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RESEARCH ARTICLE

Automatic pH control system enhances the dechlorination of 2,4,4′-trichlorobiphenyl and extracted PCBs from contaminated soil by nanoscale Fe^0 and Pd/Fe^0

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Abstract

Purpose Dechlorination of polychlorinated biphenyls (PCBs) by nanoscale zerovalent iron (NZVI) is often strongly hindered by increased pH because large amounts of H^+ ions were consumed during the surface reaction. The main objective of this work was to evaluate the effect of pH control in acid on the dechlorination processes of PCBs and to compare the dechlorination efficiency between 2,4,4′-trichlorobiphenyl (2,4,4′-CB) and the extracted PCBs from the field PCBs-contaminated soil in this system.

Methods The reaction solution pH was controlled to be weakly acid (4.90–5.10) with an automatic pH control system, in which the dechlorination of 2,4,4′-CB and extracted PCBs from a PCBs-contaminated soil by NZVI and palladized nanoscale zerovalent iron (NZVI/Pd) was investigated.

Results To control the reaction solution pH to be acid actually increased the dechlorination rate of PCBs by NZVI and NZVI/Pd. The observed normalized pseudo-first-order dechlorination rate constants (k_{obs}) of 2,4,4′-CB increased from 0.0029 min^{-1} (no pH control) to 0.0078 min^{-1} (pH control) by NZVI and from 0.0087 min^{-1} (no pH control) to 0.0108 min^{-1} (pH control) by NZVI/Pd. In the case of NZVI/Pd, the chlorines in the *para* position were much more easily dechlorinated than *ortho* position, and biphenyl was the dominating product. As the solution pH was controlled at 4.90–5.10, the dechlorination rate constants of PCB congeners extracted from soil (k_{obs}) were 0.0027–0.0033 min^{-1} and 0.0080–0.0098 min^{-1} by NZVI and NZVI/Pd, respectively.

Conclusions To keep the reaction solution to be weakly acid markedly increased the dechlorination rate of PCBs, which may offer a novel technology in the remediation of PCBs-contaminated soil.

Keywords Dechlorination · pH control system · 2,4,4′-Trichlorobiphenyl · PCBs-contaminated soil · Nanoscale Fe^0 · Nanoscale Pd/Fe^0

1 Introduction

Polychlorinated biphenyls (PCBs) as one group of persistent organic pollutants (POPs) have been banned since the late 1970s. However, their historical use has resulted in water, soil, and sediment pollution of PCBs (Rodenburg et al. 2010). So remediation of such contaminated water, soil, and sediment has become a hot spot due to their high toxicity, persistence, and strong bioaccumulation (Kimbrough 1995).

Recently, nanoscale zerovalent iron (NZVI) and palladized nanoscale zerovalent iron (NZVI/Pd) have been applied for degrading PCBs (Varanasi et al. 2007; Choi et al. 2009; Devor et al. 2009). NZVI, having a predominantly magnetite shell with large specific surface area and high surface reactivity, is found to be one of the cost-effective materials used for soil remediation (Liu et al. 2005; Yak et al. 2000; Zhang et al. 1998; Wang and Zhang 1997). However, the reactivity of NZVI markedly decreased with increased reaction time due to surface inactivation, especially in humid conditions (Wang

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et al. 2010). In addition, NZVI/Pd was a superior reductant for PCBs (Fang and Al-Abed 2008a; Xu and Bhattacharyya 2008). The role of metal additives in enhancing reactivity was ascribed to the galvanic corrosion (Xu and Zhang 2000) and the production of atomic hydrogen (Cwiertny et al. 2006). The PCBs adsorbed on the Pd or the NZVI/Pd surfaces are dechlorinated by the active hydrogen species dissolved in the Pd lattice. Complete and incomplete dechlorination of PCBs by this bimetallic iron has been reported (Grittini et al. 1995; Korte et al. 2002; Lowry and Johnson 2004).

Although the use of NZVI and NZVI/Pd for remediation of PCBs-contaminated groundwater has been previously studied, the applicability of these nanoscale particles for remediation of PCBs-contaminated soil is not well addressed. Varanasi et al. (2007) mixed iron nanoparticles into PCB-contaminated soil and attempted to maximize PCB destruction. He et al. (2009) used ZVI and Pd/Fe for remediating PCBs-contaminated soil at room temperature. However, PCBs are water insoluble and strongly adsorbed in soil colloid particles. So the dechlorination of PCBs in soil will ultimately be limited. In addition, the slow dechlorination rates of PCBs require a prolonged contact of NZVI with the PCBs. Thus, to extract PCBs from contaminated soil and treat the solution can be considered for obtaining a rapid dechlorination rate of PCBs. Xu and Bhattacharyya (2008) dealt with the modeling and experimental verification of PCB dechlorination using a porous membrane reactor embedded with Fe/Pd nanoparticles. Fang and Al-Abed (2008a) evaluated the pH effect on the dechlorination of 2-chlorobiphenyl (2-CB) by Fe/Pd and investigated the relationships between the dechlorination rates and the iron corrosion parameters.

However, the dechlorination of PCBs is pH sensitive because protons are involved (Matheson and Tratnyek 1994). Protons affected the reaction extent significantly, and the reduction rates were dependent on the pH. This also has been reported in our previous work (Wang et al. 2011). Unfortunately, previous studies just focused on controlling the initial pH, but solution pH, in fact, increased quickly and the catalyst would be deactivated (Chen et al. 2001; Choe et al. 2004). Therefore, we employed an automatic pH control system to keep reaction solution pH at 4.90–5.10 for efficient dechlorination of 2,4,4′-trichlorobiphenyl (2,4,4′-CB) and the PCBs extracted from a PCBs-contaminated soil by NZVI and Pd/NZVI. The aims of this study are (1) to evaluate the effect of automatic pH control system on the dechlorination processes of PCBs and (2) to compare the dechlorination efficiency between 2,4,4′-CB in the solution and the extracted PCBs from the PCBs-contaminated soil. Attempts were made to offer a novel technology for the remediation of PCBs-contaminated soil.

2 Materials and methods

2.1 Chemicals

2,4,4′-CB, 2-CB, 4-chlorobiphenyl (4-CB), 2,4-dichlorobiphenyl (2,4-CB), 2,4′-dichlorobiphenyl (2,4′-CB), biphenyl (BP), and PCB calibration check solution including 20 PCB congeners were 99.4+% pure and obtained from AccuStandard (New Haven, CT, USA). Iron particles in sizes ranging from 30 to 100 nm were obtained from Nanjing Emperor Nano Material Co. Ltd, China, and were stored in an anaerobic glove box (nitrogen protect system, YQX-II, Shanghai CIMO Medical Instrument Manufacturing Co. Ltd, China). $C_4H_6O_4Pd$ (≧46.0%) was obtained from Sinopharm Chemical Reagent Co. Ltd, China. Hexane [high-performance liquid chromatography (HPLC) grade] was obtained from CNW Technologies GmbH, Germany. Acetonitrile (HPLC/Spectro grade) was obtained from TEDIA Company Inc. Ltd, USA. Acetone (analytical reagent), hydrochloric acid (guaranteed reagent), and sulfuric acid (guaranteed reagent) were obtained from Nanjing Chemical Reagent Co. Ltd, China. The water used in the experiments was oxygen free, obtained by bubbling nitrogen gas overnight through milli-Q water (resistivity 18 $M\Omega\ cm^{-1}$).

2.2 Preparation of NZVI/Pd particles

The palladium was deposited on NZVI particles in an ethanol solution of palladium acetate using a method modified from the references (Fang and Al-Abed 2008b; Zhang et al. 1998). At first, the NZVI particles were moved to a plastic centrifuge tube fully filled with an ethanol solution of palladium acetate (no headspace in the tube) in the anaerobic glove box, the concentration of palladium acetate was calculated to obtain a target Pd loading of 0.5% based on the amount of NZVI. Then the tube was placed on a reciprocal shaker and shaken at 200 rpm for 2 h for complete deposition of Pd. Finally, the Pd-deposited NZVI particles (NZVI/Pd) were washed four times with oxygen-free water, each time using the same volume as the ethanol solution. After washing, the NZVI/Pd particles were ready for use in the dechlorination experiments. All batches of NZVI/Pd particles used in this study contained the same Pd target content of 0.5%.

2.3 Dechlorination of 2,4,4′-CB using an automatic pH control system

PCB solutions were prepared by dissolving a known mass of 2,4,4′-CB in acetone. In each dechlorination experiment, initial solution pH was adjusted to 5.0 by adding sulfuric acid. A 300-mL sample of 2.0±0.2 mg L^{-1} 2,4,4′-CB in 5%

acetone–water cosolvent and 1.5 g NZVI or NZVI/Pd particles were added into a 500-mL three-necked flask under anaerobic conditions. The solution of the flasks was stirred by an electric stirrer (JJ-1, Jiangsu Jintan Medical Instrument Factory, China) using PTFE stirrer bars. An automatic pH control system was used to control the pH at 4.90–5.10 throughout the whole reaction with 0.1 mM sulfuric acid. The system included an automatic pH control equipment (CD-10, Nanjing Chuan-di Instrument and Equipment Co. Ltd., China), a peristaltic pump (HL-2, Shanghai Xinbo Radio Factory, China), a pH electrode (E-201-C, Shanghai Precision and Scientific Instrument Co., China), and an electric stirrer (JJ-1, Jiangsu Jintan Medical Instrument Factory) to stir the solution in the flasks by using PTFE stirrer bars (Fig. 1). Samples were taken at predetermined time with 1-mL airtight syringes through the septa for closed-system reaction conditions. The suspension was sampled in 8-mL glass sample vials with PTFE-lined caps, prefilled with 1 mL hydrochloric acid by shaking on a vortex mixer for 1 min. The aim was to promote the dissolution of NZVI surfaces and protonation of PCB (Kim and Carraway 2000), thereby releasing the adsorbed PCB into hexane. Then the solution was extracted into 1.0 mL hexane by shaking with a reciprocal shaker for 1 h to achieve equilibrium. All dechlorination experiments were conducted in ambient conditions without oxygen.

2.4 Dechlorination of PCBs extracted from soil using an automatic pH control system

PCBs-contaminated soils were collected from a capacitor dump in Zhejiang province, China. Prior to testing, soils were air-dried and passed through a 60-mesh sieve. Physicochemical characteristics and composition of the PCBs-contaminated soil are shown in Table 1. PCBs were extracted by shaking 2 g contaminated soils with 30 mL acetone in 50-mL glass sample vials with PTFE-lined caps and ultrasonicated for 20 min. This procedure was repeated for three times, and the extracted solutions were combined (the recovery of standard 2,4,4′-CB spiked into the clean soils was 78.6–99.7%). The combined extracted solution was diluted in a 500-mL three-necked flask, initial pH was adjusted to 5.0 by adding sulfuric acid, and 1.5 g NZVI or NZVI/Pd particles were added under anaerobic conditions. The dechlorination of the extracted PCBs was carried out as performed for 2,4,4′-CB.

2.5 Analytical methods

Analysis was performed by GC/μECD (for PCBs) and HPLC (for biphenyl). Quantitative analyses of the PCB standard and samples were performed using a gas chromatograph (GC; Agilent 7890, USA) equipped with ^{63}Ni electron capture detector (ECD) and an auto-sampler. Chromatographic separations were accomplished with a 60-m HP-5 column with a 0.25 mm i.d. and 0.25 μm film thickness (J&W Scientific Inc.) using injections in the splitless mode (0.5 min). The oven temperature was held at 150°C for 2 min, increased to 280°C with a gradient of 7°C min^{-1}, and then held for 2 min. The temperatures of the injector and detector were 250°C and 300°C, respectively. Ultra-high-purity nitrogen was used as the ECD makeup gas at a flow of 30 mL min^{-1} and the carrier gas with a constant of 1.0 mL min^{-1}.

The BP concentration (one of the 2,4,4′-CB dechlorination products) was analyzed by HPLC (Agilent1100, USA) with UV detectors using 4.6×150-mm ZORBAX* ODS-C18 columns. The mobile phase consisted of 90:10 acetonitrile to water solutions and was delivered at a flow rate of 1.0 mL min^{-1}. The wavelength was set at 254 nm. The approximate detection limits were 0.1 mg L^{-1} for biphenyl.

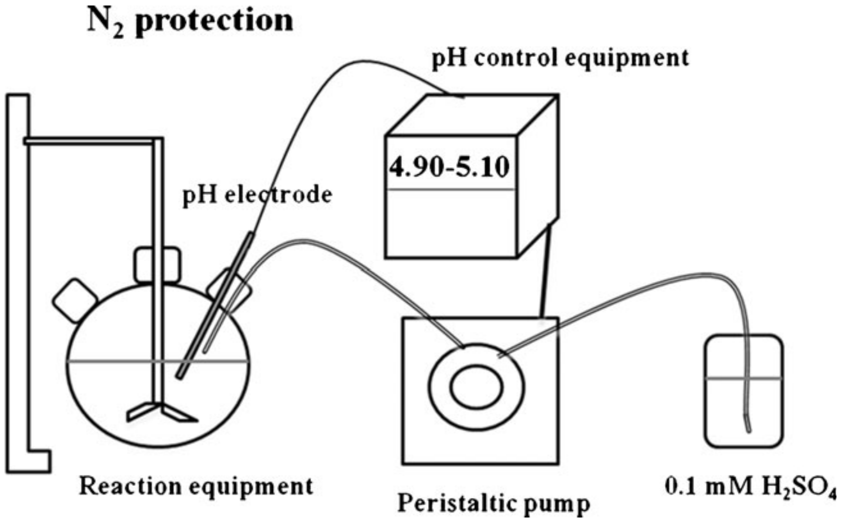


Fig. 1 Automatic pH control system

Table 1 Physicochemical characteristics and composition of the PCBs-contaminated soils

pH	DOM (mg kg^{-1})	Element (mg kg^{-1})				
		K	Ca	Mg	Al	Fe
6.30	165.5	3.60	18.2	10.0	2.60	1.00

The total concentrations of dissolved iron in aqueous solutions were determined by an atomic absorption spectrometer (Hitachi Z-2000 AAS, Japan). Five milliliters of aqueous solutions in the vials was withdrawn and filtered through a 0.22-μm membrane filter to remove fine particulates. The filtered solutions were acidified with concentrated nitric acid to pH <2. The concentration of ferrous ions was determined by the phenanthroline method (Matheson and Tratnyek 1994) with a spectrophotometer (GBC, UV-911).

The concentration of dissolved chloride ions in the solution was measured by a chloride ion-selective electrode (Pc1-1, Shanghai Precision and Scientific Instrument Co.). Solution pH was measured using a pH meter (Orion 868, USA). DOM in the contaminated soil was analyzed by total organic carbon analyzer (Muti N/C 3000, Germany). Cations in the extracted soil solution were determined by inductively coupled plasma atomic emission spectroscopy (IRIS Advantage, Thermo Electron Corporation, USA).

2.6 System mass balance

The mass balance at predetermined time was calculated as the ratio of the total PCB congeners measured to the initial PCB mass measured in the system.

$$MB(\%) = \frac{\sum(\mathrm{C_i})}{\mathrm{C_0}} \times 100 \qquad (1)$$

where C_i is the mass of all PCBs in solution at time t including all dechlorination products and the parent compound, and C_0 is the mass of the parent congener at the initial sampling event in milligrams per liter.

3 Results and discussion

3.1 Dechlorination of 2,4,4′-CB by NZVI and NZVI/Pd with and without pH control

In our earlier study, we found that solution pH was very important for the reductive dechlorination of 4-ClBP by NZVI. The dechlorination efficiency of 4-ClBP was only 53.8% after 48 h reaction as the initial pH was 4.0. During the reaction, solution pH increased quickly, which strongly inhibited the dechlorination efficiency (Wang et al. 2011). Shih et al. (2011) reported that the dechlorination rate constants of HCB linearly increased with decreasing aqueous pH values, and the dehalogenation of HCB with NZVI was favorable under acid condition. So, it is expected that pH control at acid condition will increase the dechlorination of PCBs.

Figure 2 shows that the dechlorination efficiency of 2,4,4′-CB by NZVI for 4 h was 43.4% and 81.7% without and with pH control at 4.90–5.10, respectively. The 2,4,4′-CB concentration was almost constant in the controlled treatment without NZVI. The concentration of chloride ions increased to 7.3 and 18.1 μmol L^{-1} without/with pH control, respectively, and 77.65% of the theoretical maximum was calculated by NZVI with pH control. Chuang and Larson (1995) reported that after subtraction of blanks due to background value in water, reagents, and glassware, 73% of the theoretical maximum was calculated.

To control the solution pH to be acid increased the dechlorination efficiency of 2,4,4′-CB, and shortened the reaction time. The general dechlorination reaction of PCBs by NZVI can be represented as $\mathrm{RCl} + \mathrm{H}^+ + 2\mathrm{e}^- \rightarrow RH + Cl^-$. It means that the protons in the system will significantly affect the reaction extent. Keeping the solution to be acid can provide enough protons for the dechlorination, because protons are largely consumed during the reaction.

The dechlorination of 2,4,4′-CB by NZVI/Pd was also investigated with pH control. The NZVI coated with 0.5% palladium dechlorinated 40.33% and 68.43% of 2,4,4′-CB in 30 min and 86.04% and 88.91% of 2,4,4′-CB after 4 h without/with pH control (pH 4.90–5.10). Figure 3 shows the dechlorination products of 2,4,4′-CB, and the stepwise dechlorination of 2,4,4′-CB with the formation of successive low chlorinated congeners until biphenyl was found. The concentrations of products were 0.169 mg L^{-1} for 2-CB,

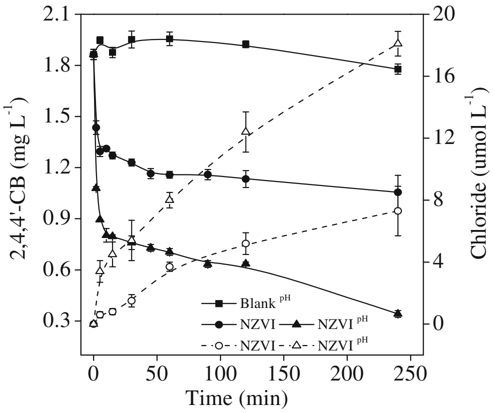


Fig. 2 Effect of pH control on the dechlorination of 2,4,4′-CB by NZVI. NZVI to solution ratio was 5.0 gL^{-1}. Initial solution pH was 5.0; *NZVI* without pH control, *NZVI^{pH}* pH control at 4.90–5.10. The *y*-axes on the *left* and *right* correspond to the concentrations of 2,4,4′-CB and chloride, respectively

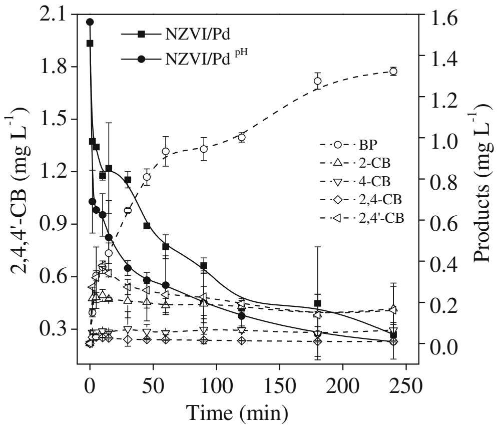


Fig. 3 Changes of 2,4,4′-CB and the intermediates formed by stepwise dechlorination with time. The initial concentration of 2,4,4′-CB was 2.0± 0.1 mg L^{-1}. The NZVI/Pd loading was 5.0 gL^{-1} of PCB solution. *NZVI/ Pd* without pH control, *NZVI/Pd^{pH}* pH control at 4.90–5.10. The *y*-axes on the *left* correspond to the concentration of 2,4,4′-CB with/without pH control, and the secondary *y*-axes on the *right* corresponds to the intermediates of 2,4,4′-CB with pH control

0.065 mg L^{-1} for 4-CB, 0.010 mg L^{-1} for 2,4-CB, and 0.162 mg L^{-1} for 2,4′-CB after 4 h, and the concentration of BP was 1.323 mg L^{-1}. 2,4,4′-CB has one Cl atom in its *ortho* or *para* positions, i.e., 2-CB and 2,4′-CB, which were formed by *para*-elimination of 2,4,4′-CB and were the most dichlorinated intermediates. Little of other theoretically possible dechlorination intermediates like 4-CB and 2,4-CB were formed by *ortho*- or *para*-elimination. This indicated that *para*-dechlorination occurred more than at *ortho* positions before conversion to BP by *ortho*-elimination in 2,4,4′-CB dechlorination. The results were in agreement with other reports (Agarwal et al. 2009; Lowry and Johnson 2004; Noma et al. 2003; Yak et al. 1999; Yang et al. 2007). Agarwal et al. (2009) found that the trends for electrophilic substitution were consistently *p*→*m*→*o* positions. Lowry and Johnson (2004) reported that non-*ortho*-substituted congeners had faster initial dechlorination rates than *ortho*-substituted congeners in the same homologue group.

Mass balances for 2,4,4′-CB were calculated in Fig. 4. Total mass balances of PCB were 85.4–98.6% for the NZVI/Pd experiment with pH control, and products mass balances ranged from 35.3% to 84.1%. Ferrous ions and total iron ions could be detected, since redox reaction took place in an aqueous solution. Figure 5 shows the concentration of ferrous ions and total iron ions when NZVI/Pd was used with/without pH control. Total iron ions and ferrous ions were 1,966 and 128.5 mg L^{-1} with pH control while just 2.605 mg L^{-1} of total iron ions by NZVI without pH control in 4 h. The concentration of the total irons without reaction pH control is in good agreement with the study of Zhang et al. (2009), which reported that the concentration of total iron and ferrous ions was about 2.5 and 1.5 mg L^{-1} for the dechlorination of 2,4-dechlorophenol by Ni–Fe nanoparticles without reaction pH control. But in our pH control system, a large amount of the total and ferrous ions was observed. The possible reason was that when the reaction pH was not controlled, ferrous ions reacted with dissolved oxygen and hydroxyls, or hydroxyl and carbonate, to form passivating layers on the surface of the nanoparticles, blocking further reaction. But when the reaction pH was controlled at 4.90–5.10, the oxides on the particles surface of NZVI or NZVI/Pd were dissolved, and the active sites of the particle surface were exposed afterwards. Thus, the iron corrosion could be accelerated to produce enough hydrogen (or hydrogen atoms) in favor of hydrogenation reaction (Kim and Carraway 2000).

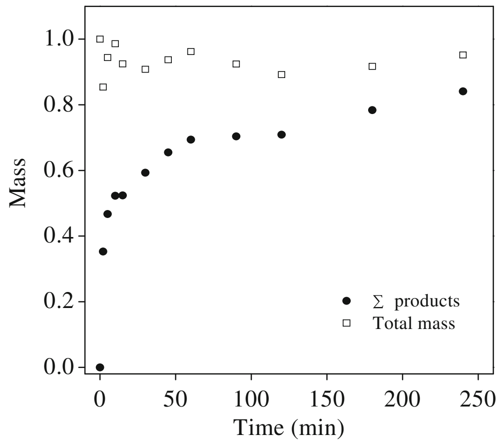


Fig. 4 Products distribution during dechlorination of 2,4,4′-CB by NZVI/Pd with pH control

3.2 Reaction kinetic study

Table 2 compared the results of 2,4,4′-CB dechlorination by NZVI and NZVI/Pd with/without pH control. All of them can be well fitted with the following pseudo-first-

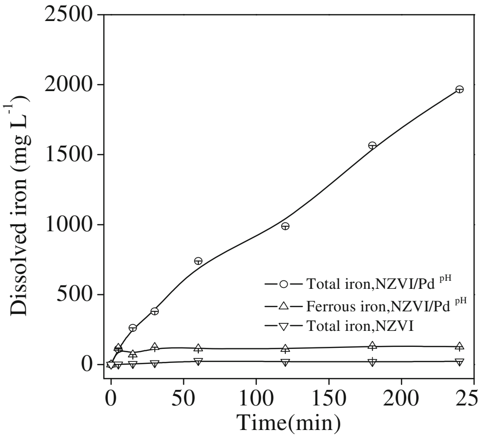


Fig. 5 Concentration of total iron and ferrous iron in the dechlorination of 2,4,4′-CB with/without pH control

Table 2 Best linear fit of first-order reaction rates for 2,4,4′-CB dechlorination with/without pH control

Composition	Reaction pH control	k_{obs} (min^{-1})	k_{SA} (10^{-4} L m^{-2} min^{-1})[a]	R^2	N[b]
NZVI	No	0.0029±0.0006	0.39	0.860	4
NZVI	Yes	0.0078±0.0012	1.04	0.919	4
NZVI/Pd	No	0.0087±0.0012	1.16	0.912	5
NZVI/Pd	Yes	0.0108±0.0016	1.44	0.918	4

[a] The normalized surface reaction rate constant; the special surface area is 15 m^2 g^{-1} and loading is 5.0 gL^{-1}; R^2 is the linearity of the data fitting

[b] N is the number of data points. Reported errors are 95% confidence intervals for pseudo-first-order fit of product data (Eq. 5)

order reaction kinetics (Lim and Zhu 2008; Xu and Bhattacharyya 2007, 2008):

$$-\frac{dC}{dt} = k_{obs}C = k_{SA}\rho_m a_S C \tag{2}$$

where C is the 2,4,4′-CB concentration (in milligrams per liter) at a sampling time (in minutes), a_S is the specific surface area of the nanoparticles (in square meters per gram), ρ_m is the loading of the nanoparticles, k_{obs} is the observed rate constant (per minute), and k_{SA} is the surface area-normalized rate constant (in liters per minute per square meter). The kinetic data for 2,4,4′-CB dechlorination were shown in Table 2. The k_{SA} values for 2,4,4′-CB by NZVI with/without pH control were determined to be 1.04×10^{-4} and 0.39×10^{-4} L m^{-2} min^{-1}, respectively, while the values for 2,4,4′-CB by NZVI/Pd were 1.44×10^{-4} and 1.16×10^{-4} L m^{-2} min^{-1} with/without pH control. The pH control to be acid significantly increased the dechlorination efficiency of 2,4,4′-CB, and application of NZVI/Pd can get better dechlorination results rather than NZVI. The dechlorination of PCB using NZVI/Pd involves the hydrogen produced at the palladium surface as a product of iron corrosion with water (Grittini et al. 1995). The Pd on the NZVI surface acts as a collector of hydrogen species that are produced by NZVI corrosion (Eqs. 4 and 5, Fang and Al-Abed 2008a). The 2,4,4′-CB adsorbed on the Pd or the NZVI/Pd surface is dechlorinated by the active hydrogen species dissolved in the Pd lattice. In addition, the continuing addition of H^+ in the reaction increased the dechlorination efficiency.

$$H_2 + RCl \rightarrow RH + H^+ + Cl^- \tag{3}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{4}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{5}$$

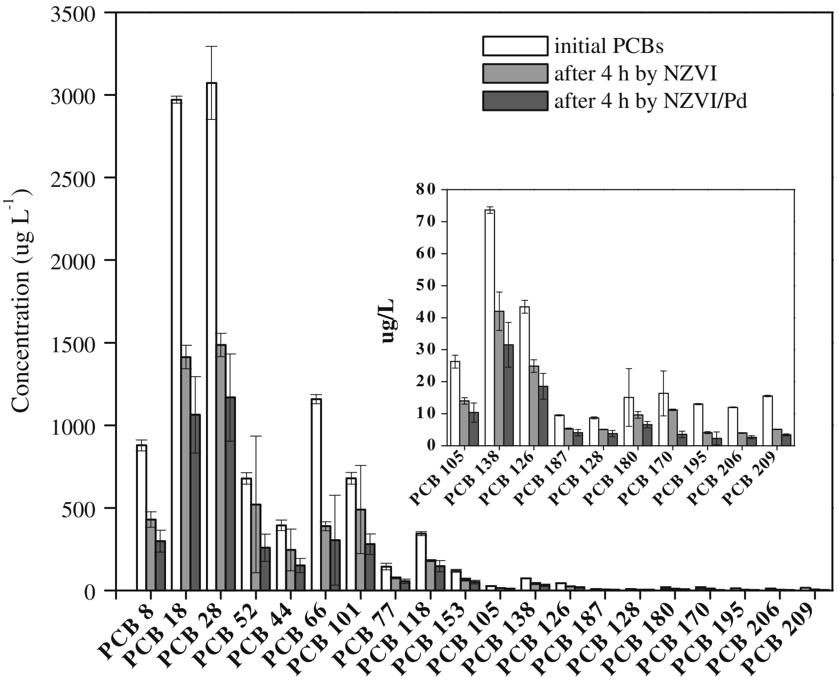
Previously reported results on PCBs and nanoscale particles measured only PCBs loss from aqueous solutions and attributed this loss to the reaction. Devor et al. (2009) reported that a pseudo-first-order rate constant of $k=1.72\times10^{-4}$ L min^{-1} g^{-1} (normalized by volume of solution and mass of Mg/Pd used) was obtained for the degradation of PCB-151 by Mg/Pd in methanol. Xu and Bhattacharyya (2007) reported that k_{SA} values were 0.017, 0.068, and 0.166 Lh^{-1} m^{-2} for Fe/Pd nanoparticles with 0.6, 2.3, and 5.6 wt.% Pd, respectively. Kim et al. (2008) reported pseudo-first-order rate constants (k_{obs}) equal of 1,2,3,4-TeCDD by Pd/nFe^{BH} was $(5.1\pm1.3)\times10^{-2}$ h^{-1}. However, the results in this study indicated that with the reaction pH control, the k_{obs} values were a little lower than the reports above. The reason was that the adsorption of PCB on NZVI surface could be neglected in this study, because acid dissoluted the passive surface and the sorbed PCBs were desorbed. Shih and Tai (2010) found that only 18% of DBZE was adsorbed on NZVI surface at pH 5, but around 43% when aqueous pH was higher than 7. Xu and Zhang (2000) reported that the initial loss of the HCB concentration was likely caused by sorption onto the particle surfaces, substantial (>70%) sorption to the iron surface was observed within the first 4 h.

3.3 Dechlorination of PCBs extracted from a PCBs-contaminated soil

The extracted PCBs from contaminated soil were investigated under the pH control system. The PCB homologue distribution was shown in Figs. 6 and 7. Di-, tri-, tetra-, and pentahomologues constitute of 97.35% of the total PCB mass, of which tri- and tetrachloride PCBs were dominant. The initial PCBs concentration in the extracted solution of PCB-contaminated soil was 10.7 mg L^{-1}, and the concentration of 2,4,4′-CB was 3.07 mg L^{-1}.

Based on the analysis by GC/μECD, the high degradation efficiency was achieved with both NZVI and NZVI/Pd, as shown in Fig. 6. After 4 h reaction with pH control, 23.17–66.90% of PCBs in the extracted solution was dechlorinated by NZVI and 56.15–82.26% by NZVI/Pd, and the dechlorination efficiency of 2,4,4′-CB was 51.63% by NZVI and 61.99% by NZVI/Pd, which were higher than the report by Varanasi et al. (2007), who found that just approximately 38% of PCBs were destroyed during mixing of soil and iron nanoparticles at room temperature. The

Fig. 6 Comparison of PCB congeners dechlorination in extracted solution from contaminated soil after 4 h with pH control by NZVI and NZVI/Pd. NZVI to solution ratio was 5.0 gL^{-1}. Reaction pH solution was adjusted as 4.90–5.10



higher dechlorination efficiency of PCBs in our study is due to two reasons. On one hand, PCBs in the contaminated soil were extracted to avoid their low diffusion from soil to nanoscale particle surface. On the other hand, the reaction pH control supplied enough H^+ ions to assure larger activity of particles.

Figure 7 shows the changes of the compound composition in the system during experimental observation up to 4 h, and the average kinetic data for PCBs congeners in the extracted solution with pH control were shown in Table 3. It indicated that the k_{obs} values had similar trend for the dechlorination of PCB congeners with different Cl numbers between using NZVI and NZVI/Pd. The average k_{obs} values from di- to hexa-decachloro PCBs were 0.0027–0.0033 and 0.0080–0.0098 min^{-1} by NZVI and NZVI/Pd, respectively. The k_{obs} value of 2,4,4′-CB was 0.0035 min^{-1} by NZVI and 0.0093 min^{-1} by NZVI/Pd. These results suggested that palladization increased the dechlorination rate for all PCB congeners, and the dechlorination rates were accelerated with lower pH. Electrons were transferred to the iron surface, and protons participated in the dechlorination of PCBs. NZVI/Pd has been reported to increase the dechlorination rates of PCBs and chlorinated benzenes by 1.5–2 orders of magnitude (Lowry and Johnson 2004; Xu and Zhang 2000).

As noted above, the dechlorination rates of PCB congeners in the extracted solution of PCBs-contaminated soil, such as 2,4,4′-CB, were slower than those of 2,4,4′-CB in the solution by NZVI and NZVI/Pd even with pH control. The reasonable explanation was that the presence of competing substrates like dissolved solids or dissolved organic matter (DOM) in the extracted solution affected the dechlorination rate of PCBs. Analysis of the PCBs-contaminated soil provided the data from Table 1. The concentration of DOM was 165.5 mg kg^{-1}, and some common cations were also detected. In this study, DOM appears to be an inhibitor for the dehalogenation of PCBs because of several aforementioned phenomena. Tratnyek et al. (2001) found that the reduction of carbon tetrachloride and trichloroethylene was inhibited by DOM. Zhang et al. (2009) reported that the introduction of humic acid decreased the removal percentage of 2,4-DCP, and the possible reason was the accumulation of adsorbed humic acid on the nanoscale Ni–Fe surface. But it is difficult to predict the net effect of natural organic matter (NOM) on the degradation kinetics of PCBs. The kinetics of PCBs transformation by NZVI might be influenced by: solubilization of PCBs by partitioning them into NOM micelles in the solution phase, enhanced absorption of contaminants by partitioning into the hydrophobic layer formed by NOM that adsorbs to NZVI particle surfaces, competition between NOM and contaminants for the surface sites where reaction occurs, and “catalysis” of contaminant reduction by redox activity of NOM that acts as electron transfer mediators at the particle–water interface (Tratnyek et al. 2001). As a consequence, later attention should be paid to the influence of organic matter which was largely contained in soils.

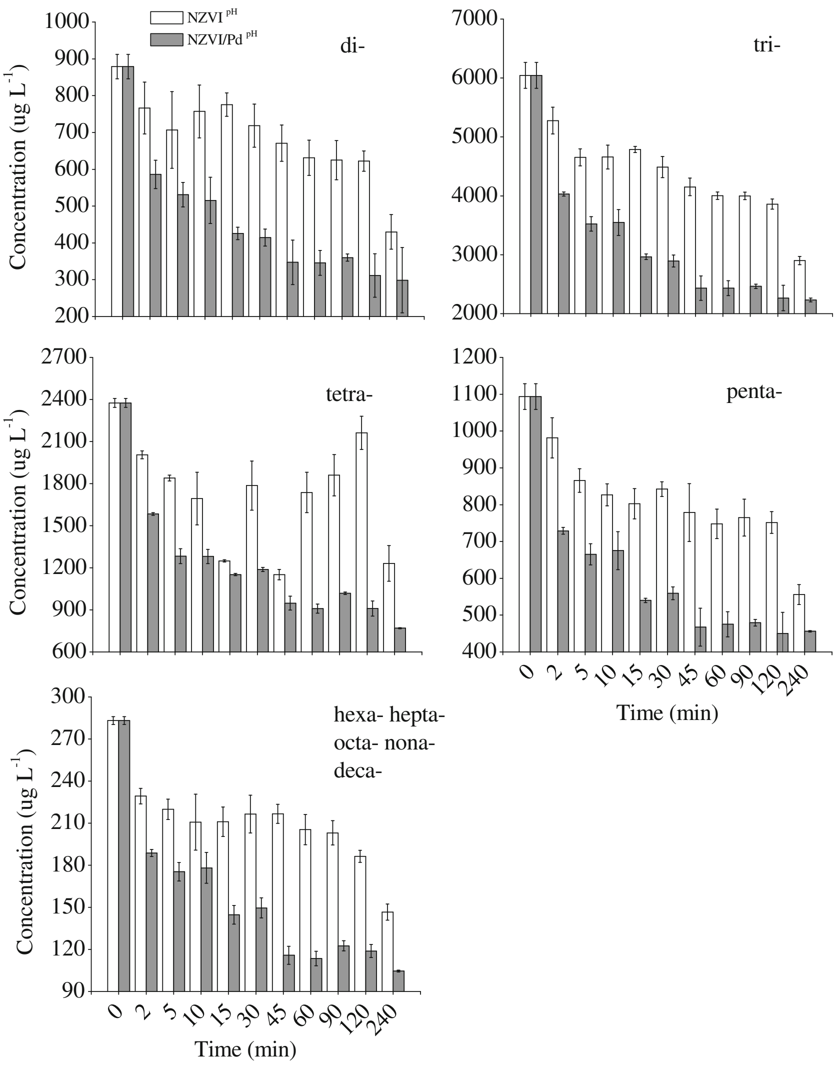


Fig. 7 The changes of the PCB congeners' composition by NZVI and NZVI/Pd with time

4 Conclusions

The automatic solution pH control in acid significantly enhanced the dechlorination efficiency of 2,4,4′-CB and the PCBs extracted from a PCBs-contaminated soil by NZVI or Pd/NZVI. The observed normalized pseudo-first-order dechlorination rate constants (k_{obs}) of 2,4,4′-CB were significantly increased with pH control. The

Table 3 Best linear fit of first-order reaction rates for PCB congeners in the contaminated soil extracted solution with pH control

PCB congeners	Composition	Average k_{obs} (min^{-1})	k_{SA} (10^{-4} L m^{-2} min^{-1})[a]	R^2	N[b]
Di-	NZVI	0.0031±0.0002	0.41	0.973	5
	NZVI/Pd	0.0091±0.0015	1.21	0.897	4
Tri-	NZVI	0.0033±0.0003	0.44	0.952	4
	NZVI/Pd	0.0098±0.0025	0.93	0.787	4
Tetra-	NZVI	0.0027±0.0004	0.36	0.931	5
	NZVI/Pd	0.0085±0.0015	1.13	0.881	4
Penta-	NZVI	0.0030±0.0003	0.40	0.966	5
	NZVI/Pd	0.0081±0.0016	1.08	0.863	4
Hexa-	NZVI	0.0030±0.0003	0.40	0.955	5
Deca-	NZVI/Pd	0.0080±0.0016	1.07	0.857	4

[a] The normalized surface reaction rate constant; the special surface area is 15 m^2 g^{-1} and loading is 5.0 gL^{-1}

[b] N is the number of data points. Reported errors are 95% confidence intervals for pseudo-first-order fit of product data (Eq. 2)

dechlorination rates of PCB congeners in the extracted solution of PCBs-contaminated soil, however, were slower than those of 2,4,4′-CB in the solution by NZVI or NZVI/Pd, even with pH control. The reasonable explanation was that the competing substrates widely existed in the extracted solution, like dissolved colloids, DOM, and other reduced substrates. The studies suggest that to keep the reaction solution to be weakly acid will markedly increase the dechlorination rate of PCBs, which may offer a novel remediation technology for the PCBs-contaminated soil.

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