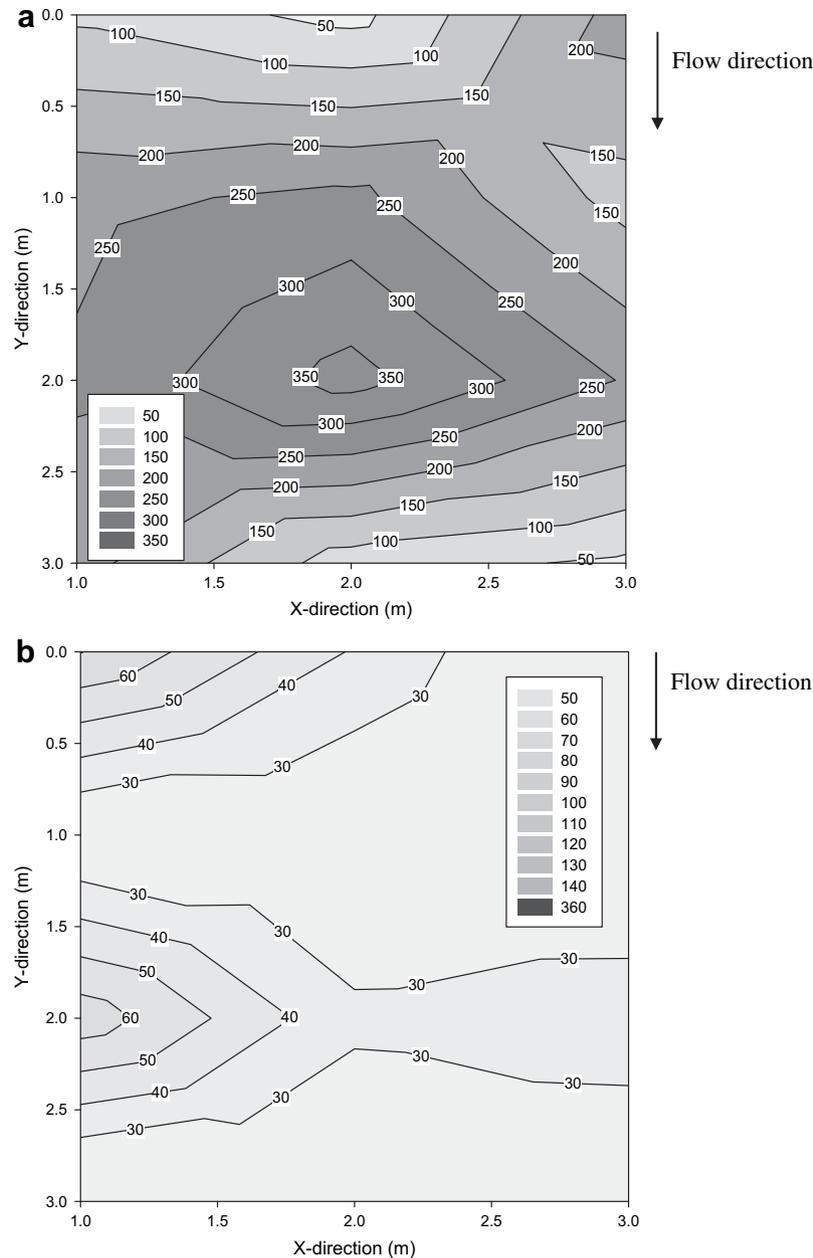
Fig. 4 – Total iron concentration distribution in the upper layer during the period of on-sited synthesized NZVI injection at (a) Day 8 and (b) Day 66. (Refer to Fig. 1 for the corresponding position of the well locations.)

reach the ratio of palladium to iron at 0.5 wt%. The NZVI mixture was then pumped into a storage tank for the injection later. The cost of on-site synthesized NZVI was approximately 200 USD/kg. It should be noted that both types of NZVI exhibited a similar behavior in terms of their influence on pH, ORP and contaminant degradation efficiency in groundwater. Therefore, data presented in this paper are primarily based on the results of the on-site synthesized NZVI study.

2.3. Characterization of NZVI

Morphological and elemental analyses of NZVI were performed by a scanning electron microscope (SEM) (Hitachi S-4300, Hitachi Science Systems, Ltd.) equipped with energy-dispersive

X-ray (EDX) at 10 kV and a transmission electron microscope (TEM) (JEOL JSM-1200EX II). A surface area analyzer (Beckman Coulter SA3100) was used to determine surface areas of NZVI. The particle size was analyzed by a particle size analyzer (Brookhaven 90Plus, Brookhaven Instruments Co.). This instrument analyzes particle sizes ranging from <1 nm to 6 μm. Diluted samples were placed in plastic cells for analysis and elapsed time was set at 30–60 s.

2.4. Injection of NZVI

In the first period of the field test, the commercial nanoiron solution was applied and monitored for three months. A total amount of 2250 L diluted commercial nanoiron solution
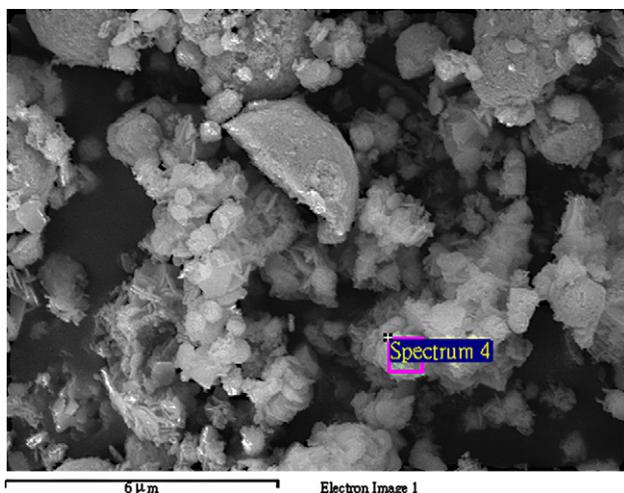
Fig. 5 – SME image of soil samples with the agglomeration of spherical iron particles.

containing 40 kg NZVI with palladium (1 wt%) was injected into the aquifer using the injection well IW-2 via gravity. The injection rate was about 1200 L/h. Five months after the end of the three-month monitoring program, the on-site synthesized
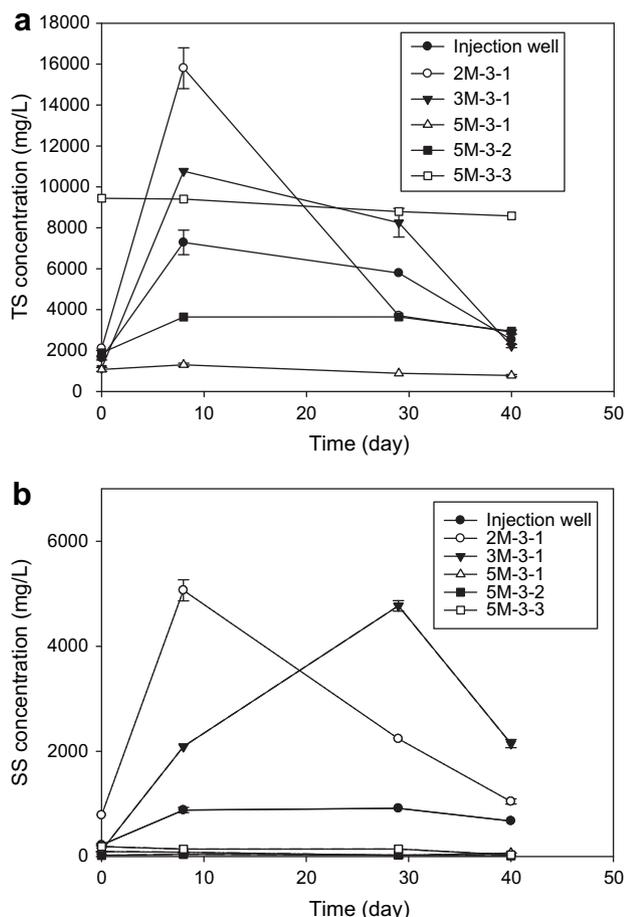

Fig. 6 – The concentration changes of (a) TS and (b) SS observed in the injection and monitoring wells.

NZVI was conducted in the second period of the trial and monitored for another three months. A total amount of 8500 L suspension containing 20 kg NZVI was injected via gravity. The first 1000 L was injected using the injection well IW-3 while the rest of NZVI suspension (7500 L) was injected using the injection well IW-1 after ten days. The 7500 L of on-site synthesized NZVI was prepared and stored for a week before deployment. Prior to the second NZVI injection, a measurement of VOC and total iron concentration was conducted to establish a new baseline for comparison with the post-injection result. It was found that the first NZVI injection resulted in a slight increase in total iron concentration from 10 ± 3 to 16 ± 9 mg/L.

2.5. Field sampling and analyses

The groundwater samples were collected using a peristaltic pump at various time intervals. A low-flow sampling technique minimizing losses of volatiles and gases was used to take samples for organic analytes. Filtered and acidified samples were analyzed by an inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 2000DV, PerkinElmer Inc.) for total iron concentrations. Triplicate analysis was performed for each sample and data were accepted only if relative standard deviation was less than 1%. Geochemical parameters of groundwater including pH, DO and ORP were measured in the field using an YSI 650 MDS-6600 probe (V2-4 Sonde, YSI Inc.). Concentrations of TS and SS were determined based on the USEPA method 160.2 (USEPA, 1999). One duplicate field sample was collected for every ten samples obtained. Duplicate samples were collected at the same time as the primary samples.

Volatile organic compounds were measured by GC/MS (Angilent 6890/5973 with a DB-624 capillary column) using a purge and trap sampling equipment (OI Analytical. Model 4560). Methane, ethane and ethene were determined from the headspace of serum vials containing water samples after equilibration. Concentrations of hydrocarbons were measured by a HP4890 GC-FID equipped with a GS-GASPRO capillary column (J&W, 30 m × 0.32 mm). Analysis was generally performed in triplicate with relative differences less than 15%.

Soil samples were obtained after 7 days of the commercial NZVI injection. The testing site was cored using 5 cm i.d. core barrels to examine the iron distribution in the aquifer. The cores were taken at the testing site near the monitoring wells (1M-2, 2M-2 and 3M-2) and the injection well (IW-2) using the Geoprobe technique. A SEM-EDX was used to identify the NZVI in the soil samples.

3. Results and discussion

3.1. Characterization of on-site synthesized and commercial NZVI

Fig. 2 shows the SEM images for the on-site synthesized and commercial NZVI, respectively. The synthesized NZVI showed a particle size in nanoscale range (Fig. S-4) while the commercial NZVI had a spherical shape and relatively large particle size. Based on the particle size analysis, the on-site
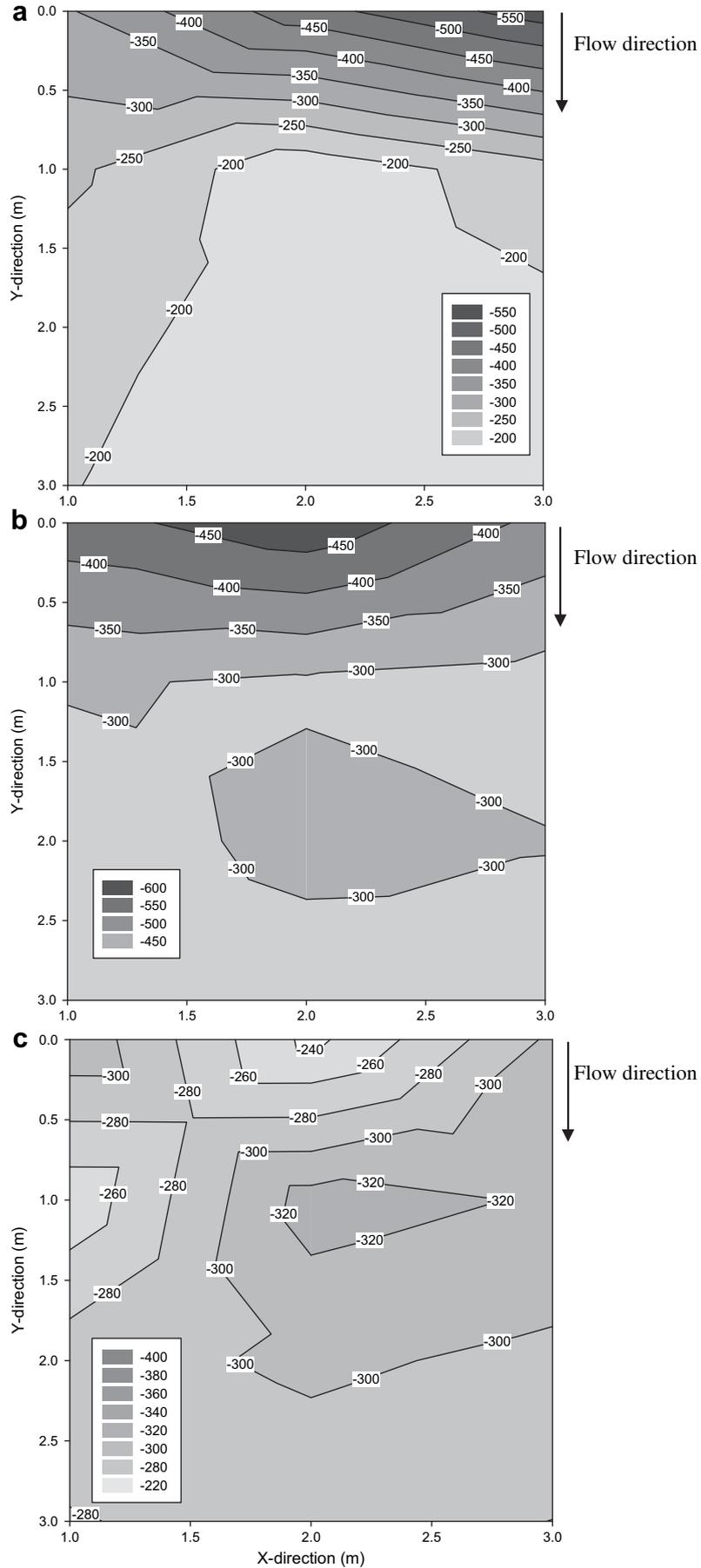
Fig. 7 – ORP changes in the upper layer during the period of on-sited synthesized NZVI injection at (a) Day 8, (b) Day 40 and (c) Day 66. (Refer to Fig. 1 for the corresponding position of the well locations.)
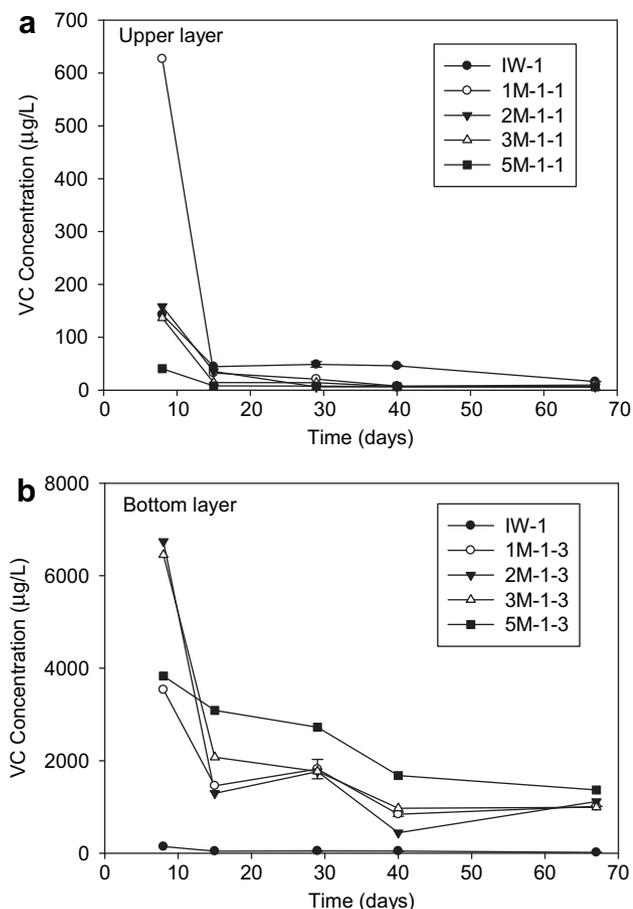
Fig. 8 – Degradation of VC in the (a) upper layer and (b) bottom layer during the NZVI injection.

synthesized NZVI had the particle size in the range of 80–120 nm whereas the commercial NZVI had the average particle size between 450 and 550 nm. The elemental analysis conducted by SEM-EDX revealed that the iron content accounted for nearly 100 wt% for commercial NZVI. The specific surface area of on-site synthesized NZVI was 29.3 m^2/g, similar to those found in literatures (Lien and Zhang, 2001; Liu et al., 2005; Ponder et al., 2000). However, the specific surface area of commercial NZVI was only approximately 4.61 m^2/g. Detail characterization of synthesized NZVI by the borohydride reduction can be found elsewhere (e.g., Nurmi et al., 2005).

3.2. Total iron concentration in groundwater and soil

Fig. 3 shows the total iron concentration change at different depths in the monitoring well (3M-1) during the period of on-site synthesized NZVI injection. As shown in Fig. 3, it is clear that the iron concentration found in the upper layer was significantly higher than that found in the middle and bottom layers. The iron concentration decreased in the order: upper layer > middle layer > bottom layer. It is believed that with the injection via gravity, much of the NZVI first seeped through channels in the unsaturated zone, causing NZVI to accumulate more in the upper layer as compared to that in the lower layer.

It should be pointed out that a significant iron concentration drop in the upper layer was observed at Day 66. This is likely because a heavy storm occurred 3 days before field sampling. Iron in the upper layer may be washed downstream or may penetrate into the bottom layer.

A concentration distribution of total iron in the upper layer determined from monitoring wells located down gradient from the injection well during the on-site synthesized NZVI injection is illustrated in Fig. 4. The injected NZVI influenced the geochemistry of the aquifer significantly. A noticeable increase in the total iron concentration at the whole testing site was observed after NZVI was injected. The iron concentration was in the range of 40–370 mg/L. In general, the iron concentration showed a tendency of decrease towards downstream. Fig. 4b shows the iron concentration distribution at the testing site after 66 days of NZVI injection. A dramatic decrease in iron concentrations with time was found. This suggested that iron either was consumed through the oxidative corrosion or transported through the groundwater flow. It should be pointed out that the total iron concentration measured in the injection well was about 2500 mg/L after 7 days of the commercial NZVI injection. It is about 7 times greater than the on-site synthesized NZVI injection. This suggested that the on-site synthesized NZVI has a better mobility than the commercial NZVI, which is at least partly due to the size effect of particles.

Fig. 5 shows the SEM image of the soil sample obtained from the injection well after 7 days of the commercial NZVI injection. Based on the SEM-EDX analysis, the agglomeration of spherical particles was determined to have the major composition of iron (81.7 wt%) suggesting they were originally from the commercial NZVI. Analysis of the concentration profile of total iron in the soil indicated that the soil iron concentration was all greater than 30 g/kg within the depth of 1–6 m. The soil iron showed the highest concentration in the vicinity of the injection well (up to 90 g/kg), which is consistent with the groundwater data. In addition, it was found that a large portion of commercial NZVI was trapped in the depth of about 3.6 m that is in a good agreement with the groundwater samples indicating the upper layer contained the highest total iron concentration among three layers.
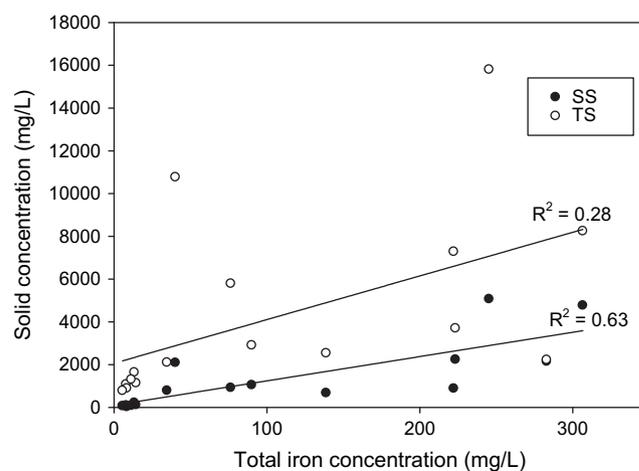

Fig. 9 – Correlation of total iron concentrations with TS and SS concentrations.
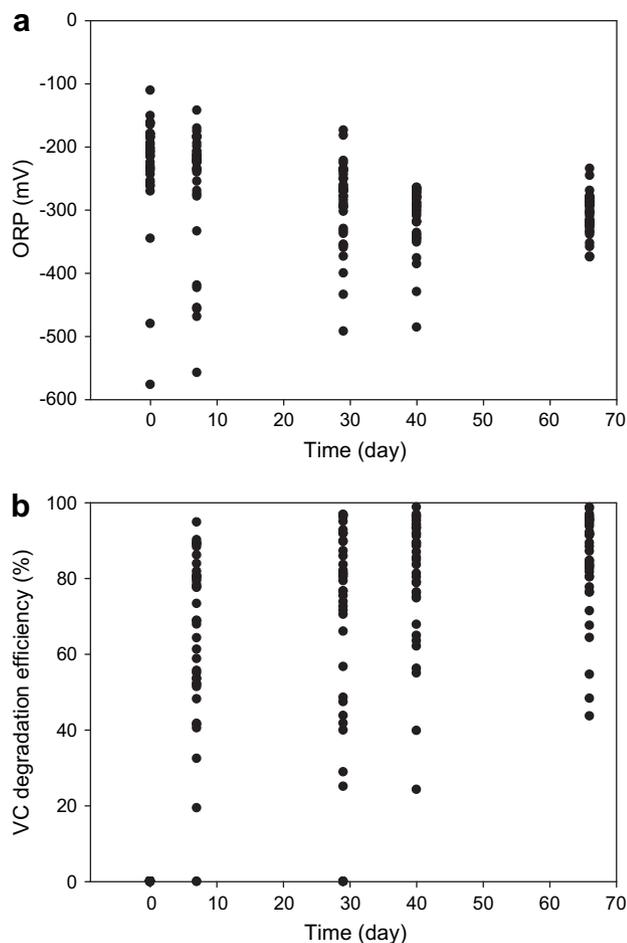
Fig. 10 – Trades of (a) ORP and (b) VC degradation efficiency at the testing site.

3.3. Electric conductivity (EC) and chloride

The EC of groundwater is dependent on the depth of the aquifer. The average EC values measured in upper, middle and bottom layer were 1.5, 8.5 and 14.5 ms/cm, respectively. A similar trend of the chloride concentration was observed. Chloride concentrations, ranging of 550–6190 mg/L, generally increased with increasing the aquifer depth. The unusual high value of chloride concentrations and EC detected in the bottom layer may be attributed to the seawater intrusion because the testing site is located near the coast.

3.4. Total solid (TS) and suspended solid (SS)

The injection of NZVI influenced the TS and SS concentration in the groundwater. A significant increase of SS and TS concentrations was observed within an effective distance of 3 m in the upper layer after the NZVI injection. As shown in Fig. 6a, the TS concentration in the upper layer peaked at Day 8 and then gradually decreased. The highest TS concentration was measured at 2 m downstream from the injection well suggesting the NZVI migration occurred. It should be noted that the TS concentration in the bottom layer was higher than that in the upper layer. For example, the TS concentration of

Day 8 measured in the upper, middle and bottom layer at the monitoring well 5M-3 was 1303, 3641 and 9401.5 mg/L, respectively. This is in a good correlation with the EC results.

The impact of NZVI on the TS concentration in the bottom layer is negligible. This is consistent with the result shown in Fig. 3 that only small amounts of NZVI were able to reach the bottom layer. Furthermore, it was found that the change of TS concentrations is minor at the furthest monitoring distance of 5 m, which may reflect the maximum mobile distance of NZVI. It is worthy of mention that although the groundwater possesses a high ionic strength in the testing site that may cause the agglomeration of NZVI and limit its movement (Phenrat et al., 2007; Saleh et al., 2008), this study has demonstrated the capability of NZVI for effective remediation of chlorinated organic solvents.

Fig. 6b illustrates the change of the SS concentration with time along the downstream path after the injection of NZVI. Compared to the TS concentration, a similar trend in the change of SS concentrations was observed. The highest concentration of SS was about 5000 mg/L measured at 2 m downstream from the injection well. Analogous to TS, no significant change of the SS concentration was found at the furthest monitoring well 5M-3.

3.5. ORP and pH

In a groundwater environment, the dissolved oxygen concentration is usually very low (e.g., <1 mg/L in this study); therefore, the predominant electron receptor is water:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{1}$$

According to the above reaction, the iron oxidation reaction should produce a characteristic increase in solution pH and a concomitant decline in the redox potential. Redox labile contaminants such as chlorinated organics can also serve as possible electron acceptors. However, these contaminants are generally present at low concentrations in the environment and typically do not strongly influence the pH or ORP profiles observed. As it has been observed in field tests of the NZVI technology, the pH and ORP profiles at given monitoring locations over time may serve as an indicator for the NZVI reactivity and to track the migration path of the nanoparticles (Elliott and Zhang, 2001; Glazier et al., 2003; Zhang, 2003).

In this study, it was found that the ORP decreased significantly from about −100 to −400 mV at the central area of the testing site after NZVI injection. The ORP distribution shown in Fig. 7 reveals that a strong reducing condition was established at the beginning while ORP values slowly increased during the course of the testing period. This corresponds to the results of the NZVI distribution shown in Fig. 4 suggesting the NZVI gradually migrated towards downstream. Overall, the data from this study suggested that NZVI is an effective means of achieving highly reducing conditions in the subsurface environment.

The impact of NZVI on groundwater pH is minor. No significant increase of pH was found in all monitoring wells where the groundwater pH was maintained under near neutral conditions (pH 6–7) except for the injection well. At the injection well, the pH value increased to 8.5 indicating the oxidation of NZVI took

place and caused the release of hydroxyl ions (Gillham and O'Hannesin, 1994).

3.6. Effectiveness of NZVI for VC degradation

The concentration profiles of VC also exhibited a dependence on the aquifer depth at the testing site. The VC concentration in the upper layer was in the range of 31.2–624.5 μg/L while VC in the bottom layer can reach up to a concentration greater than 6245 μg/L. Fig. 8 shows the VC concentration steadily decreased as the test date progressed. In general, the degradation efficiency was greater than 90% in both upper and middle layers but was about 20–85% in the bottom layer (Fig. 8). The degradation efficiency determined at most of the monitoring wells was 50–99%. The lowest degradation efficiency was about 20%, which was found in the bottom layer of the monitoring well 5M-1. Hydrocarbons including methane, ethylene and ethane were observed. High concentrations (up to 20 mg/L) of methane and ethylene were determined while the ethane concentration remained in trace amounts (at few μg/L). The formation of hydrocarbons may be resulted from the microbial activity since strongly reducing conditions are beneficial to the anaerobic bioremediation (Macé et al., 2006; USEPA, 2008). However, the cause for high hydrocarbon concentrations is still unclear at the current stage.

3.7. Correlation of TS and SS with the total iron

A challenge with evaluating the effectiveness of NZVI injection is to monitor the NZVI distribution in the aquifer. ORP and dissolved iron have been used as indicators (USEPA, 2008). In this study, geochemical parameters including ORP, pH, TS, SS and total iron concentrations were systematically monitored. It was found that the injection of NZVI resulted in a significant impact on ORP, TS, SS and total iron concentration in the groundwater. As shown in Fig. 9, the correlation analysis indicated a moderate dependence ($R^2 = 0.63$) of SS on the total iron concentration. Further, a relatively weak correlation of TS with total iron concentration was found ($R^2 = 0.28$) whereas there was no correlation between ORP and total iron concentration ($R^2 = 0.08$, Fig. S-5). This suggests that SS may have potential to serve as a proper indicator to locate the NZVI distribution in the subsurface.

The SS, TS, and total iron concentration represent the "primary" parameter that directly reflects to the iron content of injected NZVI. However, ORP can be considered as a "secondary" parameter that represents the reducing conditions caused by the redox reaction of iron and water after the post injection of NZVI. In other words, SS, TS and the total iron concentration can indicate specific groundwater conditions at a specific time while ORP reveals a bulk condition of groundwater within a period of time. As a result, it is reasonable to observe no correlation between ORP and the total iron concentration in this study.

3.8. Correlation of ORP with the VC degradation efficiency

To facilitate the evaluation process of the NZVI effectiveness, there is a need to find a simple yet reliable geochemical parameter capable of serving as a performance indicator. ORP has been extensively tested for this purpose (Elliott et al., 2008; Glazier et al., 2003; Macé et al., 2006). Fig. 10 summarizes all the data of the VC degradation efficiency and ORP measured in various time intervals from upper, middle and bottom layers during the injection of on-site synthesized NZVI. It was found that both ORP and VC degradation efficiency showed a correlative tendency as an increase in VC degradation efficiency corresponded to a decrease of ORP (Fig. 10). This is in agreement with the previous studies suggesting that ORP can act as a threshold for indicating whether or not the VC degradation takes place.

4. Conclusions

This pilot-scale field study demonstrated a successful application of nanoscale zero-valent iron (NZVI), either on-site synthesized or commercially available, for remediation of groundwater contaminated with chlorinated organic compounds. A total amount of 60 kg palladized NZVI was injected into the groundwater via gravity at a 10 m × 20 m testing site. Based on the results of this study, the following conclusions can be drawn:

- The testing site is located near the coast where the deep aquifer may be intruded by seawater. As a result, it was found that the electric conductivity, chloride, VC and TS concentration are all dependent on the aquifer depth.
- The VC degradation efficiency determined at most of the monitoring wells was 50–99%. It was greater than 90% in both upper and middle layers but was about 20–85% in the bottom layer.
- High concentrations (up to 20 mg/L) of methane and ethylene were detected. However, the cause of which is still unclear at the current stage. It is likely that enhanced bioremediation was involved at the testing site because of its strongly reducing conditions.
- NZVI is mobile in the aquifer. The effective travel distance is at least 3 m according to the SS and TS analysis.
- Correlation analysis showed a moderate dependence of the SS concentration on the total iron concentration. This suggested that SS may be used to indicate the ZVI distribution in groundwater.
- An increase in VC degradation efficiency corresponded to a decrease of ORP values, which is in agreement with the previous studies suggesting that ORP can serve as a proper indicator for the NZVI reactivity.

Appendix.
Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.watres.2009.09.012

REFERENCES

Cao, J., Elliott, D., Zhang, W.-X., 2005. Perchlorate reduction by nanoscale iron particles. Journal of Nanoparticle Research 7 (4–5), 499–506.

Choi, H., Agarwal, S., Al-Abed, S.R., 2009. Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: mechanistic aspects and reactive capping barrier concept. Environmental Science and Technology 43 (2), 488–493.

Elliott, D., Zhang, W.-X., 2001. Field assessment of nanoscale biometallic particles for groundwater treatment. Environmental Science and Technology 35 (24), 4922–4926.

Elliott, D., Lien, H.-L., Zhang, W.-X., 2008. Zerovalent iron nanoparticles for treatment of ground water contaminated by hexachlorocyclohexanes. Journal of Environmental Quality 37, 2192–2201.

Elliott, D., Lien, H.-L., Zhang, W.-X., 2009. Degradation of lindane by zero-valent iron nanoparticles. Journal of Environmental Engineering 135 (5), 317–324.

Environmental Protection Administration, Taiwan, 2006. Soil and groundwater pollution control site preliminary assessment regulations. http://law.epa.gov.tw/en/laws/278076101.html.

Feng, J., Lim, T., 2005. Pathways and kinetics of carbon tetrachloride and chloroform reductions by nano-scale Fe and Fe/Ni particles: comparison with commercial micro-scale Fe and Zn. Chemosphere 59 (9), 1267–1277.

Giasuddin, A.B.M., Kanel, S.R., Choi, H., 2007. Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. Environmental Science and Technology 41 (6), 2022–2027.

Gillham, R.W., O'Hannesin, S.F., 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. Ground Water 32 (6), 958–967.

Glazier, R., Venkatakrishnan, R., Gheorghiu, F., Walata, L., Nash, R., Zhang, W.-X., 2003. Nanotechnology takes root. Civil Engineering 73 (5), 64–69.

Government Information Office, the Republic of China, 2008. The 2008 edition of the Republic of China yearbook. http://www.gio.gov.tw/taiwan-website/5-gp/yearbook/contents.html.

He, F., Zhao, D., 2005. Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. Environmental Science and Technology 39 (9), 3314–3320.

Lien, H.-L., Zhang, W.-X., 2001. Nanoscale iron particles for complete reduction of chlorinated ethenes. Colloids and Surfaces A: Physicochemical and Engineering Aspects 191 (1–2), 97–105.

Lien, H.-L., Zhang, W.-X., 2005. Hydrodechlorination of chlorinated ethanes by nanoscale Pd/Fe bimetallic particles. Journal of Environmental Engineering 131 (1), 4–10.

Lien, H.-L., Elliott, D.W., Sun, Y.-P., Zhang, W.-X., 2006. Recent progress in zero-valent iron nanoparticles for groundwater remediation. Journal of Environmental Engineering and Management 16 (6), 371–380.

Lien, H.-L., Jhuo, Y.-S., Chen, L.-H., 2007. Effect of heavy metals on dechlorination of carbon tetrachloride by iron nanoparticles. Environmental Engineering Science 24 (1), 21–30.

Lien, H.-L., Zhang, W.-X., 2007. Nanoscale Pd/Fe bimetallic particles: catalytic effects of palladium on hydrodechlorination. Applied Catalysis B: Environmental 77 (1–2), 110–116.

Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S., Lowry, G.V., 2005. TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. Environmental Science and Technology 39 (5), 1338–1345.

Liu, Y., Phenrat, T., Lowry, G.V., 2007. Effect of TCE concentration and dissolved groundwater solutes on NZVI-promoted TCE dechlorination and H_2 evolution. Environmental Science and Technology 41 (22), 7881–7887.

Macé, C., Desrocher, S., Gheorghiu, F., Kane, A., Pupeza, M., Cernik, M., Kvapil, P., Venkatakrishnan, R., Zhang, W.-X., 2006. Nanotechnology and groundwater remediation: a step forward in technology understanding. Remediation Journal 16 (2), 23–33.

Nel, A., Xia, T., Mädler, L., Li, N., 2006. Toxic potential of materials at the nanolevel. Science 311 (5761), 622–627.

Nurmi, J.T., Tratnyek, P.G., Sarathy, V., Baer, D.R., Amonette, J.E., 2005. Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics. Environmental Science and Technology 39 (5), 1221–1230.

Nutt, M.O., Hughes, J.B., Wong, M.S., 2005. Designing Pd-on-Au bimetallic nanoparticles for trichloroethylene hydrodechlorination. Environmental Science and Technology 39 (5), 1346–1353.

Nutt, M.O., Heck, K.N., Alvarez, P., Wong, M.S., 2006. Improved Pd-on-Au bimetallic nanoparticle catalysts for aqueous-phase trichloroethylene hydrodechlorination. Applied Catalysis B: Environmental 69, 115–125.

Phenrat, T., Saleh, N., Sirk, K., Tilton, R.D., Lowry, G.V., 2007. Aggregation and sedimentation of aqueous nanoiron dispersions. Environmental Science and Technology 41 (1), 284–290.

Ponder, S.M., Darab, J.G., Mallouk, T.E., 2000. Remediation of Cr(VI) and Pb(II) aqueous solution using supported nanoscale zero-valent iron. Environmental Science and Technology 34 (12), 2564–2569.

Saleh, N., Kim, H.-J., Phenrat, T., Matyjaszewski, K., Tilton, R.D., Lowry, G.V., 2008. Ionic strength and composition affect the mobility of surface-modified Fe^0 nanoparticles in water-saturated sand columns. Environmental Science and Technology 42 (9), 3349–3355.

Sohn, K., Kang, S.W., Ahn, S., Woo, M., Yang, S.-K., 2006. Fe(0) nanoparticles for nitrate reduction: stability, reactivity, and transformation. Environmental Science and Technology 40 (17), 5514–5519.

Tratnyek, P.G., Johnson, R.L., 2006. Nanotechnologies for environmental cleanup. Nano Today 1 (2), 44–48.

United States Environmental Protection Agency (USEPA), (2008) Nanotechnology for site remediation fact sheet, EPA 542-F-08–009.

United States Environmental Protection Agency (USEPA), 1999. EPA method 160.2 (gravimetric, dried at 103–105 °C). http://www.epa.gov/region09/qa/datatables.html.

Wang, C., Zhang, W.-X., 1997. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environmental Science and Technology 31 (7), 2154–2156.

Yuan, C., Lien, H.-L., 2006. Removal of arsenate from aqueous solution using nanoscale iron particles. Water Quality Research Journal of Canada 41 (2), 210–215.

Zhang, W.-X., Wang, C.B., Lien, H.-L., 1998. Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. Catalysis Today 40, 387–395.

Zhang, W.-X., 2003. Nanoscale iron particles for environmental remediation: an overview. Journal of Nanoparticle Research 5 (3–4), 323–332.