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Effects of anions on the kinetics and reactivity of nanoscale Pd/Fe in trichlorobenzene dechlorination

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ABSTRACT

Influences of anionic co-solutes on dechlorination of 1,2,4-trichlorobenzene (124TCB) by the nanoscale Pd/Fe particles were investigated in batch experiments in the presence of an anionic solute such as nitrate, nitrite, perchlorate, phosphate, carbonate, silica, sulfate, sulfite, or sulfide. Based on the extent of inhibitory effects on the 124TCB dechlorination, the anions can be ranked in the order of: control ≈ sulfate ≈ silica < perchlorate < carbonate < nitrate < phosphate < nitrite < sulfite < sulfide. Mineralogical analysis with XRD, morphological study with SEM-EDX, and spectroscopic analysis with FTIR spectrometer of the fresh and reacted Pd/Fe samples were conducted to examine the influences of the various anions on the Pd/Fe surface. Silica and sulfate did not show any significant short-term effect on reactivity of the nanoscale Pd/Fe, because the 124TCB dechlorination reaction was only dependent on the reactivity of the Pd site that was apparently not passivated by the anions. However, sulfide and sulfite could immediately terminate the 124TCB dechlorination process. Based on the natures of their inhibitory effects on 124TCB dechlorination by the Pd/Fe, the anions can be classified as: (1) adsorption-precipitation passivating species (e.g., phosphate and carbonate), (2) redox-active species (e.g., nitrate, nitrite, and perchlorate), and (3) catalyst poisons (e.g., sulfide and sulfite).

1. Introduction

Reductive dehalogenation by zerovalent iron (ZVI) has gained acceptance as a promising treatment technology to remove halogenated organic compounds (HOCs) in groundwater or industrial effluents (Henderson and Demond, 2007; Theron et al., 2008). The reactivity of ZVI can be further enhanced by reducing its particle size to nanoscale (Nurmi et al., 2005; Tratnyek and Johnson, 2006) or depositing a catalyst metal (e.g., Pd, Ni) on its surface (Wei et al., 2006; Lim et al., 2007).

For successful applications of ZVI technology in groundwater remediation or effluent treatment, several pertinent issues need to be addressed. One of which is interference in the HOCs-ZVI interactions caused by the co-solutes present in the aqueous matrix. The co-solutes may be the redox-active species that can consume the ZVI mass through cathodic attack, or the inert species that may deposit on the iron surface resulting in formation of water-solid interfacial barrier to mass transfer, blocking of surface sites, or deactivation of surface reductive site through mineralogical modification.

Roberts and her group reported that the dissolved silica could cause an adverse effect on the reactivity of granular iron because of its corrosion-inhibiting properties (Klausen et al., 2003; Kohn and Roberts, 2006). They also reported that the dechlorination rate of trichloroethylene (TCE) could be enhanced in the short term by bicarbonate at high concentration (20 mM), but the reverse effect occurred at low bicarbonate concentration (2 mM) (Klausen et al., 2003). Tratnyek and his co-workers reported a short-term enhancement of ZVI reactivity by dissolved carbonate because of accelerated corrosion followed by gradual passivation of the iron due to formation of precipitates (Agrawal et al., 2002; Nurmi and Tratnyek, 2008). Kohn et al. (2005) reported formation of an iron carbonate hydroxide precipitate on the granular iron surface over a period of 1100 d in 2 mM $NaHCO_3$ solution. Nitrate has been reported to cause inhibition of reduction of HOCs with ZVI while being reduced to nitrite and ammonia (Farrell et al., 2000; Alowitz and Scherer, 2002). Phosphate has been reported to adversely inhibit TCE degradation by the nanoscale ZVI through forming surface complexes or precipitates on the ZVI surface (Liu et al., 2007). Devlin and Allin (2005) observed an enhanced reactivity of a granular iron caused by sulfate and chloride in 4-chloronitrobenzene reduction, due to either increased ZVI surface activity or its sorption capacity. H_2S and SO_2 gases are known Pd catalyst poisons in gas-phase reactions at elevated temperatures (Rodriguez et al.,

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1997; Kopinke et al., 2003). It is expected that the presence of dissolved sulfide and sulfite in the aqueous matrix would have a detrimental effect on the Pd/Fe activity. It appears that the anions in groundwater can interfere with the HOC dechlorination through different ways, depending on their redox properties, solubilities as iron compounds, and adsorptivities on the ZVI surface.

Chlorinated benzenes are widely used as intermediates in the syntheses of dyes, pesticides and other chemicals, space deodorants, insert and moth repellents, heat transfer agents, and solvents. They are toxic, carcinogenic, hydrophobic and biorefractory. Earlier studies have reported that they can be dechlorinated to benzene by the Pd/Fe, but are rather resistant to degradation by the unpalladized ZVI (Xu et al., 2005; Zhu and Lim, 2007).

This study was aimed at investigating how various anions found in the contaminated groundwater, surface water and industrial effluents would affect the dechlorination rate of chlorinated benzenes by nanoscale Pd/Fe, using 1,2,4-trichlorobenzene (124TCB) as a model reactant. Various instrumental techniques for surface analyses of the fresh and reacted Pd/Fe were employed to elucidate the possible mechanisms involved in the Pd/Fe deactivation by the anions. The nanoscale Pd/Fe is short-lived, because of its high reactivity and rapid corrosion once injected into water. Therefore, the short-term effects of the anions on the reactivity of nanoscale Pd/Fe toward the chlorinated benzenes are relevant and of particular concern.

2. Materials and methods

2.1. Chemicals

124TCB, 1,4-dichlorobenzene (14DCB), 1,3-dichlorobenzene (13DCB), 1,2-dichlorobenzene (12DCB) and chlorobenzene (CB) were obtained from Tokyo Kasei. Benzene was obtained from Fisher Scientific Co. Palladium (II) acetate (47% Pd) was purchased from Arofol. Assay grade ferrous sulfate was from Reachim. Sodium borohydride was supplied by Alfa Aesar. Potassium nitrate was purchased from Merck. Potassium nitrite and sodium carbonate were supplied by J.T. Baker Inc. Sodium sulfate and sodium sulfite were from AJAX Chemicals. Sodium sulfide was from Fisher Chemical. Sodium phosphate was from Fisher Scientific Co. Sodium perchlorate was from Sigma Chemical Co. All chemicals were of assay grade if not specifically noted. Milli-Q ultrapure water (18.2 MΩ cm) was used for all the experiments, and the water was adequately purged with N_2 before use to create an anoxic aqueous environment.

2.2. Synthesis of Pd/Fe

The nanoscale ZVI was first synthesized via reduction with $NaBH_4$, and the palladized ZVI was prepared by soaking the freshly synthesized nanoscale ZVI particles in an acetone solution of palladium acetate. The detailed procedure has been described elsewhere (Zhu and Lim, 2007). In the present study, Pd/Fe with a desired Pd content of 0.1% (wt/wt) was synthesized. Inductively coupled plasma-optical emission spectrometry (Optima 2000 DV) was used to determine the actual Pd contents in the synthesized Pd/Fe samples from their diluted extracts of aqua regia, and they were found to be 0.10 ± 0.01%. BET surface analysis was performed using QuantaChrome Autosorb-1 analyzer. XRD analyses of the fresh and reacted Pd/Fe were performed using Bruker AXS D8 advanced X-ray diffractometer with $\lambda = 1.5418$ Å. SEM combined with energy-dispersive X-ray (EDX) spectrometry was performed on a JSM-6360 microscope with JED-2300 X-ray analyzer. All the Pd/Fe samples were vacuum freeze-dried and then stored under nitrogen atmosphere prior to the analyses to avoid sample oxidation in air.

2.3. Dechlorination experiment

Batch experiments were carried out with each solution containing 124TCB along with one of the anions investigated. To each 70 mL serum bottle, 50 mg of the synthesized Pd/Fe was added together with 69.5 mL solution containing an anion with a known concentration. The dechlorination reaction was commenced by injecting 0.5 mL 124TCB solution, resulting in an initial 124TCB concentration (C_o) of about 0.11 mM and the Pd/Fe loading of 0.71 g L^{-1}. The bottles were placed on an orbital shaker (250 rpm) at room temperature (23 ± 1 °C). The mixing speed had been confirmed earlier as sufficient to overcome the mass-transfer limitation in the heterogeneous catalytic reaction system. The solutions were not buffered to avoid introducing possible interfering compounds to the solution matrix of the batch reaction system that might complicate the result analysis. Instead, the variations between the initial and final pH values were monitored to assist results interpretation.

At each specific time interval, one bottle was sacrificed to withdraw 2 mL solution by a gas-tight syringe with 0.2 μm filter for analysis of the parent compound and its products, while another 10 mL solution was withdrawn for chloride analysis. The initial and final pH values were recorded. The concentrations of 124TCB and its daughter products were analyzed with high performance liquid chromatography using a Perkin Elmer chromatograph equipped with a Model PE 785A UV/VIS detector. The flow injection analyzer/ion chromatograph (IC) was used to measure the concentrations of most of the anions investigated. Perchlorate was measured with the IC (Dionex ICS-1000). Bicarbonate content (as DIC) was determined using a TOC Analyzer (ASI-V, Shimadzu) and a pre-calibrated relationship of DIC and bicarbonate concentration.

3. Results and discussion

3.1. Characterizations

The BET surface area of the Pd/Fe sample was 26.3 $m^2\ g^{-1}$. The peak at 2θ of 44.8° in the XRD patterns (Fig. 1) is associated with the (1 1 0) plane of ZVI (body-centered cubic α-Fe^0). After reaction in all but the phosphate and sulfide solutions, iron oxides emerged.

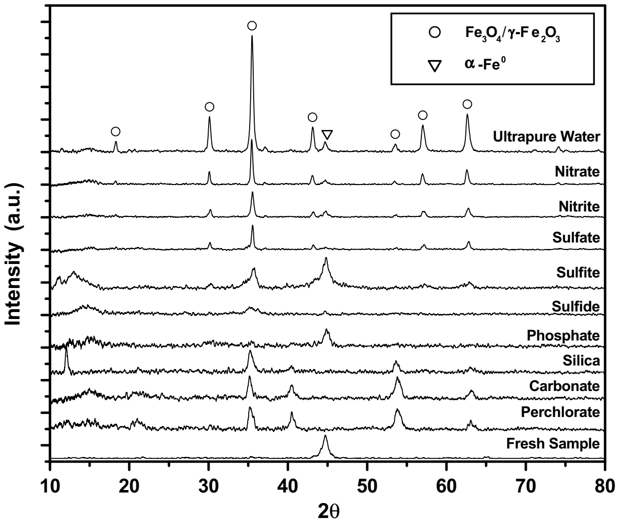

Fig. 1. XRD patterns of fresh Pd/Fe and Pd/Fe after reaction in ultrapure water and various anion solutions.

The iron oxides included magnetite/maghemite (Fe_3O_4/γ-Fe_2O_3) which are isostructural and indistinguishable in their XRD patterns. After reaction in the phosphate solution, the iron in the Pd/Fe remained in the zerovalent state, resembling that of the fresh Pd/Fe. This could be attributed to the formation of iron phosphate film that had protected the underlying ZVI from being further oxidized. In sulfide solution, there was only a trace amount of iron oxides formed after reaction in the solution.

Spherical ZVI granular particles formed aggregated structure because of magnetism (Fig. 2). Results of EDX analysis showed that Fe and O were the main elemental compositions of Pd/Fe. Our earlier X-ray photoelectron spectrometry (XPS) analysis of the fresh and reacted Pd/Fe showed the presence of Pd(0) and Fe over the surface of the fresh Pd/Fe particle (Zhu and Lim, 2007). This indicated the core/shell structure of the Pd/Fe particles included a thin iron oxide film containing Pd in the exterior of the ZVI sphere.

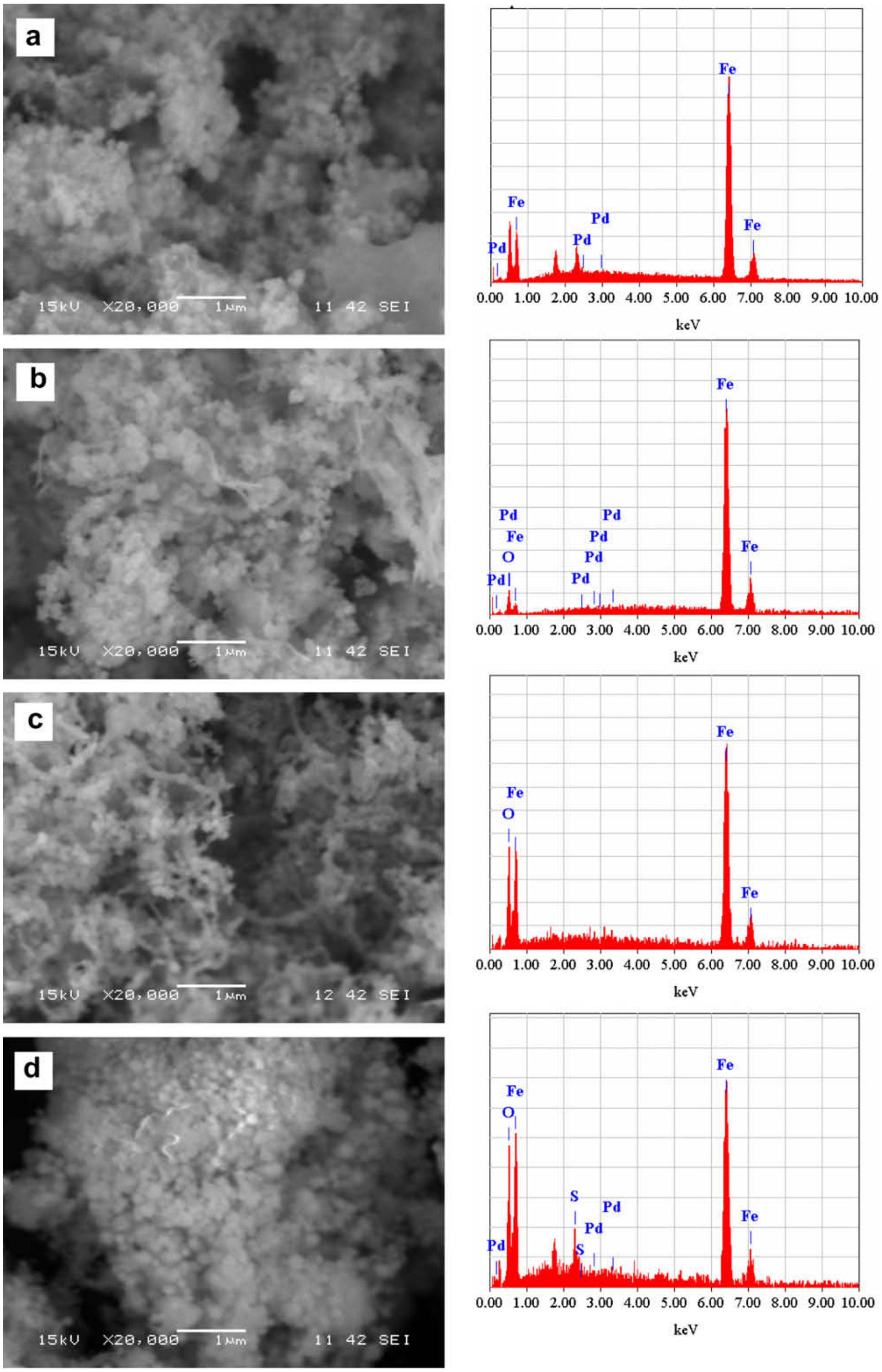

Fig. 2. SEM and EDX images of (a) fresh Pd/Fe; and Pd/Fe after reaction for 7 d in (b) ultrapure water, (c) 10 mM nitrite solution, (d) 10 mM sulfide solution.

Atomic weight-based quantitative peak area analysis of the EDX results showed that the Pd percentage of 0.23% (wt) at the outer layer was higher than the Pd content averaged over the whole Pd/Fe (0.10%).

Fig. 3 shows the FTIR spectra of the fresh Pd/Fe and reacted Pd/Fe (after 7 d of reaction in the presence of an anion). There are three main regions of interest exhibited by the spectra, i.e., the O–H stretching region from 4000 to 2000 cm^{-1}, the combination band and overtone region from 2000 to 1200 cm^{-1}, and the lattice mode and molecular anion region from 1200 to 400 cm^{-1}. The fairly broad band centered at 3385 cm^{-1} in each spectrum refers to the OH stretching vibration associated with water molecule and hydroxyl groups. Additionally, each of the spectra contains a fairly weak band near 1640 cm^{-1} that corresponds to the scissors vibration of molecular water (Su and Puls, 2004). The band at 1350 cm^{-1} and 685 cm^{-1} in the spectrum of the reacted sample in the presence of carbonate could be attributed to the precipitated carbonate on the iron oxide formed (Legrand et al., 2003). The spectral features at 1024 cm^{-1} could be assigned to P–O vibration for the reacted Pd/Fe after reaction in phosphate solution, and it indicates formation of $\equiv FePO_4$ complex on the ZVI surface (Tejedor-Tejedor and Anderson, 1990). There was no evidence showing the presences of silica, sulfate, sulfide and sulfite compounds on the surface of the reacted Pd/Fe particles. This could be due to their low concentrations in the sample.

3.2. Dechlorination mechanism and products

Benzene was the final dechlorination product throughout the course of 124TCB dechlorination with the Pd/Fe in the carbonate and perchlorate solutions, while 12DCB was the intermediate detected in the greatest quantity (Fig. 4). Other intermediates detected were 13DCB, 14DCB and CB. The product distribution for the chlorinated benzenes was generally agreeable with that observed in the ultrapure water (not shown). The carbon mass balances achieved for the dechlorination experiments conducted in various anion solutions were greater than 85%. The shortfalls could be due to adsorption of 124TCB and its products to the Pd/Fe particles, bottles and filters.

The dechlorination reaction of chlorinated benzenes with Pd/Fe was believed to follow two possible surface-mediated mechanisms involving Pd, as illustrated below.

First, the Pd site used the electron donated by ZVI to transform H^+ into a highly activated hydrogen species H^*. Second, ZVI reacted with water to produce H_2 which could be further utilized by Pd to transform into H^*. The H^* would then attack the chlorinated benzenes via electrophilic H addition to the double bond of the benzene ring, followed by the C–C scission. The overall rate-limiting step was H^* addition to the double bond of benzene ring (Keane, 2004; Mackenzie et al., 2006). A complete dechlorination of 124TCB to benzene was observed in the present study (Fig. 4).

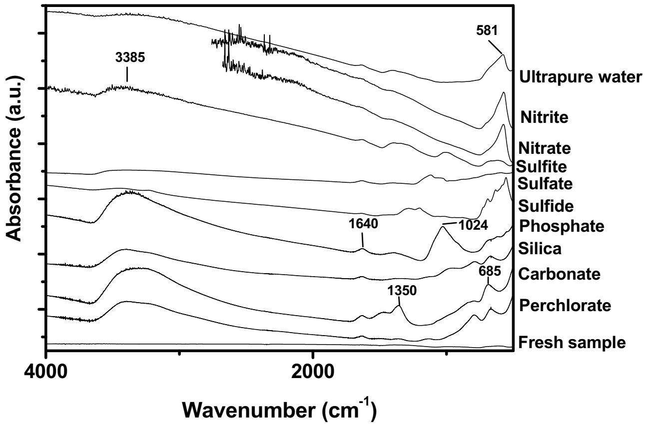

Fig. 3. FTIR spectra of fresh Pd/Fe and Pd/Fe after reaction in ultrapure water and various anion solutions.

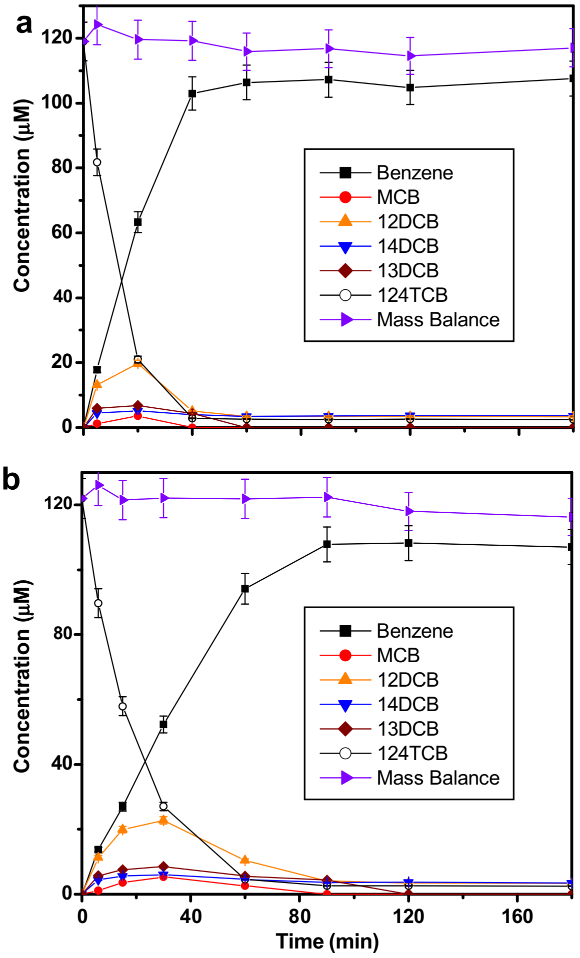

Fig. 4. 124TCB dechlorination profiles with Pd/Fe in (a) 10 mM carbonate, and (b) 2 mM perchlorate solutions.

3.3. Effects of anions on 124TCB dechlorination rates

Fig. 5 compares the results of 124TCB dechlorination in the carbonate, phosphate and silicate solutions with that of the ultrapure water. The experimental results can be well-fitted with the pseudo-first order kinetic model

$$\frac{dC}{dt} = -k_{obs}C = -k_{SA}\rho_{a}C \tag{1}$$

where k_{obs} is the pseudo-first-order rate constant (min^{-1}), k_{SA} is the normalized surface reaction rate constant ($L\,m^{-2}\,min^{-1}$), and ρ_a is the surface area concentration of Pd/Fe ($m^2\,L^{-1}$). The kinetic data for 124TCB dechlorination with the Pd/Fe in the presence of various anions are shown in Table 1, along with the observed pH changes and Pd contents after 7-d reaction.

3.3.1. ZVI-irreducible anions

Carbonate, phosphate and silica anions are considered as ZVI-irreducible (inert) solutes. Their influences on Pd/Fe reactivity towards 124TCB increased in the order of control ≈ silica < carbonate < phosphate. Previous studies reported that while carbonate

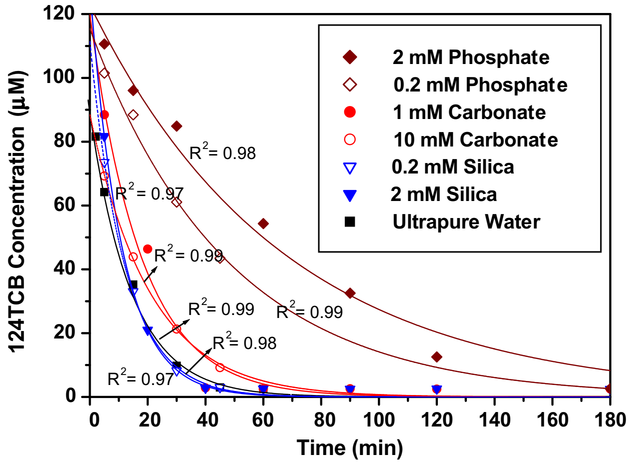

Fig. 5. Influences of phosphate, carbonate, and silica on 124TCB dechlorination by fresh Pd/Fe.

could accelerate iron corrosion and concomitantly increase HOC reduction by ZVI in the short term (Agrawal et al., 2002), it could also inhibit iron reactivity by forming complexes or precipitate coatings such as siderite, Fe-carbonate hydroxides, aragonite, or calcite on iron surface over long periods (Su and Puls, 2001; Agrawal et al., 2002; Köber et al., 2002; Klausen et al., 2003; Devlin and Allin, 2005). In the present study, the corrosion-accelerating effect by the dissolved carbonate was not observed within the first few minutes of reaction. The evidence of Fe-carbonate precipitation is shown in the FTIR spectrum of the reacted Pd/Fe (Fig. 3). Su and Puls (2004) proposed that the carbonate evidenced in the FTIR spectrum of the reacted ZVI probably existed as an inner-sphere monodentate surface complex with the iron oxides. Through rigorous analysis of 4-chloronitrobenzene dechlorination kinetics with ZVI, Devlin and Allin (2005) concluded that carbonate could affect the dechlorination through its effect on the sorption of organics to the ZVI. Thus, in the present study, it could be concluded that the formation of Fe-carbonate (either as surface complexes or precipitates) might have passivated the Pd/Fe surface, resulting in the observed inhibitory effect on the 124TCB dechlorination.

Phosphate is believed to be not competing for electrons and atomic hydrogen, with respect to HOC reduction by ZVI (Liu et al., 2007). Instead, phosphate has been reported to form inner-sphere complexes with the functional groups on the ZVI surface or co-precipitate with the released iron to form discrete solid phase on the corroded ZVI surface (Stumm and Morgan, 1996; Su and Puls, 2001). The formation of iron phosphate was confirmed by Tejedor-Tejedor and Anderson (1990) with their FTIR analysis of the phosphate compound at the goethite-water interface. Liu et al. (2007) observed formation of the sparingly soluble vivianite ($(Fe(II)_3(PO4)_2 \cdot 8H_2O)$) on the reacted nanosized ZVI in phosphate solution. In the present study, the FTIR spectral feature corresponding with $\equiv FePO_4$ complex can be observed for the reacted Pd/Fe in the phosphate solution (Fig. 3). Apparently, the adsorption or precipitation of phosphate on the Pd/Fe surface inhibited the 124TCB dechlorination significantly. The fact that phosphate forms a more insoluble precipitate with iron (e.g., vivianite) compared to carbonate explains why the former caused a larger inhibitory effect on HOC reduction than the latter, which was also observed in the present study. The distinct zerovalent state of the iron as revealed by the XRD pattern of the reacted Pd/Fe in the phosphate solution (Fig. 1) further proved the corrosion inhibition induced by the iron phosphate film on the reacted nanoparticles.

Dissolved silica is omnipresent in groundwater and surface waters. This study found that silica had insignificant effect on the 124TCB dechlorination with the nanoscale Pd/Fe (Fig. 5). This is inconsistent with the findings reported by the previous researchers who investigated granular Peerless ZVI and Master Builder ZVI and found that their reactivities in solutions containing 10–20 mg Si L^{-1} (0.36–0.71 mM) could be significantly inhibited by the adsorbed or deposited silica (Su and Puls, 2003; Kohn et al., 2005). The discrepancy may be attributed to the difference between the granular ZVI systems and the nanoscale Pd/Fe system. Silica is known as ZVI corrosion inhibitor (Kohn and Roberts, 2006) whose presence would deactivate the ZVI sites. In the ZVI system, ZVI serves as electron donor as well as adsorption site, and thus silica adsorption (or precipitation) on the ZVI would passivate these two essential functions. In contrast, in the Pd/Fe system, 124TCB can be only removed via Pd-mediated reductive dechlorination (Zhu and Lim, 2007). Furthermore, for the nanoscale Pd/Fe, hydrogen supply resulted from iron corrosion was not the

Table 1
Pseudo-first-order reaction rates for 124TCB dechlorination in various anion solutions and the corresponding0020changes of solution pH and Pd content

Solution		k_{obs} (min^{-1})	k_{SA} (10^{-3} L m^{-2} min^{-1})[a]	pH		Pd content (wt/wt%)[b]
				Initial	Final	
Ultrapure water (control)		0.088	4.73	6.5	8.8	0.070
Carbonate	1 mM	0.047	2.52	8.1	10.5	–
	10 mM	0.046	3.00	8.9	11.1	0.043
Phosphate	0.2 mM	0.021	1.12	6.1	10.6	–
	2 mM	0.015	0.80	5.9	11.1	0.077
Silica	0.2 mM	0.083	4.44	6.4	9.1	–
	2 mM	0.091	4.87	6.5	9.6	0.065
Nitrate	2 mM	0.029	1.55	4.9	9.8	–
	10 mM	0.009	0.48	5.0	10.1	0.057
Nitrite	2 mM	0.008	0.43	5.0	10.0	–
	10 mM	0.002	0.11	5.3	10.6	0.049
Perchlorate	0.2 mM	0.049	2.62	6.9	9.3	–
	2 mM	0.050	2.68	6.8	10.2	0.051
Sulfate	10 mM	0.084	4.52	6.7	9.6	–
Sulfite	2 mM	ND[c]	ND[c]	8.7	9.0	–
	10 mM			9.2	9.7	0.045
Sulfide	2 mM			9.8	9.8	–
	10 mM			10.3	9.4	0.020

[a] The normalized surface reaction rate constant; the specific surface area of ZVI is 26.3 m^2 g^{-1} and loading is 0.71 g L^{-1}.
[b] Pd:Fe ratios of samples after reaction for 7 d, with the initial Pd content of 0.10%.
[c] The reaction rates were undetectable.

limiting factor for 124TCB dechlorination because the rate of corrosion (electron donation or hydrogen release) far exceeded the dechlorination rate on the Pd sites due to the large specific area of the nanosized ZVI. Thus partial corrosion inhibition induced by the adsorbed silica on the Pd/Fe would not affect the rate of H addition to 124TCB, so long as the Pd sites were not blocked.

3.3.2. ZVI-reducible anions

Nitrate, nitrite, and perchlorate are ZVI-reducible anions, and they may react with ZVI as follows:

$$NO_3^- + H_2O + Fe \rightarrow NO_2^- + 2OH^- + Fe^{2+} \tag{2}$$

$$NO_3^- + 6H_2O + 4Fe \rightarrow NH_3 + 9OH^- + 4Fe^{2+} \tag{3}$$

$$2NO_3^- + 6H_2O + 5Fe \rightarrow N_2 + 12OH^- + 5Fe^{2+} \tag{4}$$

$$NO_2^- + 5H_2O + 3Fe \rightarrow NH_3 + 7OH^- + 3Fe^{2+} \tag{5}$$

$$ClO_4^- + H_2O + Fe \rightarrow ClO_3^- + 2OH^- + Fe^{2+} \tag{6}$$

Nitrite or nitrate adversely affected the 124TCB dechlorination rates (Fig. 6). For example, the k_{obs} values decreased 3-fold when 2 mM nitrate was introduced, and 10-fold when the concentration was 10 mM (Table 1). Nitrite exhibited even greater adverse effects on the 124TCB dechlorination reaction compared with nitrate.

Examinations of the reacted Pd/Fe did not show noticeable presence of any nitrogen compound (as can be inferred from Figs. 2c and 3). Thus, the substantial decreases of k_{obs} values in nitrite or nitrate solutions was believed to be mainly due to 124TCB competition with the anions for the reductive sites on the Pd/Fe particles. This is evidenced by the observed decreases of nitrate or nitrite concentrations in the experiments (data not shown). Nitrite exerted a greater effect than nitrate on the 124TCB dechlorination by Pd/Fe, due to its higher competition ability. It was also reported that in the granular ZVI system nitrite could be more readily degraded than nitrate, with its removal rate being 1.5–15 times faster than nitrate (Alowitz and Scherer, 2002). It is worth noting that dechlorination experiments in the presence of nitrite and nitrate at 10 mM resulted in 40 and 20% 124TCB, respectively, remaining in solutions after 7 d of reaction. This indicated that nitrate or nitrite could passivate the ZVI surface through consumption of iron mass, hindering further 124TCB reductive dechlorination.

Perchlorate is highly soluble in water. Its major source is ammonium perchlorate, which is used as a solid propellant for rockets, missiles, and pyrotechnic devices, and also in other commercial products. Perchlorate has been detected in the contaminated terrestrial waters, and the detected concentrations were up to 1.7 mg L^{-1} (Moore et al., 2003). Table 1 shows that perchlorate had a moderate inhibitory effects on 124TCB dechlorination rate, and the effects were rather consistent over its concentrations of 0.2–10 mM. The study by Moore et al. (2003) showed that perchlorate could be also reductively degraded on iron surfaces, though the removal rates were very slow (<66% removal in 336 h). The slow perchlorate reduction process by Pd/Fe was also observed in the present study (data not shown). Therefore, the effect of perchlorate on 124TCB dechlorination rate was not as profound as those demonstrated by nitrate and nitrite.

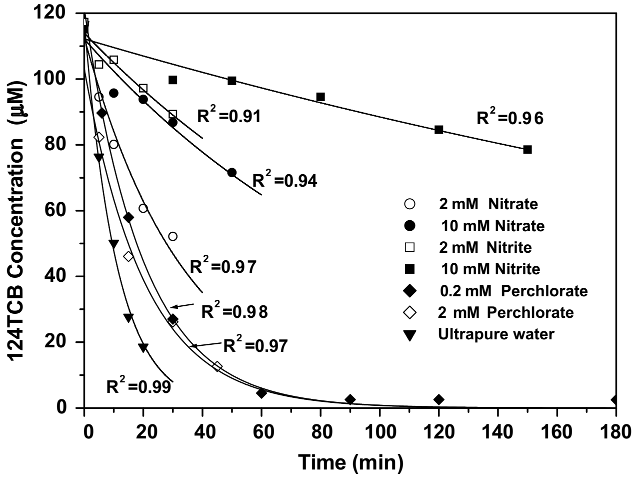

Fig. 6. Influences of nitrate, nitrite, and perchlorate on 124TCB dechlorination by fresh Pd/Fe.

3.3.3. Pd poisons

Sulfate is ubiquitous in the terrestrial waters and wastewaters. It is readily reduced by bacteria to the reduced sulfur species. Our preliminary study showed that sulfate did not cause any significant effect on 124TCB dechlorination by the nanoscale Pd/Fe particles. However, the dissolved sulfide and sulfite did exhibit detrimental effects on the 124TCB dechlorination by the Pd/Fe. For example, in the presence of sulfide (2 mM), there was almost no 124TCB dechlorination detected. This might be attributed to either the formation of FeS film that prevented the access of 124TCB to Pd/Fe or Pd poisoning by sulfide. The second phenomenon was believed to prevail because the EDX and XRD results (Figs. 1 and 2d) did not indicate presence of substantial sulfur species on the reacted Pd/Fe (after 7 d of reaction). To confirm the Pd poisoning phenomenon, two additional experiments were carried out in 2 mM Na_2S solution and ultrapure water (as control), respectively, to investigate 124TCB dechlorination by Pd/γ-Al_2O_3 as catalyst and H_2 as electron (or hydrogen) donor (instead of ZVI). The result showed that in the Na_2S solution, there was no noticeable 124TCB degradation in 96 h, while 124TCB was completely dechlorinated within 24 h in the absence of sulfide. Thus, it was believed that Pd poisoning could be the reason for the absence of 124TCB dechlorination in the Pd/Fe system since Pd was the dominant active site in the reaction. The possible mechanism resulting in the Pd poisoning could be sulfur diffusion into the bulk of the Pd metal or formation of adsorbed layer of sulfur compounds on Pd that would block or modify charge mobility at Pd sites (as proposed by Lowry and Reinhard, 2000). Analysis of the sulfur-fouled Pd catalysts with XPS by Chaplin et al. (2007) showed formation of PdS complex during sulfide fouling, and its regeneration was possible with sodium hypochlorite and hot air at 120 °C.

Catalyst deactivation also appeared to occur in the sulfite solution. There was no noticeable 124TCB dechlorination over a reaction period of 7 d at both 2 and 10 mM sulfite solution. Sulfite might have deactivated Pd by being chemisorbed to the Pd sites and preventing their accessibility to 124TCB. This speculation has been confirmed by Schuth et al. (2000) who investigated Pd deactivation by sulfite during HOCs hydrodechlorination with dissolved H_2.

3.4. Changes in pH and Pd contents

Table 1 shows that generally the final pH values of the solutions with an anionic solute were slightly higher than that in the ultrapure water (control). Nevertheless, there is no clear correlation between the degree of inhibitory effects induced by the anion added and the solution pH. Previous researchers investigating pH effects on TCE and carbon tetrachloride dechlorination concluded that the pH effects on reactivity of the nanoscale ZVI were weak at pH above 8 (Liu and Lowry, 2006). Thus, the preceding discussions of the anion effects on 124TCB dechlorination remain valid.

The Pd contents in the Pd/Fe reacted for 7 d generally decreased in all experiments. An earlier study revealed that Pd islets on the ZVI could be dislodged when the underlying ZVI undergoing severe corrosion after aging (Zhu and Lim, 2007). In the present study, however, one should note that the kinetics results presented in Table 1 were analyzed over a short-term reaction period over which catalyst dislodgment could be negligible. Furthermore, there is no clear relationship between the final Pd content (after 7-d reaction) and the relative significance of the anions in their inhibitory effects on 124TCB dechlorination. Therefore, the factor of varying degrees of Pd losses in various anion solutions can be ruled out in the preceding discussions of anion effects on the 124TCB dechlorination.

4. Conclusions

This study provides useful performance assessment on the nanoscale Pd/Fe particle for its application in dispersed forms for treating contaminated aquifers or wastewater effluents. While the nanoscale Pd/Fe particles are effective in treating chlorinated benzenes in the aqueous phase, several anions found in the terrestrial waters and wastewaters may adversely affect the dechlorination reaction. Based on the observed degrees of inhibitory effects they imposed on the nanoscale Pd/Fe reactivity toward 124TCB, the anions can be ranked in the increasing order of: control $\approx$ sulfate $\approx$ silica < perchlorate < carbonate < nitrate < phosphate < nitrite < sulfite < sulfide. The order is different from that reported for HOC dechlorination with the nanoscale ZVI (Liu et al., 2007). The inconsistency could be due to the difference between the reaction mechanisms involved in the ZVI system and the Pd/Fe system.

The anions can be grouped into three groups according to the natures of their inhibitory effects on the dechlorination reaction: (1) adsorption-precipitation passivating species, such as phosphate and carbonate that can block the adsorptive and reductive sites on Pd/Fe surface; (2) redox-active species such as nitrate, nitrite and perchlorate that can compete for the Pd/Fe reductive sites; and (3) Pd catalyst poisons, such as sulfide and sulfite.

Besides the aqueous matrix effect, another challenge for cost-effective applications of the Pd/Fe nanoparticles in groundwater treatment is to protect the particles from the rapid Fe consumption or corrosion when injected into the groundwater. In this context, coatings with surfactants or polyelectrolytes may be a feasible solution. For water treatment, the treatment system with mineral-supported Pd and H_2 bubbling may be a competitive option to the Pd/Fe nanoparticles, for its efficient use of the hydrogen and ease of Pd regeneration.

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