



# Enhanced degradation of trichloroethylene in nano-scale zero-valent iron Fenton system with Cu(II)

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## ABSTRACT

Degradation of trichloroethylene (TCE) in nano-scale zero-valent iron (nZVI) Fenton system with Cu(II) was investigated in a closed batch system. TCE was significantly degraded (95%) in 10 min in nZVI Fenton system with 20 mM Cu(II) at initial pH 3, while slight degradation (25%) was observed in nZVI Fenton system without Cu(II) at the same experimental condition. Aqueous Fe(II) concentration proportionally increased (1.2–19.6 mM) with increasing Cu(II) concentration (1–20 mM). Surface analyses using X-ray spectroscopy showed that metallic Cu was formed on the nZVI surface and surface Fe(0) decreased by 1.4 times after the addition of Cu(II) to nZVI suspension. Kinetic rate constant for TCE degradation at 15.3 mM nZVI ( $4.1989 \text{ min}^{-1}$ ) increased by 1.8 times till the increase of nZVI concentration by 5 times and then showed a saturation pattern at higher nZVI concentration. As Cu(II) concentrations increased in the Cu/nZVI Fenton system, the rate constant increased linearly ( $R^2 = 0.979$ ). No significant difference has been observed in the degradation kinetics of TCE by Cu/nZVI Fenton at pH 3 and pH 6 ( $4.8720 \text{ min}^{-1}$  vs.  $4.9858 \text{ min}^{-1}$ ), whereas the kinetics by nZVI Fenton at pH 6 were 1.6 times faster ( $0.0318 \text{ min}^{-1}$ ) than at pH 3 ( $0.0194 \text{ min}^{-1}$ ).

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## 1. Introduction

Chlorinated organic compounds (COCs) have been commonly used in the dry cleaning and degreasing industries as solvents. The release of COCs is of significant public health and environmental concerns due to their harmful characteristics such as carcinogenicity, toxicity, and flammability [1]. The COCs are much denser than water and persistent in natural environment therefore, the remediation of soil and groundwater contaminated by COCs is considered to be much more difficult than that by any other hydrocarbons [2]. Trichloroethylene (TCE) is one of the most well-known COCs ubiquitously found in contaminated soil and groundwater. The United States Environmental Protection Agency has classified it as a probable human carcinogen (Class B2) and issued its maximum contaminant level at  $5 \mu\text{g L}^{-1}$  by the Safe Drinking Water Act [3].

Over the last decades, a great deal of effort has been done to develop and improve remedial alternatives to clean soil and groundwater contaminated by COCs. Chemical oxidation processes using ozone [4], titanium dioxide [5] and Fenton reagents [6] have been known as effective processes to treat wastewater and contaminated groundwater. Fenton reaction among the processes

has attracted an attention due to its strong oxidative capacity for organic contaminants [7]. The main reaction mechanism to produce a representative oxidant from conventional Fenton process is the decomposition of  $\text{H}_2\text{O}_2$  to hydroxyl radical ( $\text{OH}^\bullet$ ) in the presence of Fe(II). Hydroxyl radical from the Fenton process is a powerful and nonselective oxidant, which it can easily react with most of organic compounds. The pH of Fenton process, however, should be kept in acidic range, to avoid the precipitation of  $\text{Fe}(\text{OH})_{3(s)}$ , which is an well known drawback of the process [6]. To overcome these limitations, including early termination of the reaction, Fenton-like reaction and modified Fenton reaction have been studied extensively. Chelate based Fenton reaction using citrate [8], humate [9], and N-(2-hydroxyethyl)iminodiacetic acid [10] has been reported to enhance the degradation of volatile organic compounds at neutral pH by producing stable iron (Fe(II) or Fe(III))–chelate complexes and avoiding iron precipitation. In addition, chitosan has been used as a natural chelating agent to degrade aromatic contaminants [11]. Heterogeneous Fenton-like systems using solid iron sources (e.g., goethite [12], pyrite [13], ferrihydrite, hematite, lepidocrocite, and magnetite [14]) to produce  $\text{OH}^\bullet$  instead of aqueous Fe(II) have been developed as alternative Fenton technologies. In goethite Fenton reaction, formation of chloride as a major transformation product has been reported during the oxidative degradation of COCs [12]. In addition, both magnetite and pyrite Fenton reactions enhanced oxidative degradation of 2,4,6-trinitrotoluene without accumulation of potential toxic transformation products [14]. Zero-valent

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iron (ZVI) has been previously used as a potential iron source for Fenton-like reaction [15,16]. It has been reported that pH of ZVI suspension differently affected the initiation of ZVI Fenton reaction, i.e., ZVI Fenton reaction for the removal of As(III) occurred at the pH range of 3–9 [15], however the Fenton reaction for the removal of 4-chlorophenol hardly occurred at circumneutral pHs [16]. Recently, nano-scale ZVI (nZVI) with enhanced reactivity due to the increased surface area is widely applied to the remediation of contaminated soil and groundwater, as well as wastewater treatment [17,18]. It has been also reported that nZVI particles are more reactive than micro-scale ZVI due to the high surface area [19]. Fenton-like reaction with nZVI showed oxidative degradation of 4-chloro-3-methyl phenol [20], molinate [21], and pentachlorophenol [22]. To enhance the reactivity of nZVI Fenton by producing reactive oxidants, transition metals such as Ni(II) were added to the nZVI Fenton system. A bimetallic Ni/nZVI Fenton reaction, however, did not show the enhanced formation of  $\text{OH}^\bullet$ . Instead, it formed Fe(IV) which can be used for the oxidative removal of As(III) followed by co-precipitation and/or sorption on iron oxides [23]. To our best knowledge to date, no significant research has been conducted to characterize the bimetallic nZVI Fenton reaction for the oxidative degradation of COCs and to identify its reaction mechanism.

In this research, TCE, nZVI, and Cu(II) were selected as representative target chlorinated organic compound, heterogeneous iron source, and bimetallic additive to characterize Cu/nZVI Fenton system for the degradation of TCE and to identify its reaction mechanism. Cu(II) was chosen to enhance the reactivity of nZVI Fenton system, since Cu could be a better metallic additive than Ni. This is based on the fact that electron affinity of Cu (1.235 eV) is higher than that of Ni (1.156 eV) [24]. Batch kinetic tests were conducted to investigate the degradation kinetics of TCE during the Cu/nZVI Fenton reaction, to evaluate the effect of environmental factors (concentrations of nZVI and Cu(II) and initial pH) on the degradation kinetics, and to identify its reaction mechanism. Spectroscopic and microscopic analyses on the surface of Cu/nZVI were conducted to explore the bimetallic Fenton reaction mechanism during the oxidative degradation of TCE.

## 2. Experimental

### 2.1. Chemicals

Chemicals used in this study were ACS grade or higher. These included TCE (99.5%, Sigma), hydrogen peroxide (30 wt%, Kanto), copper(II) chloride dehydrate (97.5%, Kanto), sodium hydroxide (97%, Sigma), ferric chloride (98%, Sigma), sodium borohydride (99%, Sigma), and ferrous sulfate heptahydrate (99%, Sigma). HPLC grade solvents were used to prepare samples. Deaerated deionized water (DDW) was used to protect the oxidation of nZVI in suspension state before starting Cu/nZVI Fenton reactions. For more information, please refer to “Chemicals” in the [Supporting Information](#).

### 2.2. Synthesis of nZVI

nZVI was synthesized following the reduction method using borohydride solution. For more information, please refer to “Synthesis of nZVI” in the [Supporting Information](#).

### 2.3. Experimental procedures

Batch kinetic experiments were conducted to characterize oxidative degradation of TCE in Cu/nZVI Fenton system using 24 mL of amber borosilicate glass vials with open-top cap with three layered septum system [25]. Samples and controls using nZVI were prepared in an anaerobic chamber. An exact amount of nZVI (0.2 g)

was transferred to the vials and DDW adjusted with 3 M  $\text{H}_2\text{SO}_4$  was poured into each vial to keep suspension pH low (at pH 3) for Fenton reaction. An exact amount (200  $\mu\text{L}$ ) of Cu(II) stock solution (2.34 M) was added to each vial to produce bimetallic Cu/nZVI. The vial was sealed with the septum system, taken out of the anaerobic chamber, and mixed by an orbital shaker for 1 h at 200 rpm at room temperature ( $25 \pm 0.5^\circ\text{C}$ ). Variation of Fe(II) and Fe(III) concentrations with respect to different Cu(II) concentrations (1, 10, 20 mM) on nZVI surface was observed under the experimental conditions. Oxidative degradation was initiated by spiking 100  $\mu\text{L}$  of methanolic TCE stock solution (125 mM) with gastight microsyringe (Hamilton Co.) [25] and adding 450  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$  into the each vial, resulting in 0.53 mM of TCE and 188 mM of  $\text{H}_2\text{O}_2$ , respectively. Each vial was mounted on a tumbler providing an end-over-end rotation at 7 rpm at room temperature for complete mixing. Degradation kinetics of TCE was monitored by measuring its aqueous concentration at each sampling time. Control tests to investigate any possible loss of TCE and classic Fenton experiment to compare with the degradation kinetics of TCE by Cu/nZVI Fenton reaction can be referred to the [Supporting Information](#). For more information on batch mechanistic experiments to examine the role of Cu(II) for the oxidative degradation of TCE in the nZVI Fenton system and the parametric study to investigate the effect of nZVI and Cu(II) loadings and initial pH on the oxidative degradation of TCE, please refer to “Experimental procedures” in the [Supporting Information](#).

### 2.4. Analytical procedures

TCE concentration in aqueous sample was measured by a gas chromatograph with an electron capture detector (GC/ECD) [25]. For surface analyses, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) and X-ray photoelectron spectroscopy (XPS) were used. For more information, please refer to “Analytical procedures” in the [Supporting Information](#).

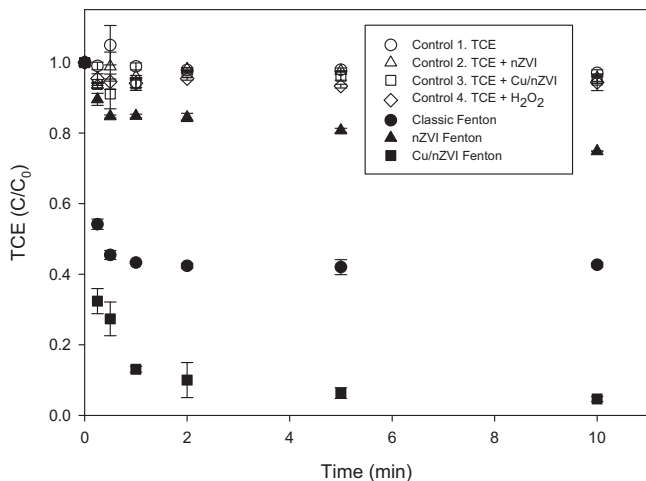
### 2.5. Data treatment

To investigate the characteristics of Cu/nZVI Fenton reaction by comparing TCE degradation kinetics, the experimental data obtained in early stage ( $t < 2$  min) were fitted by a pseudo-first-order kinetics law and kinetic rate constants at different experimental conditions were estimated and compared. For more information, please refer to “Data treatment” in the [Supporting Information](#).

## 3. Results and discussion

### 3.1. Oxidative degradation of TCE by nZVI suspension in the presence of Cu(II)

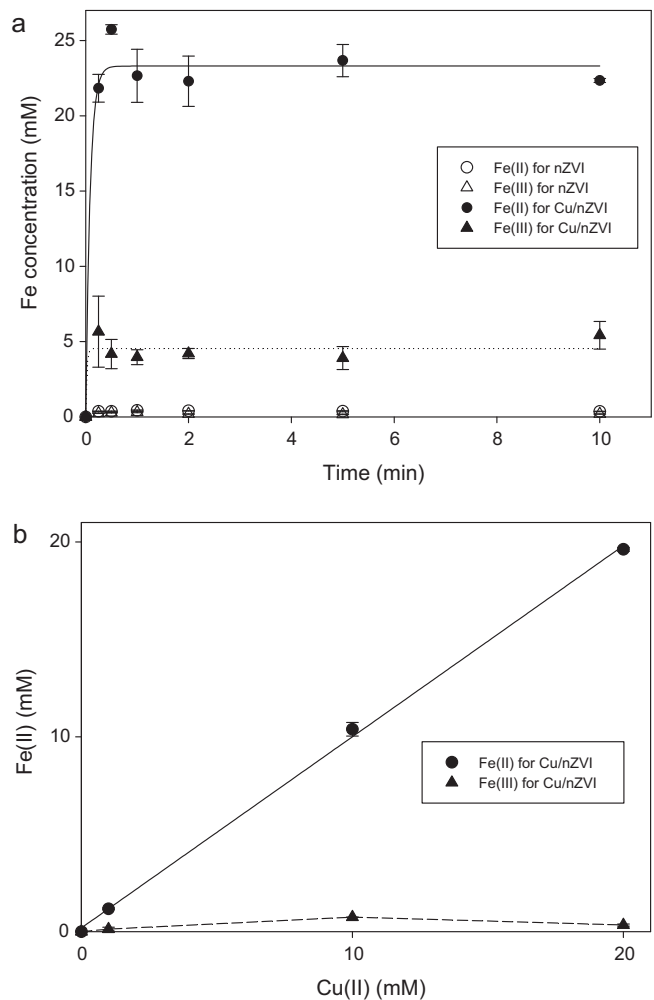
**Fig. 1** shows the degradation of TCE by nZVI Fenton reaction in the presence of Cu(II) at pH 3. TCE removals in four controls were less than 10% showing that no significant losses by volatilization, sorption, and oxidation by hydrogen peroxide occurred during experimental runs. A slight degradation of TCE (25%) was observed when nZVI was only applied as a Fenton reagent to the reaction system, while more than 95% of TCE was oxidatively degraded in nZVI suspension with Cu(II) in 10 min. Compared to the removals of TCE by nZVI Fenton with and without Cu(II), TCE removal by classic Fenton (57%) stayed between those with and without Cu(II). Low reactivity caused by an early termination of classic Fenton reaction was due to a quenching reaction consuming hydroxyl radical by aqueous Fe(II) (i.e.,  $\text{Fe}^{2+} + \text{OH}^\bullet \rightarrow \text{Fe}^{3+} + \text{OH}^-$ ) at high iron concentrations [8,12,26]. nZVI Fenton without Cu(II) showed much slower TCE removal kinetics than the classic Fenton, which is due to very low aqueous Fe(II) content (0.39 mM) released from



**Fig. 1.** Comparison of nZVI Fenton and Cu/nZVI Fenton reactions for the oxidative degradation of TCE. Error bars are ranges of standard deviation of relative TCE concentration. Experimental condition:  $[TCE]_0 = 0.53$  mM,  $[nZVI]_0 = [Fe(II)]_0 = 153$  mM,  $[Cu(II)]_0 = 20$  mM,  $[H_2O_2]_0 = 188$  mM, and initial pH 3.

nZVI surface (Fig. 2(a)). In contrast, we have measured 59.2 times higher aqueous Fe(II) (23.09 mM) in bimetallic Cu/nZVI suspension resulting in the highest TCE removal. This remarkable removal of TCE in the nZVI Fenton system with Fe(II) was due to the continuous supply of increased Fe(II) from nZVI surface which can continuously produce  $OH^\bullet$  via a reaction with  $H_2O_2$  (Fig. 2(a)). The enhancement in oxidative degradation of TCE by Cu/nZVI Fenton system attributed to the increase of aqueous Fe(II) was much more remarkable as the addition of Cu(II) increased. Aqueous Fe(II) was observed to be proportionally increased (1.2–19.6 mM) as the increase of Cu(II) concentration (Fig. 2(b)) but Fe(III) content was very low and irrelevant to the increase of Cu(II). Surprisingly, the added Cu(II) and released Fe(II) concentrations were almost stoichiometrically identical. This indicates that Cu(II) added to nZVI suspension potentially played an important role in the release of Fe(II) from the nZVI surface via oxidative substitution of Fe(0) by Cu(II). The increased aqueous Fe(II) was able to react with  $H_2O_2$  to produce higher content of  $OH^\bullet$  to enhance the oxidative degradation of TCE. Computer simulation using an equilibrium model (PHREEQC) was conducted to investigate potential Cu species in the bimetallic Cu/nZVI suspension at the same experimental conditions before initiating the degradation. The result shows that Cu(0) and  $Cu_2O$  were the main Cu species in Cu/nZVI surfaces at equilibrium pH (5.5). The reduced Cu species were bound on positively charged nZVI surface (point of zero charge ( $PZC_{nZVI}$ ) = 7.7–8.1, [27,28]) after the oxidative substitution of Fe(0) and subsequent release of Fe(II) from the nZVI surfaces. Standard redox potential of  $Cu^{2+}/Cu^0$  ( $E^0_{Cu^{2+}/Cu(s)} = +0.34$  V at 298 K) is much higher than that of  $Fe^{2+}/Fe^0$  ( $E^0_{Fe^{2+}/Fe(s)} = -0.44$  V at 298 K), suggesting that Cu(II) can be reduced to Cu(0) species by electron transfer from nZVI surface during the oxidative substitution and oxidized iron, Fe(II), can be subsequently released to bulk aqueous solution [27,29]. Metals such as Cu, Ni, and Co can easily form complexes on the surface of solid iron in aqueous system [30,31].

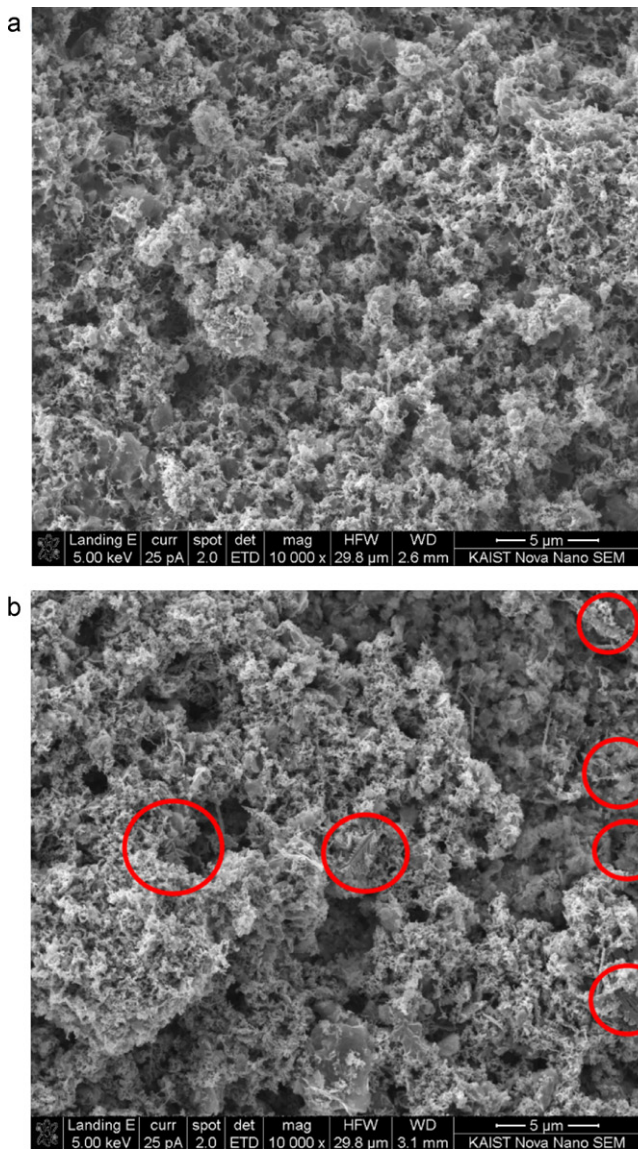
Fig. 3 shows that SEM/EDS images of nZVI in the absence (Fig. 3(a)) and presence of 20 mM Cu(II) (Fig. 3(b)). We observed a bulbous shape of mixed iron (oxy)hydroxides layer in nZVI sample due to the increased iron corrosion at initial pH 3 [32], while Cu/nZVI sample showed micron-sized dendrites formed by Cu embedded on the fractured surfaces of nZVI structure [33]. Cu peak shown in EDS spectrum (Fig. 3(c)) clearly indicates that the dendrite-structured Cu was adsorbed on the surface of nZVI. The



**Fig. 2.** Concentration profiles of aqueous Fe(II) and Fe(III) released from nZVI surface (a) in the presence and absence of Cu(II), (b) the concentration profiles at different Cu(II) concentrations. Experimental condition: (a)  $[nZVI]_0 = 153$  mM,  $[Cu(II)]_0 = 20$  mM, and initial pH 3, (b)  $[nZVI]_0 = 153$  mM,  $[Cu(II)]_0 = 1, 10,$  and  $20$  mM, and initial pH 3.

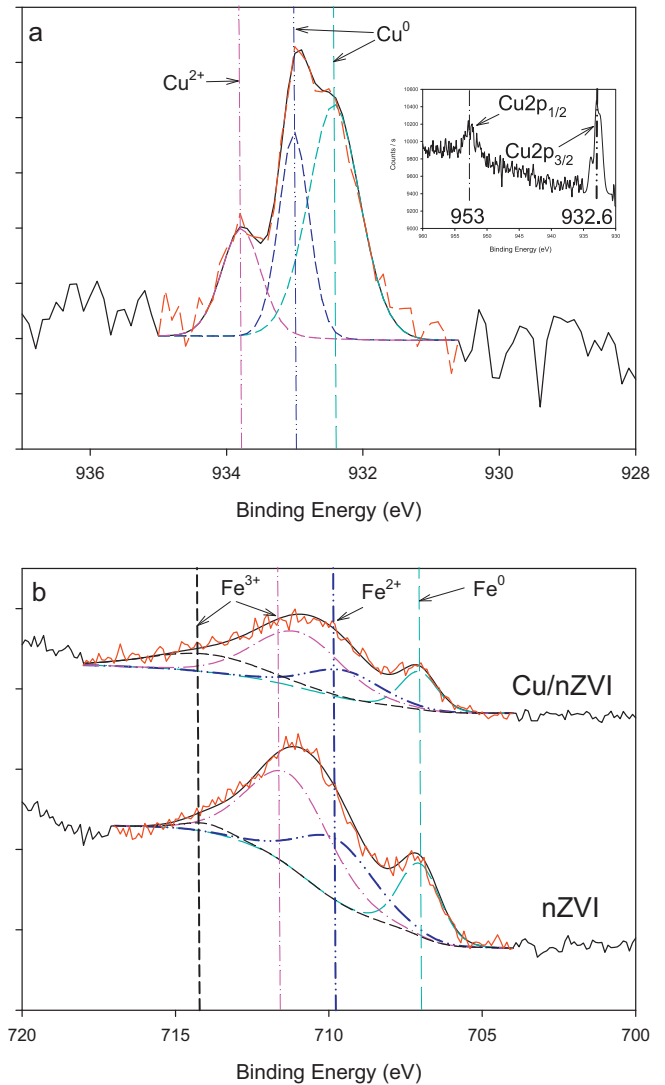
atomic composition of Fe and Cu were 82.78% and 17.22%, which was approximately a 5:1 ratio. Surface area of Cu/nZVI ( $24.04$  m<sup>2</sup>/g) was 2.1 times lower than that of nZVI ( $50.17$  m<sup>2</sup>/g), which is due to the formation of micron-size dendrites on the surface of nZVI. XPS analysis to investigate the change of redox states of Cu and Fe species on nZVI surface in nZVI Fenton system with and without Cu(II) was conducted to evaluate if the electron transfer from the nZVI surface occurred. The recorded Cu 2p and Fe 2p photoelectron profiles from nZVI and Cu/nZVI are shown in Fig. 4. Two peaks centered at 932.6 and 953 eV assigned as Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> clearly appeared in XPS spectrum of Cu/nZVI sample (Fig. 4(a)). The narrow region spectra for Cu 2p<sub>3/2</sub> in solid phase obtained from the Cu/nZVI sample were composed of three identical peaks at 932.4, 933.04, and 933.86 eV, respectively. The binding energies for Cu(0) and Cu(II) were reported to be detectable at 932.47–932.8 [34,35] and 933.8–934.2 eV [36]. Therefore, the XPS spectrum in Fig. 4(a) shows the existence of Cu(0) and Cu(II) of which surface composition is 82.11% and 17.89% (Table 1), respectively. This indicates that most of added Cu(II) was reduced to Cu(0) on the surface of nZVI. In the case of Fe species, the narrow region spectrum for Fe 2p<sub>3/2</sub> was composed of four identical peaks at 706.83–707.06, 709.5–709.7, 711.02–711.26, and 714 eV (Fig. 4(b)). It has been reported that the binding energies for Fe(0), Fe(II), and Fe(III) are exhibited at 706.8, 709–709.5, 711–714 eV, respectively [37,38].





**Fig. 3.** SEM images of (a) nZVI, (b) Cu/nZVI mixture, and (c) EDS spectrum of Cu/nZVI. Experimental condition:  $[\text{nZVI}]_0 = 153 \text{ mM}$ ,  $[\text{Cu(II)}]_0 = 20 \text{ mM}$ , and initial pH 3.

Fig. 4(b) shows the change of peak intensity of Fe species ( $\text{Fe(0)}$ ,  $\text{Fe(II)}$ , and  $\text{Fe(III)}$ ) on the surface of nZVI, before and after addition of  $\text{Cu(II)}$ . The peak intensities of  $\text{Fe(0)}$  and  $\text{Fe(II)}$  decreased and that of  $\text{Fe(III)}$  increased on the nZVI surface after  $\text{Cu(II)}$  addition. Table 1 shows percent composition of Fe and Cu species on nZVI surfaces



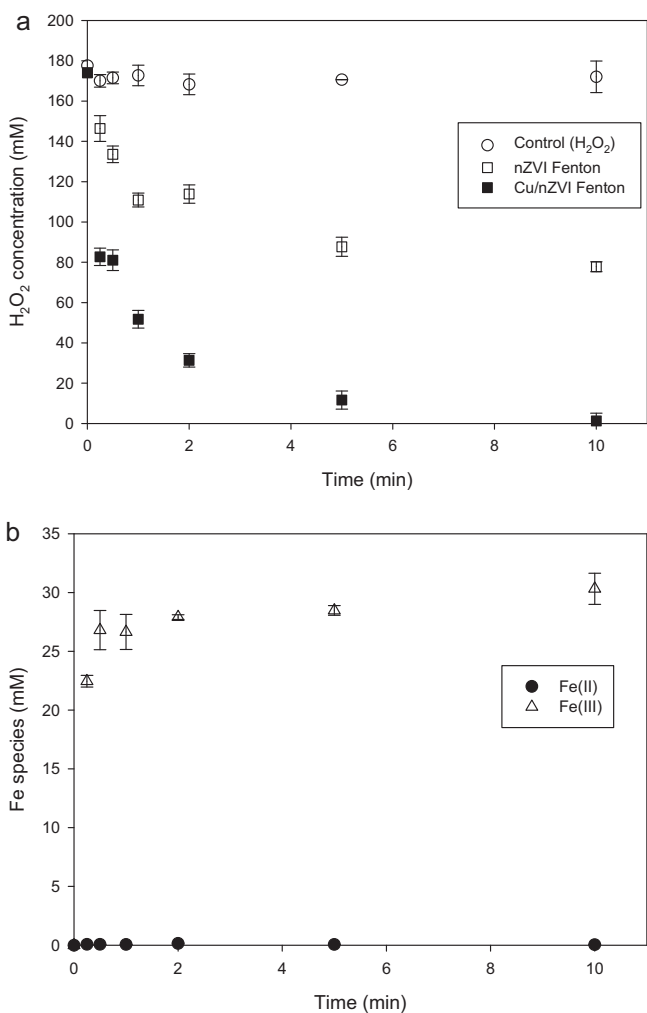
**Fig. 4.** XPS spectra of (a)  $\text{Cu}(2p)$  in Cu/nZVI mixture, (b)  $\text{Fe}(2p_{3/2})$  in nZVI sample with and without  $\text{Cu(II)}$ . Experimental condition:  $[\text{nZVI}]_0 = 153 \text{ mM}$ ,  $[\text{Cu(II)}]_0 = 20 \text{ mM}$ , and initial pH 3.

before and after  $\text{Cu(II)}$  addition. The percent compositions of  $\text{Fe(0)}$ ,  $\text{Fe(II)}$ , and  $\text{Fe(III)}$  on nZVI surface without  $\text{Cu(II)}$  were 19.02%, 29.76%, and 51.22%. The low surface composition of  $\text{Fe(0)}$  and high surface composition of  $\text{Fe(III)}$  may be due to the oxidation of nZVI surface by atmospheric oxygen during the sample preparation for XPS analysis. After the addition of  $\text{Cu(II)}$ , the surface composition of  $\text{Fe(0)}$  and  $\text{Fe(II)}$  decreased by 1.4 and 1.5 times, respectively (13.68 and 19.81%) and that of  $\text{Fe(III)}$  increased by 1.3 times (66.51%). The decrease of surface  $\text{Fe(0)}$  was attributed to the electron transfer to  $\text{Cu(II)}$  to form  $\text{Cu(0)}$  on the surface of nZVI and the decrease of surface  $\text{Fe(II)}$  was due to its dissolution to bulk aqueous solution to balance the sorbed cations caused by the oxidative substitution. Based on the above results, the formation of a representative oxidant in Cu/nZVI Fenton reaction can be summarized by the following three chemical reactions:

**Table 1**  
Change in chemical composition of Fe and Cu species with and without  $\text{Cu(II)}$ .

Reactants	$\text{Fe}^0$ (%)	$\text{Fe}^{2+}$ (%)	$\text{Fe}^{3+}$ (%)	$\text{Cu}^0$ (%)	$\text{Cu}^{2+}$ (%)
nZVI	19.02	29.76	51.22	–	–
Cu/nZVI	13.68	19.81	66.51	82.11	17.89

Experimental conditions:  $25 \pm 1^\circ \text{C}$ . Cu/nZVI sample was prepared in initial pH 3 suspensions and dried in an anaerobic chamber for 24 h.



**Fig. 5.** (a) Variation of H<sub>2</sub>O<sub>2</sub> concentration at different types of Fenton reaction. (b) Concentration of Fe(II) and Fe(III) in Cu/nZVI Fenton system. Experimental condition: [TCE]<sub>0</sub> = 0.53 mM, [nZVI]<sub>0</sub> = 153 mM, [Cu(II)]<sub>0</sub> = 20 mM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 188 mM, and initial pH 3.

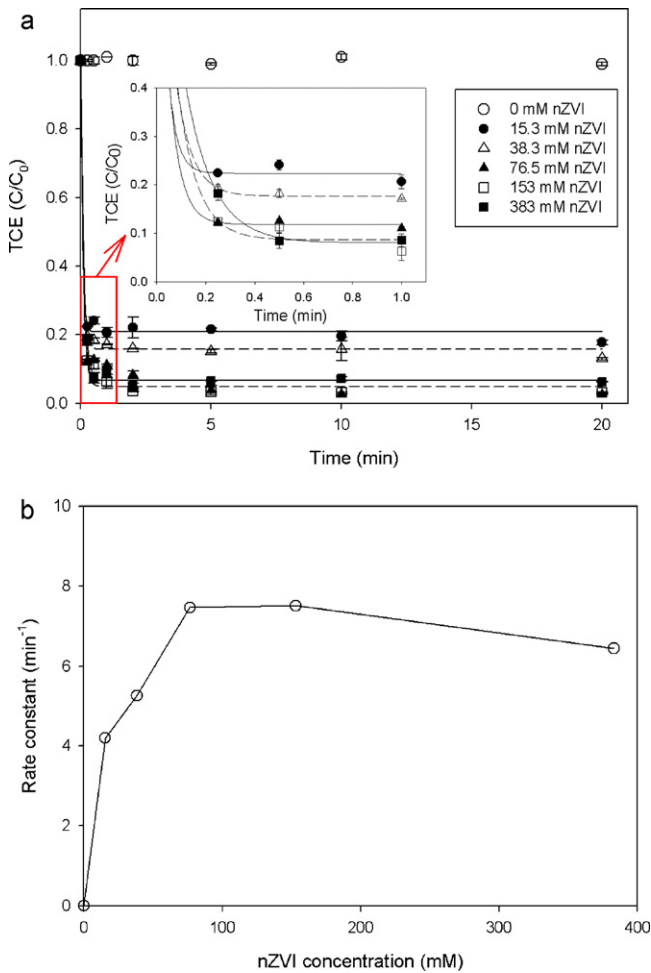


Fig. 5(a) shows variation of H<sub>2</sub>O<sub>2</sub> concentration in nZVI Fenton reactions with and without Cu(II). Control samples without nZVI addition did not show any significant losses of H<sub>2</sub>O<sub>2</sub> in 10 min, indicating no significant formation of OH<sup>•</sup> throughout the experiment. Both nZVI reaction with and without Cu(II) showed a rapid consumption of H<sub>2</sub>O<sub>2</sub> in 2 min and then much slower consumption. Almost 100 mM of H<sub>2</sub>O<sub>2</sub> was consumed in nZVI Fenton system without Cu(II), which is 1.8 times lower consumption than nZVI Fenton with Cu(II) consumed. This is because Fe(II) generation by the oxidation of nZVI surface with H<sub>2</sub>O<sub>2</sub> (Reaction (2)) was not enough to fully consume H<sub>2</sub>O<sub>2</sub> and limited, therefore aqueous Fe(II) concentration to initiate the Fenton reaction by forming OH<sup>•</sup> with H<sub>2</sub>O<sub>2</sub> was low. H<sub>2</sub>O<sub>2</sub> in Cu/nZVI Fenton system was almost fully decomposed, suggesting that adding Cu(II) to nZVI suspension can enhance the reactivity of nZVI Fenton system by producing more OH<sup>•</sup>. In addition, we observed variation of the concentration on aqueous Fe species during the degradation of TCE by Cu/nZVI Fenton reaction (Fig. 5(b)). Fe(II) concentration in aqueous solution

was low (<0.15 mM) during the reaction, while Fe(III) concentration rapidly increased to 28 mM in 2 min and then slowly increased. This indicates that increased Fe(II) released from Cu/nZVI surfaces (Reactions (1) and (2)) rapidly produced sufficient amount of OH<sup>•</sup> and Fe(III) via oxidation by H<sub>2</sub>O<sub>2</sub>. Therefore, Cu/nZVI Fenton reaction can be continued to fully degrade TCE, which cannot be observed in nZVI Fenton and classic Fenton reactions. The experimental results suggest that the degradation of TCE in nZVI Fenton system can be enhanced by adding metal cations such as Cu(II) to induce better conditions for the supply of Fe(II) (Reactions (1) and (2)) and generation of OH<sup>•</sup> (Reaction (3)) leading to full degradation of TCE by the continuous and reactive Fenton reaction. In addition, the highest TCE removal in Fig. 1 indicates that Reaction (3) is a rate determining step for Fe(II) oxidation and OH<sup>•</sup> formation in the Cu/nZVI Fenton reaction. Based on the results from SEM/EDS and XPS analyses (Figs. 3 and 4) with Fe(II) measurement at different Cu(II) concentrations (Fig. 5), a reaction mechanism of oxidative TCE degradation in Cu/nZVI Fenton system can be suggested by the following four steps: (1) added Cu(II) contacts nZVI by mixing and Fe(II) is released from nZVI surface via oxidative substitution of Fe(0) by Cu(II), (2) Cu species reduced by Fe(0) on the nZVI surface (i.e., Cu(0) and Cu<sub>2</sub>O) form surface complexes and they are bound on the positively charged nZVI surface due to the lower suspension pH than PZC<sub>nZVI</sub>, (3) OH<sup>•</sup> is produced by aqueous Fe(II) oxidation with H<sub>2</sub>O<sub>2</sub> and it attacks TCE in Cu/nZVI suspension, and (4) aqueous Fe(II) can be produced by direct oxidation with H<sub>2</sub>O<sub>2</sub> on nZVI surface therefore OH<sup>•</sup> can be continuously produced to fully degrade TCE. The degradation of TCE by Cu/nZVI Fenton reaction may follow similar oxidative degradation pathways of Fenton reactions previously reported, resulting in the transformation of low molecular acids (dichloroacetic-, formic-, glyoxylic-, and oxalic acids), CO<sub>2</sub>, and chloride [39]. No measurements of transformation products of TCE by Cu/nZVI Fenton reaction were carried out in this research.

### 3.2. Effect of nZVI and Cu(II) concentrations and initial pH on the degradation kinetics of TCE

Fig. 6(a) shows the degradation kinetics of 0.53 mM TCE in Cu/nZVI Fenton system at five different nZVI concentrations at initial pH 3. Oxidative degradation of TCE increased as the nZVI concentration increased to 76.5 mM and then showed a saturation pattern accompanied by a slight decrease of degradation rate. An estimated kinetic rate constant of TCE at 15.3 mM nZVI (4.1989 min<sup>-1</sup>) increased by 1.8 times as the nZVI concentration increased by 5 times (76.5 mM). This indicates that Fe(II) released from nZVI surfaces by oxidative substitution by Cu(II) and direct oxidation with H<sub>2</sub>O<sub>2</sub> increased the formation of OH<sup>•</sup> as the nZVI concentration increased to 76.5 mM and it affected overall degradation kinetic rates. Due to the oxidative substitution by Cu(II), an equivalent amount of Fe(II) could be released from nZVI surfaces and produce reactive OH<sup>•</sup> at 15.3 mM nZVI, resulting in a steep increase of kinetic rate constant (Fig. 6(b)). As nZVI concentration increased to 76.5 mM, aqueous Fe(II) released from the surface increased due mainly to the direct oxidation of nZVI surface by H<sub>2</sub>O<sub>2</sub>. Fe(II) content released from nZVI by Reaction (2) seems to be lower than that by Reaction (1), which leads to a gradual increase of kinetic rate constants by 76.5 mM nZVI. A slight increase in kinetic rate constant (7.5138 min<sup>-1</sup>) was observed as nZVI concentration was doubled up (153 mM nZVI) and then the rate constant decreased to 6.4475 min<sup>-1</sup> as it was increased by 5 times (383 mM nZVI). The result indicates once optimal amount of nZVI was introduced to the system, further addition of nZVI did not positively affect the degradation of TCE. As the nZVI concentration increased to 383 mM, aqueous Fe(II) concentration could increase continuously and reach an excessive Fe(II) condition causing a quenching reaction easily. Therefore, OH<sup>•</sup> produced during the

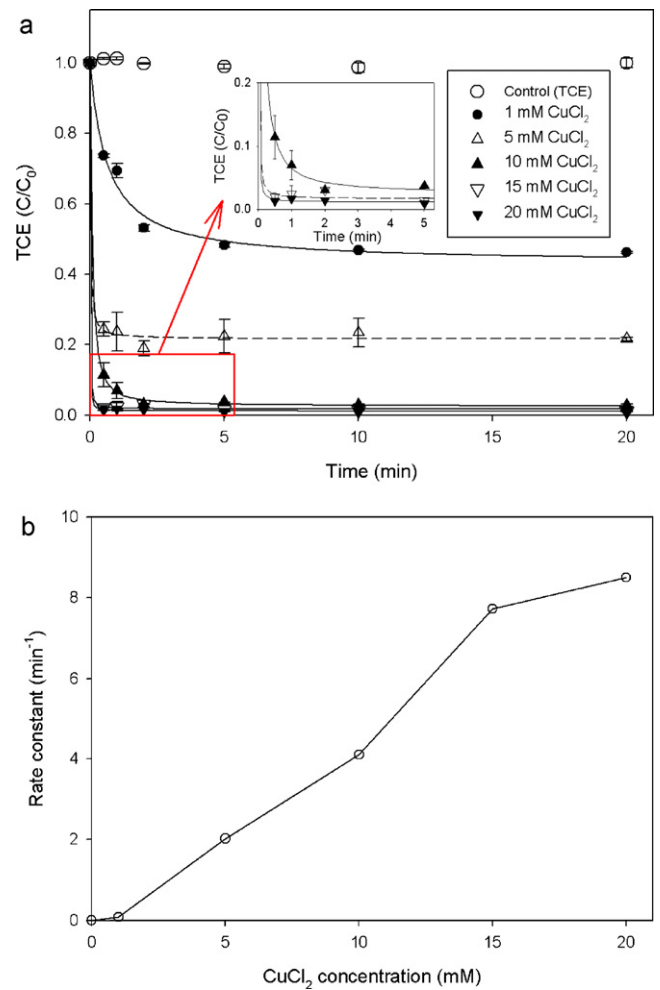


**Fig. 6.** (a) Effect of nZVI content on the oxidative degradation of TCE in Cu/nZVI Fenton system. (b) Variation of kinetic rate constants at different nZVI contents. Experimental condition:  $[TCE]_0 = 0.53$  mM,  $[Cu(II)]_0 = 20$  mM,  $[H_2O_2]_0 = 188$  mM, and initial pH 3.

Cu/nZVI Fenton reaction can be consumed by the excessive Fe(II) [8,26]. This may properly explain the slight increase and decrease of kinetic rate constants at higher nZVI concentrations.

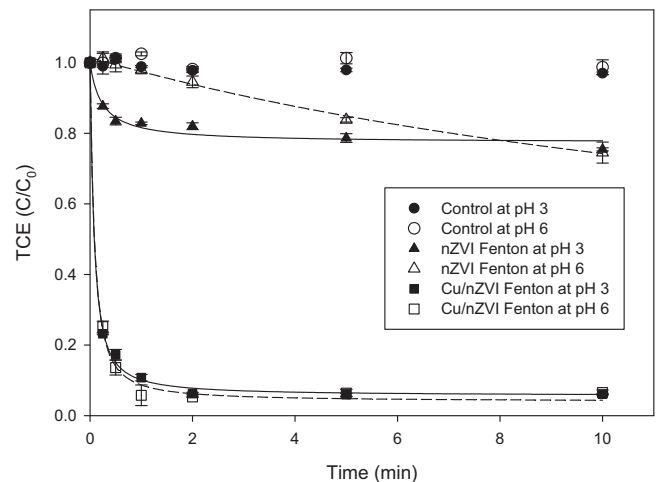
Fig. 7(a) shows the degradation kinetics of TCE in the Cu/nZVI Fenton system at different Cu(II) concentrations. As Cu(II) concentration increased, the kinetic rate constant for TCE degradation increased linearly ( $R^2 = 0.979$ ) (Fig. 7(b)). This seems to be mainly caused by the increased Fe(II) released from the surface of nZVI by the oxidative substitution by the increase of Cu(II) addition. The increased Fe(II) subsequently produced higher concentration of  $OH^\bullet$ , leading to the greater kinetic rate constant for TCE degradation.

Fig. 8 shows the degradation kinetics of TCE at different initial pHs in nZVI and Cu/nZVI Fenton systems. Degradation profiles of TCE in the Cu/nZVI Fenton system at initial pH 3 and 6 showed a similar degradation pattern, while the degradation profiles in the nZVI Fenton system at pH 3 and 6 looked different. The kinetic rate constants for the degradation of TCE by the Cu/nZVI Fenton at pH 3 ( $4.8720$  min<sup>-1</sup>) and 6 ( $4.9858$  min<sup>-1</sup>) were almost same, while those by nZVI Fenton at pH 3 ( $0.0194$  min<sup>-1</sup>) and 6 ( $0.0318$  min<sup>-1</sup>) were different each other. pH of Cu/nZVI suspension starting with initial pH at 3 was kept relatively constant around pH 3 so that the Fenton system can produce sufficient amount of Fe(II) to form  $OH^\bullet$  by the oxidation with  $H_2O_2$ . Although we kept initial pH of nZVI suspension at 6, the pH of Cu/nZVI suspension decreased before initiating the Fenton reaction due to the release of protons during the



**Fig. 7.** (a) Effect of Cu(II) concentration on the oxidative degradation of TCE in Cu/nZVI Fenton system. (b) Variation of kinetic rate constants at different Cu(II) concentrations. Experimental condition:  $[TCE]_0 = 0.53$  mM,  $[nZVI]_0 = 153$  mM,  $[H_2O_2]_0 = 188$  mM, and initial pH 3.

oxidative substitution of Fe(0) by Cu(II) on the surface of nZVI [40], resulting in the similar favorable pH condition ( $\sim$ pH 3) to initiate the Fenton reaction. This leads to the similar degradation pattern of TCE in Cu/nZVI Fenton system at the different pHs. The difference



**Fig. 8.** Effect of initial suspension pH on the oxidative degradation of TCE in nZVI Fenton and Cu/nZVI Fenton systems. Experimental condition:  $[TCE]_0 = 0.53$  mM,  $[nZVI]_0 = 153$  mM,  $[Cu(II)]_0 = 20$  mM, and  $[H_2O_2]_0 = 188$  mM.



between degradation pattern and kinetics of TCE by nZVI Fenton system at pH 3 and 6 resulted from the availability of Fe(II) to react with H<sub>2</sub>O<sub>2</sub> at the beginning of the Fenton reaction. The pHs of both nZVI suspensions were kept relatively constant around pH 3 and 6 before the initiation of Fenton reaction. Fe(II) produced at pH 6 was mainly originated from iron dissolution [16,20], while Fe(II) produced at pH 3 can be more easily generated from both iron corrosion and oxidation with H<sub>2</sub>O<sub>2</sub>. TCE was abruptly degraded (17%) in 30 s in nZVI Fenton system at initial pH 3, followed by slow degradation kinetics. This subsequent slow degradation of TCE may be due to limited generation of Fe(II) from nZVI surface after 30 s, resulting in less decomposition of H<sub>2</sub>O<sub>2</sub> (Fig. 5). TCE was degraded more slowly in nZVI Fenton system at initial pH 6 than at initial pH 3, showing a gradual decrease of TCE. At early stage, decomposition of H<sub>2</sub>O<sub>2</sub> in the nZVI Fenton system at initial pH 3 was much faster than that at initial pH 6 but the decomposition of H<sub>2</sub>O<sub>2</sub> in the system at initial pH 6 became greater as the reaction proceeded (Fig. S1). This is due to the slow and gradual dissolution of Fe(II) from the nZVI surface at pH 6 compared to the fast and abrupt Fe(II) dissolution at pH 3. The addition of Cu(II) to nZVI suspension at pH 6 enhanced the production of Fe(II) from nZVI surface by decreasing pH and oxidative substitution and promoted reactivity of nZVI Fenton system. Similar degradation pattern was found in additional experiment using natural soil suspension (pH 6.2). A slight decrease of TCE (14%) by classic Fenton in the soil suspension was observed, while more than 80% of TCE was oxidatively degraded in Cu/nZVI Fenton system in 10 min (Fig. S2). Relatively high pH condition in the soil suspension made the classic Fenton reaction difficult to occur. Low removal of TCE in the classic Fenton reaction was due mainly to the sorption of TCE on soil surface. The experimental results imply that Cu(II) addition may induce and/or promote reactivity of the Fenton reaction applied to the remediation of sites contaminated with TCE at circum-neutral pH condition.

#### 4. Conclusions

Characteristics of a heterogeneous Cu/nZVI Fenton system have been investigated. Cu/nZVI Fenton system has shown much more enhanced degradation of TCE than nZVI Fenton and classic Fenton systems at initial pH 3 and 6. Variations of Fe(II), Fe(III), and H<sub>2</sub>O<sub>2</sub> concentrations before and during the Fenton reaction also indicated that Cu/nZVI Fenton is much efficient system for TCE removal than nZVI Fenton. Based on the results from SEM/EDS and XPS analyses with Fe(II) measurement at different Cu(II) concentrations, a reaction mechanism of oxidative TCE degradation in Cu/nZVI Fenton system can be suggested by the following four steps: (1) release of Fe(II) from nZVI surface via oxidative substitution of Fe(0) by Cu(II), (2) reduction of Cu species by Fe(0) on the nZVI surface, (3) production of OH• by aqueous Fe(II) oxidation with H<sub>2</sub>O<sub>2</sub> and degradation of TCE by OH radical in Cu/nZVI suspension, and (4) release of Fe(II) by a direct oxidation with H<sub>2</sub>O<sub>2</sub> on nZVI surface and continuous production of OH• to fully degrade TCE. The effect of nZVI concentration on the degradation kinetics of TCE in the Cu/nZVI Fenton system showed once optimal amount of nZVI was added to the system, further addition of nZVI did not significantly enhance the degradation of TCE. TCE degradation linearly increased as Cu(II) concentration increased to 20 mM. Experimental results from the evaluation of initial pH effect on the degradation of TCE in Cu/nZVI Fenton system showed that the release of Fe(II) from nZVI surface initially controlled by the oxidative substitution was not significantly influenced by initial pH. This implies that the Cu/nZVI Fenton system could be applied to the remediation of sites contaminated with TCE at circum-neutral pH. Cu/nZVI system developed in this study can solve technological problems such as low operation pH by providing the low pH condition automatically (i.e., by providing

protons to the sites) and early termination of Fenton reaction frequently found in classic Fenton system. The experimental results and reaction mechanism obtained from this research can provide basic knowledge for the development of novel technologies using bimetallic Fenton reactions to remediate soil and groundwater contaminated with chlorinated organics effectively and be applied to the operation of enhanced bimetallic Fenton systems. Finally, high cost of bimetallic Fenton systems due to the use of precious metals (Pd, Pt, and Au) can be mitigated by applying Cu.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.10.056.

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