Coupled reduction of chlorinated hydrocarbons and heavy metals by zerovalent silicon

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Abstract The feasibility of using zerovalent silicon (Si^0) as a novel reductant to remove chlorinated compounds and heavy metals in contaminated sites was investigated. The kinetics and degradation mechanism of carbon tetrachloride (CT) by Si^0 were also examined. Results showed that zerovalent silicon could effectively dechlorinate the chlorinated compounds. A nearly complete dechlorination of CT by Si^0 was obtained within 14 h. The produced concentrations of chloroform (CF) accounted for 71–88% loss of CT, showing that reductive dechlorination is the major degradation pathway for the degradation of chlorinated hydrocarbons by Si^0. The degradation followed pseudo first-order kinetics and the normalized surface reaction rate constant (k_{sa}) for CT dechlorination ranged between 0.0342 and 0.0454 L m^{-2} h^{-1} when CT concentrations were in the range of 3–20 μM. A linear relationship between the k_{sa} and pH value was also established. In addition, zerovalent silicon has a high capability in the removal of heavy metals. 83% of Cr(VI) was removed by 0.5g Si^0 within 5 h, which is higher than that by Fe^0. The removal efficiency of divalent metal ions by Si^0 followed the order of Cu(II) > Pb(II) > Ni(II). This indicates that zerovalent silicon is an alternative reductant and can undergo coupled reduction of heavy metals and chlorinated hydrocarbons in contaminated groundwater.

Keywords Chlorinated hydrocarbons; coupled reduction; heavy metals; pseudo first-order kinetics; zerovalent silicon (Si^0)

Introduction

Chlorinated hydrocarbons and heavy metals are the most often found toxic chemicals in contaminated aquifers. Several studies (Matheson and Tratnyek, 1994; Su and Puls, 1999; Doong *et al*., 2003) have recently addressed the importance of abiotic degradation using zerovalent metals to remove the chlorinated hydrocarbons and heavy metals under anaerobic conditions. Results of feasibility studies (Lien and Zhang, 1999; Scherer *et al*., 2000) demonstrated that granulated iron is effective on the dechlorination of chlorinated solvents. Orth and Gillham (1996) used zerovalent iron to dechlorinate TCE and found that ethene and ethane were the major degradation products. Sequential reductive dehalogenation and β-elimination are believed to be the major pathways for the degradation of chlorinated aliphatic compounds. Factors influencing the reductive dechlorination of chlorinated compounds include the reactivity of individual contaminants, pH values, and the available concentration and specific surface area of metals (Matheson and Tratnyek, 1994; Lien and Zhang, 1999).

Although zerovalent iron can decompose chlorinated hydrocarbons effectively, questions remain to be answered on the increase in pH value during the dechlorination processes and the long-term effectiveness of a permeable reactive barrier (PRB) packed with iron. Zerovalent iron is thermodynamically unstable and produces hydroxide ions in aqueous solution, resulting in the increase in pH up to 10–12. Several zerovalent metals such as nickel and zinc were used as alternative reductants to dechlorinate toxic chemicals. However, the release of the dissolved metal ion species from the surface of metals limited the development of using such materials as novel reductants for the remediation of contaminated sites. Zerovalent silicon (Si^0) is widely used in the semiconductor industry and is the

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subject of numerous investigations such as in nanotechnology. Also, Si^0 has a lower redox potential ($E_H^0 = -0.807$ V) when compared to iron ($E_H^0 = -0.44$ V). This indicates that silicon is a strong reductant and could be an electron donor for the reduction of contaminants. A previous study showed that the combination of zerovalent silicon and iron can accelerate the dechlorination rate of PCE (Doong *et al.*, 2003). However, the effect of environmental parameters, such as concentration of contaminant and pH on the dechlorination of chlorinated hydrocarbons by Si^0 has not been well-understood. Also, the removal of heavy metal ions by Si^0 received less attention. Therefore, the purpose of this study was to understand the transformation of carbon tetrachloride (CT) and heavy metals using zerovalent silicon as an electron donor and to evaluate the feasibility of using silicon as a novel material to remediate contaminated sites. The effects of pH and the initial CT concentration on the dechlorination efficiency and rate of CT under anoxic condition were also investigated in this study.

Materials and methods

Chemicals
All chemicals were used as received without further treatment. 2-(*N*-cyclohexylamino) ethanesulfonic acid (CHES buffer) (>99.5%, reagent grade) was purchased from Aldrich Co. (Milwaukee, WI). Methylene chloride (DCM) (> 99.8%, GC grade) was obtained from J.T. Baker Co. (Philipsburg, NJ). Carbon tetrachloride (CT) (> 99.8%, GC grade), chloroform (CF) (> 99.8%, GC grade), tris(hydroxymethyl) aminomethane (Tris buffer), and zerovalent silicon (> 99.5%) were purchased from Merck Co. (Darmstadt, Germany). All the solutions were prepared using distilled deionized water and were deoxygenated in vacuum-sealed bottles under N_2 atmosphere. The surface of zerovalent silicon, measured by BET N_2 adsorption analyzer (Micromeritics, ASAP 2000), was 1.69 m^2/g.

Dechlorination experiments
Experiments were conducted in batch-fed modes using untreated silicon. N_2-purged 70 mL serum bottles were filled with 40 mL of deoxygenated buffer solution and zerovalent silicon. 50 mM Tris buffer solution was used to control the pH at 8.3 in the Si^0–H_2O system. The serum bottles were sealed with Teflon-lined rubber septa and aluminium crimp caps (The Wheaton Co., NJ). An aliquot of the stock solutions of chlorinated compounds dissolved in methanol or heavy metal ions in distilled deionized water was delivered into serum bottles by a gas-tight syringe to obtain the final concentrations of 20 μM for CT or 50 μM for heavy metals. The total volume of the liquid phase was 40 mL, resulting in a 30-mL headspace left for analysis. The bottles were incubated with an orbital shaker at 150 rpm and at 25 ± 1°C in the dark. Parallel experiments were also carried out without the addition of zerovalent silicon (blank control).

Analytical methods
The headspace analytical technique for the determination of chlorinated hydrocarbons was used in this study. The concentrations of chlorinated hydrocarbons and their products in the headspace of the test bottles were monitored by drawing 60 μL of gas in the headspace with a 100 μL gas-tight syringe. The mixture was injected into a gas chromatograph (GC) (Perkin-Elmer, Autosystem) equipped with a flame ionization detector (FID) and an electron capture detector (ECD). A 60-m VOCOL fused-silica megabore capillary column (0.545 mm × 3.0 μm, Supelco Co.) was used for separating the chlorinated compounds. The column was connected to FID and ECD simultaneously by a Y-splitter with 40% of the flow (1.85 ml/min) to ECD for better identifying and quantifying the chlorinated hydrocarbons. The column temperature was maintained at 90°C isothermally with the nitrogen

gas (N_2) as the carrier gas. The relative standard deviation (RSD) for GC analysis was controlled within 10%. The serum bottles were opened after the headspace analysis and the pH was measured using a pH meter equipped with a pH electrode.

Cr(VI) was determined using the diphenylcarbazide (DPC) method. 1.5 ml of samples were withdrawn using a N_2-purged syringe, centrifuged at 14,000 rpm for 10 min and then acidified to pH < 2 by HNO_3. 0.2 ml of DPC in acetone was then added into the supernatant, left for 4 min and the concentration of Cr(VI) was determined using UV-Vis spectroscopy at 540 nm. Heavy metals in aqueous solutions including Cu, Pb and Ni were analyzed by atomic absorption spectrometry.

Results and discussion

Dechlorination of carbon tetrachloride by Si[0]

Figure 1 illustrates the dechlorination of various concentrations of CT by 0.3 g Si[0] at pH 8.3 under anoxic conditions. The concentrations of CT used in this study were in the range of 3–20 μM. No obvious degradation of CT was observed in the absence of Si[0]. Addition of Si[0] significantly enhanced the dechlorination efficiency and rate of CT. A nearly complete dechlorination of CT by Si[0] was observed within 14 h. Chloroform (CF) was found to be the dominant product during the dechlorination processes. The produced concentrations of CF increased upon increasing initial CT concentrations and maximum concentrations of 2.12–15.9 μM were observed. This corresponds to 71–88% loss of CT, showing that reductive dechlorination is the major degradation pathway for the dechlorination of CT by zerovalent silicon.

Previous studies depicted that the dechlorination of chlorinated hydrocarbons by zerovalent metals is a surface-mediated reaction and is first-order with respect to not only the contaminant concentration but also the available amounts of the specific surface area of metals (Johnson *et al*., 1996; Doong *et al*., 2003). Therefore, the dechlorination rate of CT can be described by a pseudo first-order rate equation:
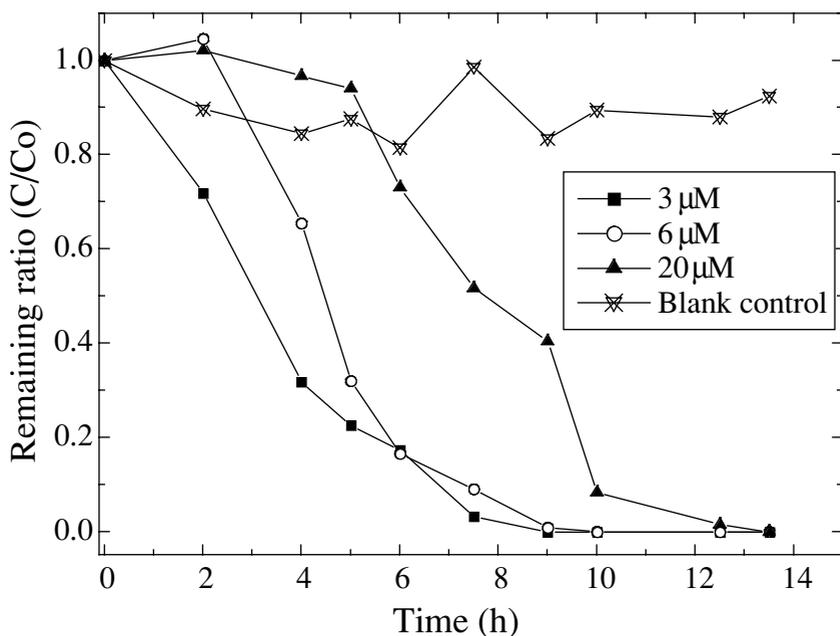
Figure 1 The dechlorination of CT by zerovalent silicon at pH 8.3 under anoxic condition

$$\ln\left(\frac{[\text{CHC}]_t}{[\text{CHC}]_0}\right) = -k_{\text{obs}}t \qquad (1)$$

$$\ln\left(\frac{[\text{CHC}]_t}{[\text{CHC}]_0}\right) = -k_{\text{sa}}\rho_a t \qquad (2)$$

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where $[\text{CHC}]_0$ and $[\text{CHC}]_t$ are the concentrations of chlorinated hydrocarbons at the initial time and at time t, respectively, k_{obs} is the pseudo first-order rate constant (h^{-1}), k_{sa} is the normalized surface reaction rate constant ($L\,m^{-2}\,h^{-1}$), and ρ_a is the surface area concentration of silicon ($m^2\,L^{-1}$). Table 1 shows the normalized surface reaction rate constants (k_{sa}) for CT dechlorination and the maximum CF concentrations at various initial concentrations of CT. The k_{obs} for CT dechlorination increased from 0.347 h^{-1} at 3 µM to 0.460 h^{-1} at 20 µM. This corresponds to the k_{sa} values of 0.0342–0.0454 $L\,m^{-2}\,h^{-1}$, showing that the degradation rate increased positively with increasing initial CT concentrations.

It is noted that a lag time was needed for CT to onset the dechlorination reaction by Si^0. This delay may be attributed to the existence of a hydrogen-terminated surface of Si^0. Due to the high reactivity of silicon, the silicon surfaces are often etched with aqueous hydrogen fluoride (HF) and with 40% ammonium fluoride (NH_4F) to form hydrophobic and hydrogen-terminated silicon (H-Si) that is fairly stable under atmospheric conditions (Zhou *et al.*, 2001). The hydrogen-terminated silicon will be further oxidized to an Si-OH surface when it is exposed to air containing water for several hundred minutes. Morita *et al.* (1989) examined the possible factors influencing the formation of native silicon oxide on the surface of silicon in air or in ultrapure water and found that native silicon oxide would be formed on Si wafer at room temperature with the coexistence of water and oxygen in the air. Therefore, hydrogen-terminated silicon and silicon oxide would appear on the surface of silicon used in this study. To understand the surface characteristics of silicon on the dechlorination, 20 µM of CT was re-spiked into the solution after 24 h of incubation. As depicted in Figure 2, the re-spiked CT was completely dechlorinated within 2 h without the lag time. The k_{sa} value was 0.221 $L\,m^{-2}\,h^{-1}$, which was 5 times higher than that for the first amendment. This result clearly shows that the surface characteristics of zerovalent silicon significantly influence the dechlorination efficiency and rate of CT. Since the existence of hydrogen-terminated silicon lowered the dechlorination rate of CT, the addition of hydroxide ion may solubilize the hydrogenated silicon surface to enhance the dechlorination rate. Therefore, the effect of pH on the dechlorination of CT by zerovalent silicon was further investigated.

Effect of pH value

pH is an important factor influencing the dechlorination efficiency and rate of chlorinated hydrocarbons by Si^0. To understand the dechlorination behavior of CT over a wide range of pH, a series of buffered solutions containing 0.6 g Si^0 and 10 µM of CT were used. Tris buffer was used to control the pH at 7.2–8.9 and CHES buffer was used at pH 9.5. Figure 3 illustrates the effect of pH on the reductive dechlorination of CT by Si^0. CT cannot be dechlorinated within 16 h at pH 6.5, while a complete dechlorination was observed when

Table 1 The maximum concentration of CF produced and the pseudo first-order rate constants for CT dechlorination at pH 8.3

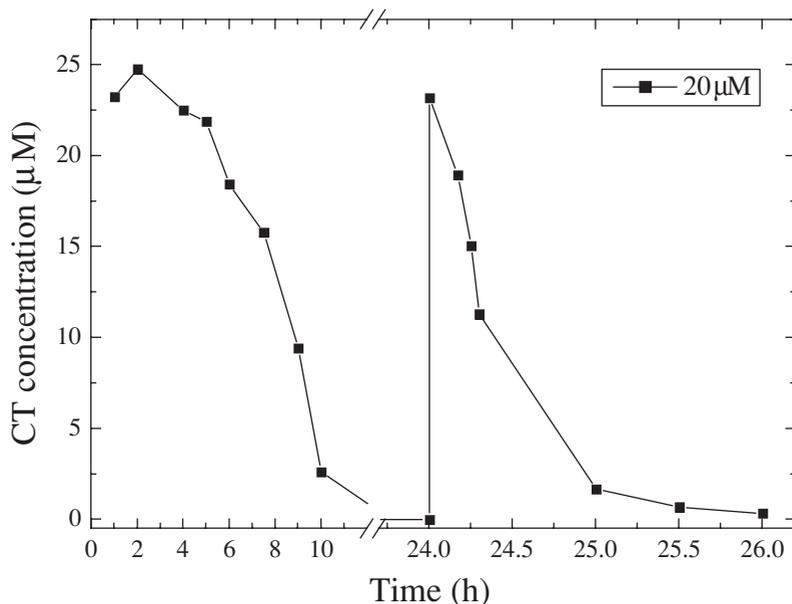| CT concentration (µM)	Maximum CF concentrations produced (µM)	Rate constant for CT dechlorination	
		k_{obs} (h^{-1})	k_{sa} ($L\,m^{-2}\,h^{-1}$)
3	2.12	0.347	0.0342
6	5.28	0.389	0.0384
20	15.8	0.460	0.0454

Figure 2 The dechlorination of the re-amended carbon tetrachloride by Si⁰ at pH 8.3 after the incubation of 24 h

the pH value was higher than 7.2. The dechlorination efficiency and rate increased upon increasing pH values, suggesting that hydroxide ions (OH⁻) can activate the silicon surface for reaction. The production of CF at various pH values ranged between 7.7 and 8.5 µM, which corresponded to 77–85% of CT reduction. However, only trace amounts of dichloromethane (DCM) were detected, proving again that sequential reductive dechlorination is the main dechlorination pathway for chlorinated hydrocarbons in the presence of Si⁰ and the dechlorination rate is much less favorable for low chlorinated compounds.

The dechlorination of CT at various pH values also followed a first-order rate equation. Table 2 illustrates the effect of pH on the rate constant for CT dechlorination and the
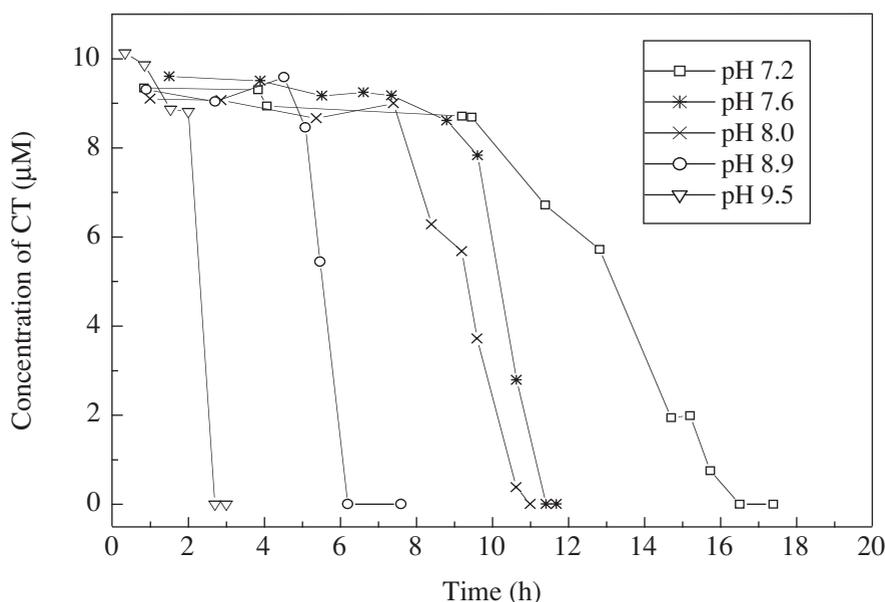

Figure 3 The pH effect on the dechlorination of carbon tetrachloride by Si⁰ under anoxic conditions

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Table 2 Effect of pH on the produced chloroform concentration and the pseudo first-order rate constants for CT dechlorination by 0.6 g Si^0 at various pH values ranging between 7.2 and 9.5. The concentration of CT was 10 μM

pH value	Maximum CF concentrations produced (μM)	Rate constant for CT dechlorination	
		k_{obs} (h^{-1})	k_{sa} ($L m^{-2} h^{-1}$)
7.2	8.05	0.501	0.0247
7.6	8.32	0.805	0.0397
8.0	8.14	1.105	0.0545
8.9	8.23	1.564	0.0771
9.5	7.66	2.109	0.104

production of CF by 0.6 g Si^0 under anoxic conditions. The k_{sa} increased linearly from 0.0247 to 0.104 L h^{-1} m^{-2} when pH values increased from 7.2 to 9.5. A linear relationship between k_{sa} and pH was also observed ($r = 0.996$, $n = 5$), showing that the degradation rate of CT was first-order dependent on the pH values. It is noted that the produced CF concentration at pH 9.5 is relatively lower than those at pH 7.2–8.9, presumably due to the further dechlorination of CF to dichloromethane.

Removal of heavy metals by Si^0

Several heavy metal ions such as arsenic (As) and chromium (Cr) have been demonstrated to be removed by zerovalent iron in the contaminated groundwater (Alowitz and Scherer, 2002; Manning et al., 2002). However, the removal of heavy metals by Si^0 remains unclear. Figure 4 shows the removal of Cr(VI) by zerovalent silicon at pH 8.3. Control experiments without Si^0 showed no obvious loss of contaminant over the experimental period of 5 h. In the presence of Si^0, however, Cr(VI) concentration decreased linearly with time and a removal ratio of 83% was observed within 5 h. Addition of Fe^0 has less effect on the removal of Cr(VI). The aqueous Cr(VI) concentration decreased from 50 μM to 30.3 μM within 5 h when 0.5 g Fe^0 was added into the solution. The combination of 0.5 g Si^0 and 0.5 g Fe^0 removed contaminant significantly and a nearly complete removal of Cr(VI) was
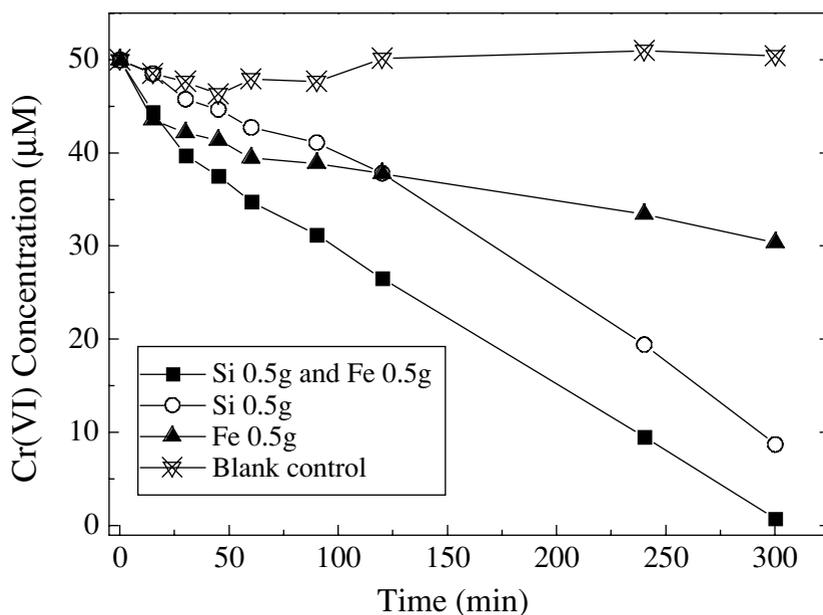

Figure 4 The removal of Cr(VI) in solutions containing zerovalent silicon and zerovalent iron
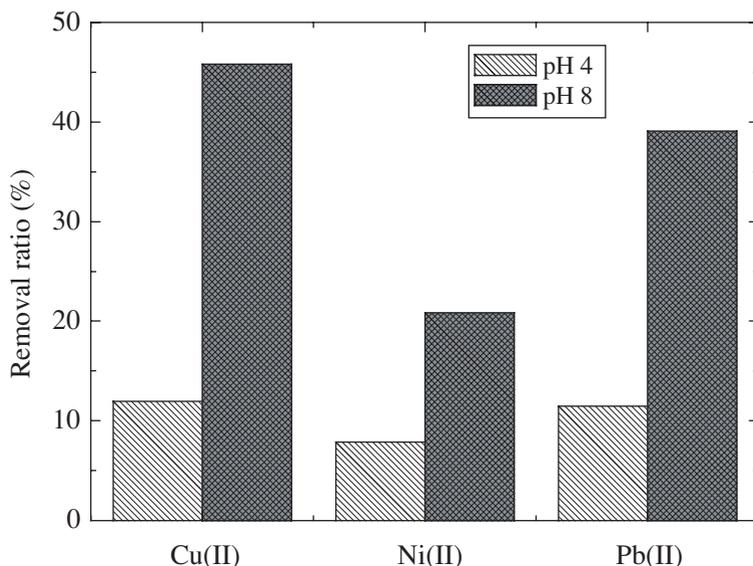
Figure 5 The removal efficiency of heavy metal ions by Si^0 at various pH values

observed within 5 h. It is noted that the reduction pattern of Cr(VI) in the Si^0/Fe^0 system was similar to that by Si^0 only, showing that Si^0 is more efficient than zerovalent iron in the reduction of Cr(VI).

Zerovalent silicon can also remove Cu(II), Ni(II), and Pb(II) effectively. Figure 5 illustrates the removal of 50 μM heavy metal ions by Si^0 at various pH values. The removal efficiency of metal ions by Si^0 followed the order of Cu(II) > Pb(II) > Ni(II). Also, pH is an important factor influencing the reduction ratio of metal ions by Si^0. Only 8–12% of metal ions were removed at pH 4, while the removal ratios were 3 to 4 times higher than that at pH 4 when the pH value increased to 8. This means that high pH can enhance the reduction efficiency of metal ions, presumably due to the activation of the active sorption sites on the surface of silicon at high pH values.

Conclusions

Results obtained in this study demonstrate that zerovalent silicon can reduce the chlorinated compounds and heavy metal ions effectively. A nearly complete dechlorination of CT in the concentration range of 3–20 μM was observed within 14 h. Reductive dechlorination was shown to be the major degradation pathway for the dechlorination of CT by Si^0. The degradation followed pseudo first-order kinetics with respect to the CT concentrations and pHs. A linear relationship between the k_{sa} and the environmental factors was also established. Moreover, zerovalent silicon can remove Cr(VI) effectively. The reduction efficiency of metal ions by Si^0 followed the order of Cu(II) > Pb(II) > Ni(II). These results clearly show that zerovalent silicon is a novel material that can be used in PRB as an alternative reductant for effectively remediating the contaminated sites.

Acknowledgement

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