



Humic acid and metal ions accelerating the dechlorination of 4-chlorobiphenyl by nanoscale zero-valent iron

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Abstract

Transformation of polychlorinated biphenyls (PCBs) by zero-valent iron represents one of the latest innovative technologies for environmental remediation. The dechlorination of 4-chlorobiphenyl (4-CIBP) by nanoscale zero-valent iron (NZVI) in the presence of humic acid or metal ions was investigated. The results showed that the dechlorination of 4-CIBP by NZVI increased with decreased solution pH. When the initial pH value was 4.0, 5.5, 6.8, and 9.0, the dechlorination efficiencies of 4-CIBP after 48 hr were 53.8%, 47.8%, 35.7%, and 35.6%, respectively. The presence of humic acid inhibited the reduction of 4-CIBP in the first 4 hr, and then significantly accelerated the dechlorination by reaching 86.3% in 48 hr. Divalent metal ions, Co^{2+} , Cu^{2+} , and Ni^{2+} , were reduced and formed bimetallics with NZVI, thereby enhanced the dechlorination of 4-CIBP. The dechlorination percentages of 4-CIBP in the presence of 0.1 mmol/L Co^{2+} , Cu^{2+} and Ni^{2+} were 66.1%, 66.0% and 64.6% in 48 hr, and then increased to 67.9%, 71.3% and 73.5%, after 96 hr respectively. The dechlorination kinetics of 4-CIBP by the NZVI in all cases followed pseudo-first order model. The results provide a basis for better understanding of the dechlorination mechanisms of PCBs in real environment.

Key words: 4-chlorobiphenyl; nanoscale zero-valent iron; humic acid; metal ions; dechlorination

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Introduction

Polychlorinated biphenyls (PCBs) consist of 209 congeners that are very persistent to degradation and hazardous to the biosphere. Due to their high stability and thermal properties, PCBs have been widely used as a heat-transfer medium in electrical transformers and capacitors, and their production ended in most countries in the 1970s.

Because of their high stability, low aqueous solubility, and high organic affinity, PCBs are difficult to be treated (Borja et al., 2005). The most common destructive technique is incineration, which, however, often produces more toxic by-products (i.e., polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-furans) (Wu et al., 2005). Destruction of PCBs by reactive nanoscale zero-valent metals is one of the latest innovative technologies (Shih et al., 2009; Lim and Lastoskie, 2009; Varanasi et al., 2007; Lowry and Johnson, 2004; Hadnagy et al., 2004; Wang and Zhang, 1997). The use of reactive nanoscale zero-valent metals, which have a larger specific surface area and higher surface reactivity, has been documented to work efficiently for the reductive dechlorination of PCBs

and other chlorinated compounds for several years (Shih et al., 2009). The remediation of contaminants by nanoscale zero-valent iron is a process that is largely controlled by surface reactions, especially those involving the iron oxide formation under ambient environmental conditions.

NZVI is effective for the removal of chlorinated compounds, and its reactivity is highly controlled by its surface characteristics. The mechanisms regarding PCBs dechlorination by NZVI have been reported in some previous studies (Shih et al., 2009; Zheng et al., 2009; He et al., 2009). However, little is known about their removal in real environment (Sharma et al., 2009; McDonough, 2008; Xie et al., 2009). Natural organic matter (NOM) is ubiquitous in shallow aquifers where remediation technologies based on Fe^0 are most applicable. The kinetics of contaminant transformation by Fe^0 might be influenced by: (1) the solubilization of contaminants by partitioning into NOM micelles in the solution phase, (2) the enhanced absorption of contaminants by partitioning into the hydrophobic layer formed by NOM that adsorbs to Fe^0 particle surfaces, (3) the competition between NOM and contaminants for the surface sites where reaction occurs, and (4) the “catalysis” of contaminant reduction by redox activity of NOM that acts as electron transfer mediators at the particle–water

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interface. These effects might occur independently or in combination, so it is difficult to predict their net effect on contaminant degradation kinetics (Tratnyek et al., 2001). However, limited studies have reported the effects of NOM on the decomposition of some other contaminants by Fe^0 (Tratnyek et al., 2001; Zhang et al., 2009; Rao et al., 2009; Lu et al., 2009; Giasuddin et al., 2007).

Zhang et al. (2009) found the introduction of HA decreased the removal of 2,4-DCP. Rao et al. (2009) reported that the removal rate of arsenic by Fe^0 was inhibited in the presence of HA probably because of the formation of soluble Fe-humate in the groundwater which hindered the formation of iron precipitates.

Besides the effect of organic compounds, NZVI is also effective for inactivating dissolved metals. These dissolved metals can be reduced by NZVI to their lower oxidation states and co-precipitated with ferric oxyhydroxide on the surface of NZVI particles. The metallic system has been further advanced for enhanced reactivity through the deposition of a discontinuous layer of noble metals on the substrate-metal surface and the manipulation of its properties in the nanoscale regime. Because of its high reactivity, the nanoscale bimetallic system seems promising for the treatment of aqueous PCBs in groundwater or equivalent because the dechlorination reaction occurs in water-metal interface (Choi et al., 2009). Several studies showed that the deposition of small amounts of second metals such as Ni, Co, Cu and Pd onto iron surface could enhance the dechlorination of chlorinated hydrocarbons (Shih et al., 2009; Zheng et al., 2009; He et al., 2009; Agarwal et al., 2009; Xu and Bhattacharyya, 2008; Fang and Al-Abed, 2008a, 2008b).

In this study, the reduction of 4-CIBP by NZVI under different pH and in the presence of NOM and metal ions was studied in water batch reactors. The aim is to explore the dechlorination process of 4-CIBP in simulating the real environmental condition.

1 Materials and methods

1.1 Chemicals

Iron particles ranging in sizes from 30 to 100 nm were obtained from Nanjing Emperor Nano Material Co., Nanjing, China. The PCB, used in this study, was congener-003 (4-chlorobiphenyl, 4-CIBP), which was 98.8% pure and obtained from J&K Scientific Inc., China (CAS No. 2051-62-9). Humic acid (HA) was purchased from Sigma-Aldrich Co., America. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were obtained from Shanghai Anpel Co., China. Hexane (GC grade) and acetone (Optima grade) were obtained from Fisher Scientific, UK. HCl (12 mol/L) was analytical grade. The water used in the experiments was oxygen-free, obtained by bubbling nitrogen gas overnight through milli-Q water (resistivity 18 M Ω /cm).

1.2 Sacrificial batch reactions

The batch dechlorination reaction of 4-CIBP was conducted in 40 mL serum glass vials. In each vial, 0.300 g

NZVI was added into 30 mL of 4-CIBP solution. Solution pH was adjusted using sulfuric acid or sodium hydroxide to attain the desired pH values, and was measured using a standard pH meter (Thermo Orion 868, America). HA (10 mg/L) was added to examine its effect on the reduction of 4-CIBP by NZVI. The effect of metal ions on the dechlorination of 4-CIBP was evaluated by adding 0.1 mmol/L metal ions (Co^{2+} , Cu^{2+} and Ni^{2+} respectively) into the serum bottles. Control experiments without the addition of NZVI were run identically. The initial pH was 4.0, and the concentration of 4-CIBP (aqueous stock solution of 4-CIBP in acetone) was 5.0 mg/L. The existence of 5% cosolvent acetone in the stock solution has little effect on the reduction of 4-CIBP by NZVI.

All pre-processors were operated in anaerobic glove box (nitrogen protected system), YQX-II, Shanghai CIMO Medical Instrument Manufacturing Co., China. The serum glass vials were sealed with Teflon-lined silicon septa and placed on an orbital shaker at 140 r/min, 25°C in the dark during the experiment. 4-CIBP and HA were found to significantly adsorb on the surface of NZVI. For the dechlorination of 4-CIBP, extraction at predetermined time intervals was modified by the addition of 0.50 mL hydrochloric acid to 1.00 mL suspension to promote the dissolution of NZVI surfaces and protonation of 4-CIBP (Kim and Carraway, 2000). For analyzing the loss of total 4-CIBP, 1.00 mL of supernatant was withdrawn from the selected reaction vials. Then, the two kinds of aqueous extraction solutions were transferred to an 8-mL vial containing 2.00 mL of hexane respectively. The vials were placed on the vortex mixer for 1 min, and then shaken on a reciprocal shaker for 1 hr to achieve extraction equilibrium.

1.3 Analytical methods

One milliliter of the top extracts was transferred to 2 mL GC vials from the extraction bottles, and analyzed for 4-CIBP using a Hewlett Packard (HP, USA) 6890N Gas Chromatograph with an electron capture detector (GC/ECD). A BD-5 column (J&W scientific Inc., China) with 30.0 m \times 0.32 mm \times 0.25 μm was used. Samples (1.0 μL) were injected using an auto sampler (HP 6890 Series, USA). The carrier gas flow rate (He, UHP zero grade) was 1 mL/min. The make-up gas (N_2) flow rate was 60 mL/min. The injection temperature was 250°C, and the detector temperature was 300°C. The oven temperature was hold at 150°C for 2 min, ramped to 280°C at 10°C/min, and hold at 280°C for 2 min.

Five milliliters of aqueous solutions in the vials were withdrawn and filtered through a 0.22- μm membrane filter to remove fine particulates. The deposition of metal ions on the NZVI was calculated by the change of metal ion concentration before and after the reaction. The filtered solutions were then acidified using concentrated nitric acid to pH < 2, and heavy metals including Fe, Cu, Ni and Co were determined by an atomic absorption spectrometer (Hitachi Z-2000 AAS, Japan).

Concentrations of chloride were determined by a chloride ion-selective electrode (pHs-3B, Shanghai Precision & Scientific Instrument Co., China). Ten milliliters of

aqueous solution in the vials were withdrawn for Cl^- and pH measurement.

2 Results and discussion

2.1 Dechlorination of 4-CIBP by NZVI at various pH

Solution pH is generally important for the reductive dechlorination of chlorinated organic compounds (Song and Carraway, 2005). The dechlorination of 4-CIBP by NZVI from three batches was conducted at various pH. Figure 1a shows the effects of different initial pH on the dechlorination of 4-CIBP by NZVI. When the initial pH values were 4.0, 5.5, 6.8 and 9.0, the concentrations of 4-CIBP decreased to 46.2%, 52.2%, 64.3% and 64.4% of the initial respectively after 48 hr reaction, while the concentration of 4-CIBP maintained to be almost constant in the control treatments without NZVI. The results suggest that the hydrogen ions largely enhanced the dechlorination process and are consumed during the reaction, so a lower pH could supply more protons in the solution and thus enhance the dechlorination as illustrated by the following reactions (Varanasi et al., 2007).

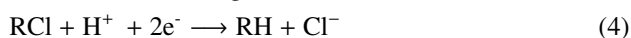
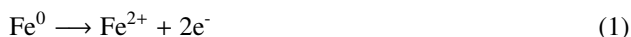


Figure 1b shows the variation of the pH values with time. When the initial pH was 4.0, 5.5, 6.8, solution pH values changed to near 7.5 quickly, and then varied little until the end of reaction. But when the initial pH was 9.0, the solution pH kept steady with the time. Low pH favors more iron surface sites available for the reaction with chlorinated molecules, promotes the corrosion rate and leads to the release of chloride ions. When the pH was 4.0 or 5.5, the oxides on the particles were probably dissolved, and more surface active sites could be exposed. Therefore, low pH accelerated the dechlorination of 4-CIBP. The solution pH increased even if the initial pH was low. At higher pH, carbonate and hydroxide coatings were undoubtedly formed, which inhibited the further decomposition of iron surface and hindered the access of 4-CIBP to the NZVI surface (Fang and Al-Abed, 2008b; Jovanovic et al., 2005).

As shown in Fig. 1c, the change of solution chloride ion concentration with time was investigated. The concentration of Cl^- increased with increasing reaction time, and reached the maximum at pH 4.0. It indicated that NZVI was a reactive metal and could be an effective enhancer for the dechlorination of 4-CIBP. Chuang and Larson (1995) found that the chlorine atoms removed during dechlorination had been largely or entirely converted to chloride ions. Lowry and Johnson (2004) found Pd/Peerless Fe^0 and nanoscale zero-valent iron tended to dechlorinate PCBs in a predictable manner with chlorine removal from each position following the general trend para \geq meta > ortho chlorines.

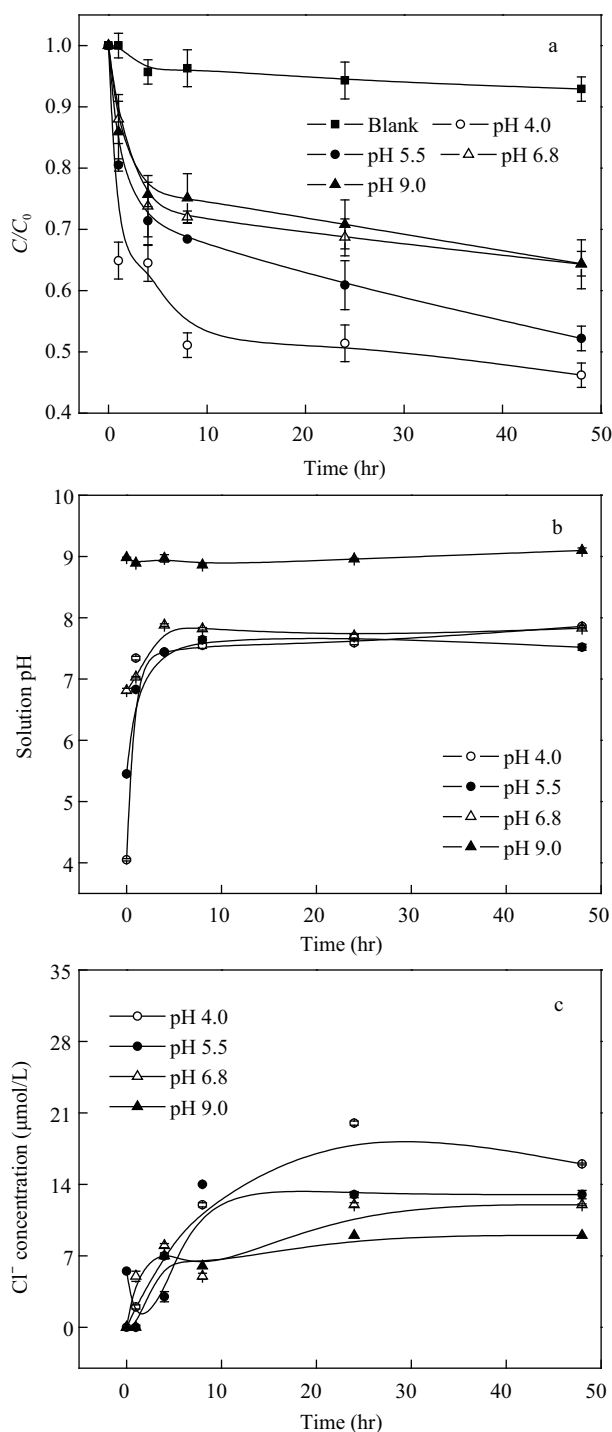


Fig. 1 Effect of initial solution pH on the dechlorination of 4-CIBP by NZVI. (a) change of C/C_0 of 4-CIBP with reaction time where C and C_0 are 4-dBP concentrations at time t and 0, respectively; (b) variation of pH with time at the different initial pH; (c) solution Cl^- concentration. Conditions: initial solution 4-CIBP concentration was 5.0 mg/L, NZVI to solution ratio was 10 g/L.

2.2 Effect of humic acid on the reduction of 4-CIBP by NZVI

As shown in Fig. 2a, the existence of humic acid gave notable increases in the dechlorination of 4-CIBP. After 96 hr reaction, the dechlorination efficiency of 4-CIBP in the presence of HA was 87.2%, while it was only 65.0% without HA addition. Adsorption of HA and 4-CIBP on the NZVI was examined in the same treatments. As shown

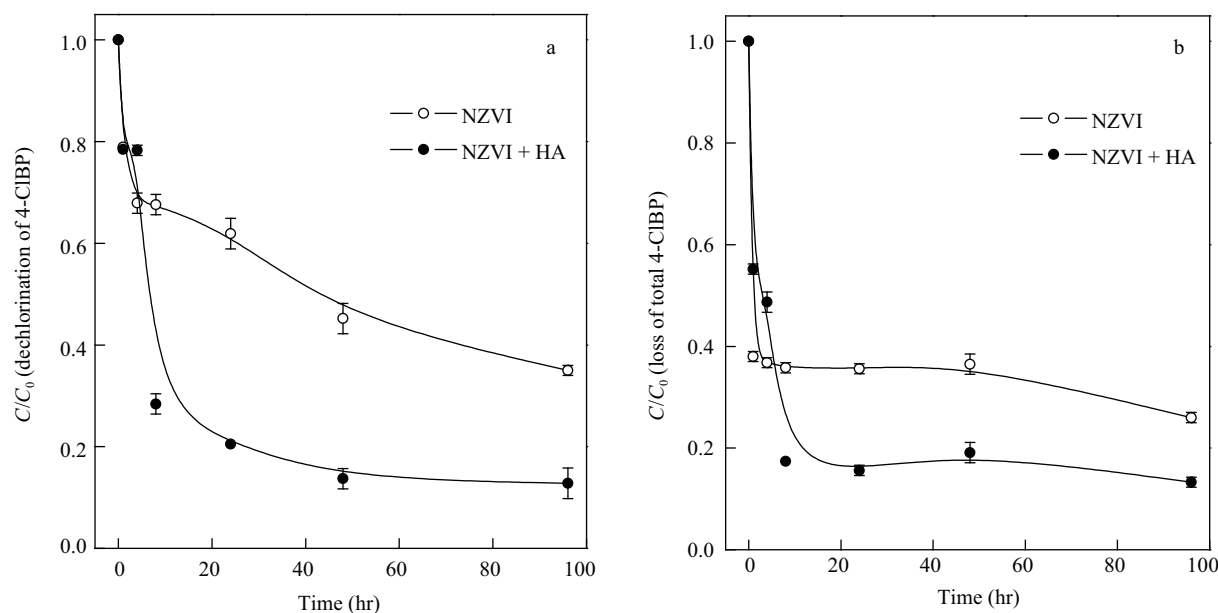


Fig. 2 Comparison of dechlorination and adsorption of 4-CIBP by NZVI in the presence/absence of HA. (a) effect of HA on the dechlorination of 4-CIBP; (b) effect of HA on the loss of total 4-CIBP. Conditions: initial solution HA concentration was 10 mg/L, NZVI to solution ratio was 10 g/L, and initial solution 4-CIBP concentration was 5.0 mg/L, initial solution pH was 4.0.

in Fig. 2b, solution 4-CIBP concentrations decreased significantly in a very short time. After 8 hr, the loss of mass of 4-CIBP were 82.6% with HA and 64.2% without HA. The aim we took two extraction methods was to compare the dechlorination of 4-CIBP by NZVI with the sorption of 4-CIBP onto the HA-coated NZVI. After 1 hr reaction, there were distinct difference between dechlorination efficiency (21.5%) and adsorption percentages (20.3%) in the presence of HA, and 21.1% and 23.3% in the absence of HA (adsorption percentages = the loss of total 4-CIBP – dechlorination percentages). When the reaction went on, the sorption of 4-CIBP onto the NZVI or the HA-coated NZVI was also dechlorinated by NZVI. The result showed that HA and 4-CIBP quickly adsorbed on the NZVI. Deng et al. (2003) reported that there were two types of surface sites on the NZVI: the reactive sites responsible for the reduction and the non-reactive sites for the adsorption. The reactive site density was generally estimated to be only 2% of the total surface sites. Adsorption reaction took place on both the reactive and non-reactive sites, but dechlorination reaction occurred only on the reactive sites.

An interesting phenomenon from Fig. 2 was that the reduction of 4-CIBP was inhibited by HA in the first 4 hr, however, it was observed that the addition of HA accelerated the reduction rate of 4-CIBP subsequently. With respect to the effect of HA on the 4-CIBP reduction by NZVI, several hypotheses were tested to identify the mechanisms. After 4 hr reaction, the loss of total 4-CIBP was 63.2% without HA and 51.3% with HA. The inhibitory effect of HA on 4-CIBP reduction suggests that competition occurred between HA and 4-CIBP for the surface sites on the NZVI. The complexation between HA and the generated Fe(II) may inhibit the corrosion of NZVI. But in the later reaction, the reduction rate of 4-CIBP in the presence of HA increased significantly. The possible reasons are that polyphenols in the HA can reduce Fe^{3+} to Fe^{2+} , the excavation of active surface sites by

dissolution of passive iron oxides accelerated the reduction of 4-CIBP, and the redox-active moieties in the HA or Fe-HA complexes acted as reductants to reduce 4-CIBP or serve as electron-transfer mediators from underlying NZVI to 4-CIBP (Xie and Shang, 2005). Doong and Lai (2006) observed the dual roles of humic acid acting as both an inhibitor to compete for the reactive sites with tetrachloroethylene and an electron shuttle to effectively accelerate the dechlorination efficiency in the ZVI system.

Figure 3a shows that solution chloride concentration increased with the time in the batch experiments. The concentration of chloride ions was 13 $\mu\text{mol/L}$ without HA and 20 $\mu\text{mol/L}$ with HA after 48 hr. It was notable that the increasing trends were irregular. This is probably due to the fact that the released chloride ions could be easily adsorbed onto Fe-HA complexes at the lower pH. Chuang and Larson (1995) found after subtraction of blanks due to the effect of water, reagents, and glassware, 73% of the theoretical maximum Cl^- concentration was calculated. As shown in Fig. 3b, the solution pH in the absence of HA increased sharply to around 7.3 in the first hour, and then gradually increased to 8.2 in 96 hr. In the presence of 10 mg/L HA, the solution pH increased to about 6.4 and were stabilized in this value which was lower than that in the absence of HA. This indicates that HA acted as a buffer in the reaction system.

The amount of Fe ions in the solution was also determined since the redox reaction took place in an aqueous solution. Dissolved iron in solutions increased within 1 hr, and then decreased gradually in the system of NZVI (Fig. 3c). However, in the presence of HA it did not increase until after 8 hr of reaction. The possible reason is that Fe^0 was firstly oxidized to Fe^{2+} in a Fe^0 -water system (Manning et al., 2002). But when pH was at neutral and alkaline, Fe would exist in the form of hydroxide. In the presence of HA, increasing dissolved iron at early stage of reaction was possibly resulted from the formation

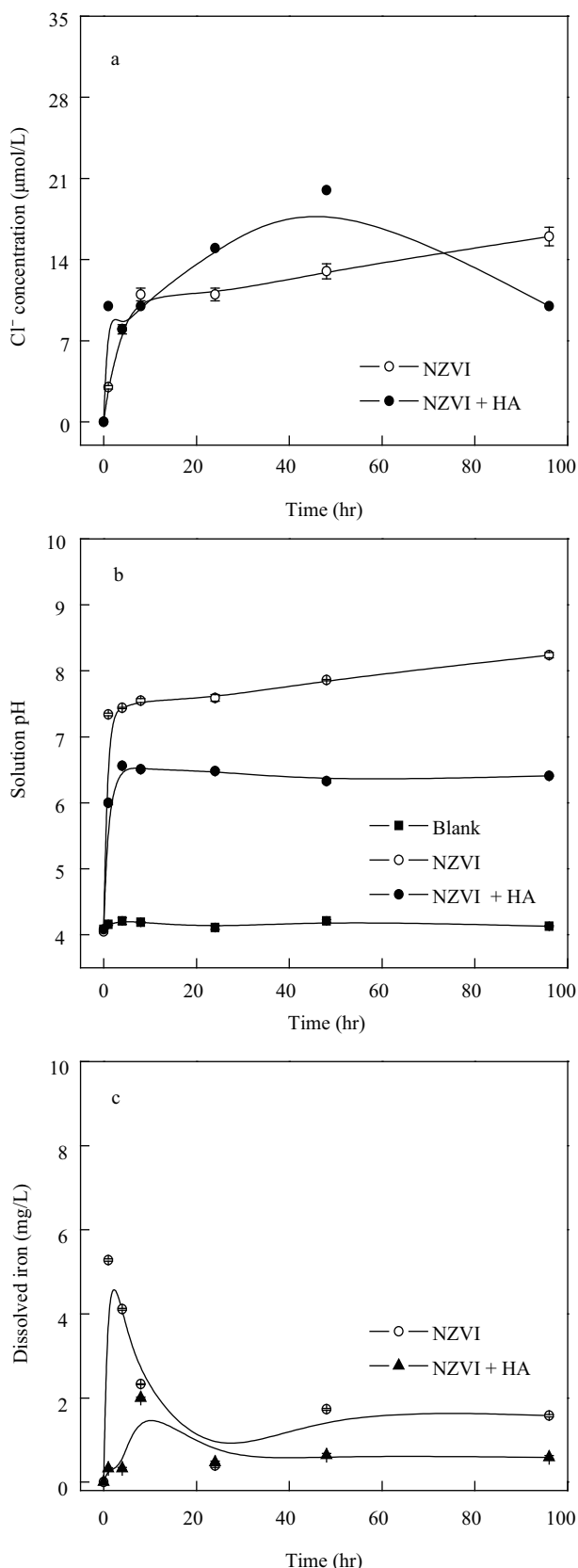


Fig. 3 Effect of HA on the dechlorination of 4-ClBP by NZVI. (a) solution Cl^- concentration; (b) solution pH; (c) dissolved iron concentration.

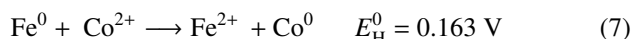
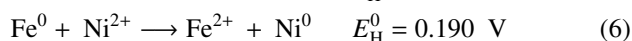
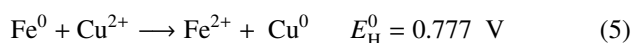
of soluble Fe-humate which subsequently suppressed the formation of iron (hydr)oxides (Liu et al., 2008). The decreased dissolved iron could be resulted from the saturation of HA complexation sites with dissolved iron from

the continuous corrosion of NZVI.

2.3 Effect of metal ions on the dechlorination of 4-ClBP by NZVI

Figure 4 shows the dechlorination of 4-ClBP by the NZVI in the presence and absence of 0.1 mmol/L divalent metal ions. In the absence of metal ions, 65.0% of the initial 4-ClBP was dechlorinated by the NZVI in 96 hr. Addition of metal ions enhanced the dechlorination efficiency of 4-ClBP. Dechlorination percentages of 4-ClBP in the presence of 0.1 mmol/L Co^{2+} , Cu^{2+} and Ni^{2+} after 96 hr were 67.9%, 71.3% and 73.5%, respectively. The presence of Ni^{2+} obviously enhanced the reduction of 4-ClBP.

Divalent metal ions could be reduced to zerovalent metals by NZVI (Doong and Lai, 2006) as shown in Reactions (5)–(7), resulting in the formation of bimetallic system to accelerate the dehydrogenation of PCBs.



where, E_{H}^0 is the redox potential relative to the standard hydrogen electrode potential at 25°C. The Ni^{2+} , Cu^{2+} and Co^{2+} ions were adsorbed onto the surface of NZVI rapidly and the concentration of metal ions in the aqueous solution decreased to about zero in a very short time (Fig. 5c). It suggests that most metal ions were deposited on the surface of NZVI (Doong and Lai, 2006). To prove this, the deposition of metal ions on NZVI was detected. As shown in Fig. 5d, concentrations of these divalent metal ions deposited on the NZVI increased sharply and then decreased. This indicated that they acted as a bimetallic system, which had catalytic ability, and dramatically accelerated the reductive dechlorination. Figure 5a, b shows the solution pH and the change of dissolved iron concentration, which were similar to the effect by HA.

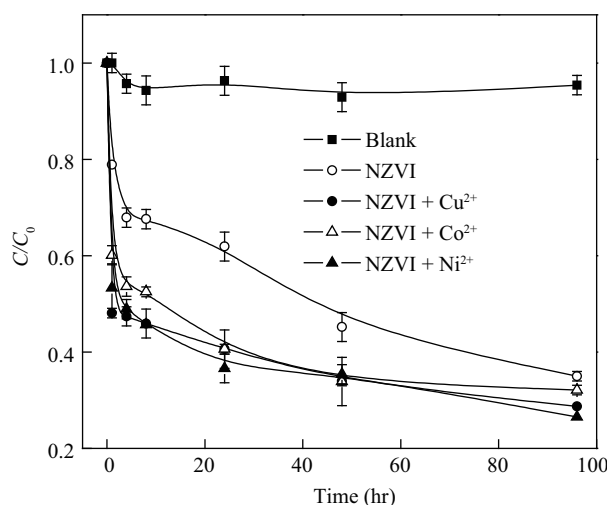


Fig. 4 Effect of metal ions (0.1 mmol/L Cu^{2+} , Co^{2+} , Ni^{2+}) on the dechlorination of 4-ClBP by NZVI. The ratio of NZVI to solution was 10 g/L, the initial solution pH was 4.0, and the initial solution 4-ClBP concentration was 5.0 mg/L.

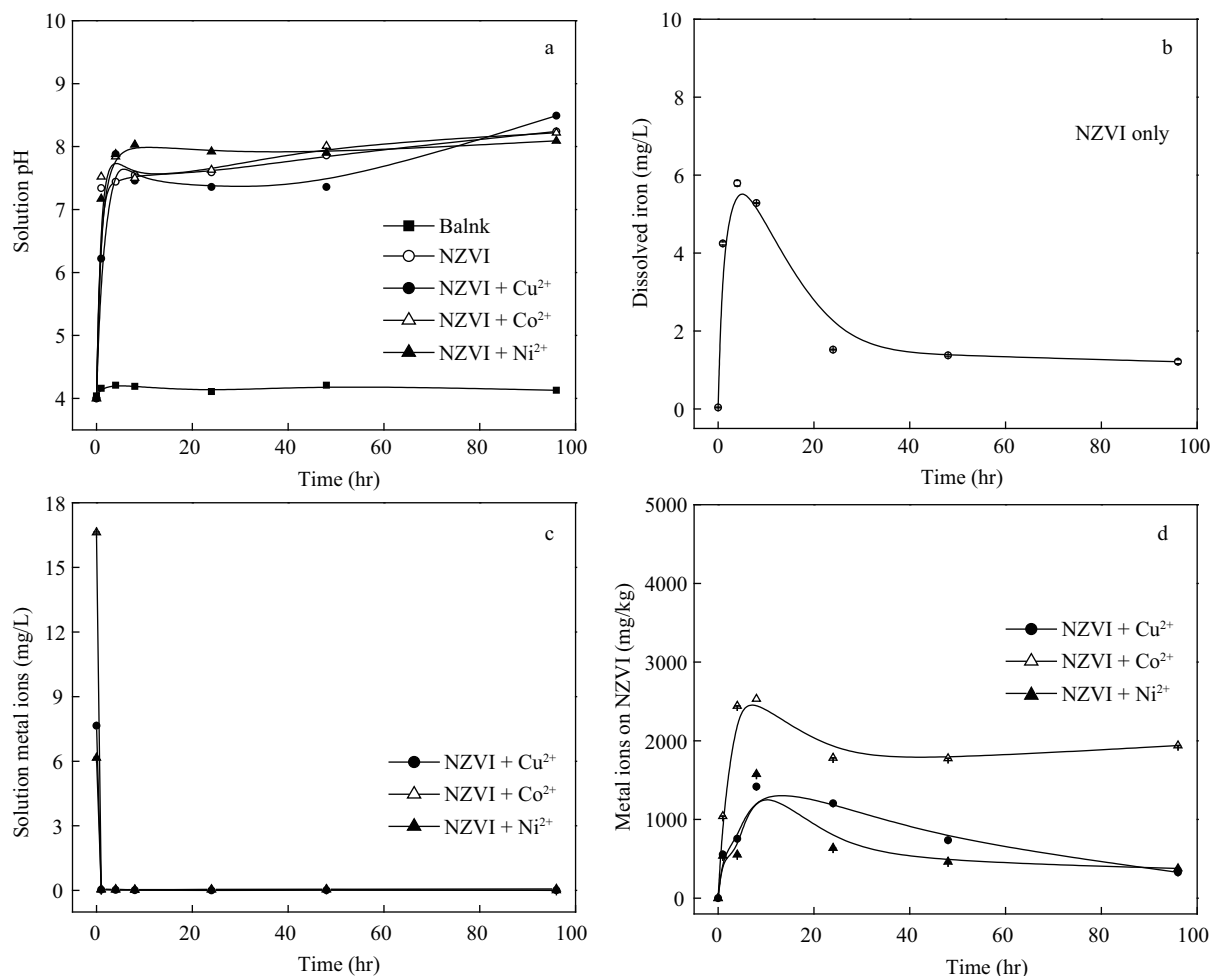


Fig. 5 Effect of metal ions on the reaction of 4-CIBP in liquid phase with the NZVI. (a) the change of solution pH; (b) dissolved solution iron concentration in the absence of metal ions; (c) concentration changes of solution divalent metal ions; (d) divalent metal ions deposited on the surface of NZVI.

2.4 Reaction kinetic studies

Figure 2a and 4 show the results of 4-CIBP dechlorination by NZVI in the presence/absence of HA, Ni^{2+} , Cu^{2+} and Co^{2+} . The experimental results can be well fitted with the pseudo first-order kinetic model:

$$\frac{dC}{dt} = -k_{\text{obs}}C \quad (8)$$

where, C (mg/L) is the 4-CIBP concentration at time t (hr) and k_{obs} (hr^{-1}) is the observed rate constant. The kinetic data for 4-CIBP are shown in Table 1, along with

Table 1 Pseudo first-order reaction for the reduction of 4-CIBP by NZVI in the presence of HA and metal ions

Composition	k_{obs}^a (hr^{-1})	N_d	R^2	pH	
				Initial	Final
NZVI	0.0092 ± 0.002	7	0.961	4.05	8.24
NZVI + HA	0.0808 ± 0.025	7	0.888	4.08	6.41
NZVI + Cu^{2+}	0.0323 ± 0.010	7	0.985	4.00	8.22
NZVI + Co^{2+}	0.0220 ± 0.004	7	0.991	4.00	8.49
NZVI + Ni^{2+}	0.0382 ± 0.006	7	0.993	4.00	8.09

k_{obs} is the pseudo first-order initial rate constant for the dechlorination reaction of 4-CIBP; N_d is the number of data points; R^2 is coefficient of determination, a measure of the proportion of variability in a data set.

^a 95% confidence interval was provided for all the values of first-order rate constant.

the observed pH changed after 96 hr reaction. The values of k_{obs} were 0.0808 and 0.0092 hr^{-1} with and without HA, respectively. The dechlorination was clearly increased significantly with the addition of HA. Considering the effects of Ni^{2+} , Cu^{2+} and Co^{2+} , the k_{obs} values were 0.0382, 0.0323 and 0.0220 hr^{-1} , respectively.

3 Conclusions

NZVI showed substantial activity in the dechlorination of 4-CIBP in acidic solution. The reduction of 4-CIBP by NZVI was inhibited by HA in the first 4 hr but then was accelerated. Divalent metal ions are quickly reduced by the NZVI, and then enhanced the dechlorination efficiency of 4-CIBP. The results obtained from this study can provide a basis for better understanding of the dechlorination of 4-CIBP in the real environment.

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References

- Agarwal S, Al-Abed S R, Dionysiou D D, 2009. A feasibility study on Pd/Mg application in historically contaminated sediments and PCB spiked substrates. *Journal of Hazardous Materials*, 172(2-3): 1156–1162.
- Borja J, Taleon D M, Aurensenia J, Gallardo S, 2005. Polychlorinated biphenyls and their biodegradation. *Process Biochemistry*, 40(6): 1999–2013.
- 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 & Technology*, 43(2): 488–493.
- Chuang F W, Larson R A, 1995. Zero-valent iron-promoted dechlorination of polychlorinated-biphenyls (PCBs). *Environmental Science & Technology*, 29(9): 2460–2463.
- Deng B L, Hu S D, Whitworth T M, Lee R, 2003. Trichloroethylene reduction on zero valent iron: Probing reactive versus nonreactive sites. In: Chlorinated Solvent and Dnapi Remediation – Innovative Strategies for Subsurface Cleanup (Henry S M, Warner S D, eds.). ACS Symposium Series, 837: 181–205.
- Doong R A, Lai Y L, 2006. Effect of metal ions and humic acid on the dechlorination of tetrachloroethylene by zero valent iron. *Chemosphere*, 64(3): 371–378.
- Fang Y, Al-Abed S R, 2008a. Correlation of 2-chlorobiphenyl dechlorination by Fe/Pd with iron corrosion at different pH. *Environmental Science & Technology*, 42(18): 6942–6948.
- Fang Y X, Al-Abed S R, 2008b. Dechlorination kinetics of monochlorobiphenyls by Fe/Pd: Effects of solvent, temperature, and PCB concentration. *Applied Catalysis B-Environmental*, 78(3-4): 371–380.
- 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 & Technology*, 41(6): 2022–2027.
- Hadnagy E, Gardner K H, Spear J M, Aulisio D, Calante I, 2004. *In situ* PCB dechlorination in sediments using nanoscale and microscale zero-valent iron. *Abstracts of Papers of the American Chemical Society*, 228: 601–601.
- He N, Li P J, Zhou Y C, Ren W X, Fan S X, Verkhozina V A, 2009. Catalytic dechlorination of polychlorinated biphenyls in soil by palladium-iron bimetallic catalyst. *Journal of Hazardous Materials*, 164(1): 126–132.
- Jovanovic G N, Znidarsic-Plazl P, Sakrithichai P, Al-Khaldi K, 2005. Dechlorination of *p*-chlorophenol in a microreactor with bimetallic Pd/Fe catalyst. *Industrial & Engineering Chemistry Research*, 44(14): 5099–5106.
- Kim Y H, Carraway E R, 2000. Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons. *Environmental Science & Technology*, 34(10): 2014–2017.
- Lim D H, Lastoskie C M, 2009. Density functional theory studies on the relative reactivity of chloroethenes on zerovalent iron. *Environmental Science & Technology*, 43(14): 5443–5448.
- Liu T Z, Tsang D C W, Lo I M C, 2008. Chromium(VI) reduction kinetics by zero-valent iron in moderately hard water with humic acid: Iron dissolution and humic acid adsorption. *Environmental Science & Technology*, 42(6): 2092–2098.
- Lowry G V, Johnson K M, 2004. Congener-specific dechlorination of dissolved PCBs by microscale and nanoscale zerovalent iron in a water/methanol solution. *Environmental Science & Technology*, 38(19): 5208–5216.
- Lu J J, Li Y, Yan X M, Shi B Y, Wang D S, Tang H X, 2009. Sorption of atrazine onto humic acids (HAs) coated nanoparticles. *Colloids and Surfaces a – Physicochemical and Engineering Aspects*, 347(1-3): 90–96.
- Manning B A, Hunt M L, Amrhein C, Yarmoff J A, 2002. Arsenic(III) and arsenic(V) reactions with zerovalent iron corrosion products. *Environmental Science & Technology*, 36(24): 5455–5461.
- McDonough, K M, Fairey J L, Lowry G V, 2008. Adsorption of polychlorinated biphenyls to activated carbon: Equilibrium isotherms and a preliminary assessment of the effect of dissolved organic matter and biofilm loadings. *Water Research*, 42(3): 575–584.
- Rao P H, Mak M S H, Liu T Z, Lai K C K, Lo I M C, 2009. Effects of humic acid on arsenic(V) removal by zero-valent iron from groundwater with special references to corrosion products analyses. *Chemosphere*, 75(2): 156–162.
- Sharma B, Gardner K H, Melton J, Hawkins A, Tracey G, 2009. Evaluation of activated carbon as a reactive cap sorbent for sequestration of polychlorinated biphenyls in the presence of humic acid. *Environmental Engineering Science*, 26(9): 1371–1379.
- Shih Y H, Chen Y C, Chen M Y, Tai Y T, Tso C P, 2009. Dechlorination of hexachlorobenzene by using nanoscale Fe and nanoscale Pd/Fe bimetallic particles. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 332(2-3): 84–89.
- Song H, Carraway E R, 2005. Reduction of chlorinated ethanes by nanosized zero-valent iron: Kinetics, pathways, and effects of reaction conditions. *Environmental Science & Technology*, 39(16): 6237–6245.
- Tratnyek P G, Scherer M M, Deng B L, Hu S D, 2001. Effects of natural organic matter, anthropogenic surfactants, and model quinones on the reduction of contaminants by zero-valent iron. *Water Research*, 35(18): 4435–4443.
- Varanasi P, Fullana A, Sidhu S, 2007. Remediation of PCB contaminated soils using iron nano-particles. *Chemosphere*, 66(6): 1031–1038.
- Wang C B, Zhang W X, 1997. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental Science & Technology*, 31(7): 2154–2156.
- Wu W H, Xu J, Zhao H M, Zhang Q, Liao S J, 2005. A practical approach to the degradation of polychlorinated biphenyls in transformer oil. *Chemosphere*, 60(7): 944–950.
- Xie L, Shang C, 2005. Role of humic acid and quinone model compounds in bromate reduction by zerovalent iron. *Environmental Science & Technology*, 39(4): 1092–1100.
- Xie M, Yang Z Y, Bao L J, Zeng E Y, 2009. Equilibrium and kinetic solid-phase microextraction determination of the partition coefficients between polychlorinated biphenyl congeners and dissolved humic acid. *Journal of Chromatography A*, 1216(21): 4553–4559.