

Synergistic Effect of Copper Ion on the Reductive Dechlorination of Carbon Tetrachloride by Surface-Bound Fe(II) Associated with Goethite

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The dechlorination of carbon tetrachloride (CT) by Fe(II) associated with goethite in the presence of transition metal ions was investigated. X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD) were used to characterize the chemical states and crystal phases of transition metals on solid phases, respectively. CT was dechlorinated to chloroform (CF) by 3 mM Fe(II) in 10 mM goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$) suspensions. The dechlorination followed pseudo-first-order kinetics, and a rate constant (k_{obs}) of 0.036 h^{-1} was observed. Transition metal ions have different effects on CT dechlorination. The addition of Ni(II), Co(II), and Zn(II) lowered the k_{obs} for CT dechlorination, whereas the amendment of 0.5 mM Cu(II) into the Fe(II)–Fe(III) system significantly enhanced the efficiency and the rate of CT dechlorination. The k_{obs} for CT dechlorination with 0.5 mM Cu(II) was 1.175 h^{-1} , which was 33 times greater than that without Cu(II). Also, the dechlorination of CT by surface-bound iron species is pH-dependent, and the rate constants increased from 0.008 h^{-1} at pH 4.0 to 1.175 h^{-1} at pH 7.0. When the solution contained Cu(II) and Fe(II) without goethite, a reddish-yellow precipitate was formed, and the concentration of Fe(II) decreased with the increase in Cu(II) concentration. XPS and XRPD analyses suggested the possible presence of Cu_2O and ferrihydrite in the precipitate. Small amounts of aqueous Cu(I) were also detected, reflecting the fact that Cu(II) was reduced to Cu(I) by Fe(II). A linear relationship between k_{obs} for CT dechlorination and the concentration of Cu(II) was observed when the amended Cu(II) concentration was lower than 0.5 mM. Moreover, the k_{obs} for CT dechlorination was dependent on the Fe(II) concentration in the 0.5 mM Cu(II)-amended goethite system and followed a Langmuir–Hinshelwood relationship. These results clearly indicate that Fe(II) serves as the bulk reductant to reduce both CT and Cu(II). The resulting Cu(I) can further act as a catalyst to enhance the dechlorination rate of chlorinated hydrocarbons in iron-reducing environments.

Introduction

Chlorinated hydrocarbons are one of the major contaminants in soils and groundwaters (1, 2). The dechlorination of

chlorinated hydrocarbons by iron species has recently received much attention. In many natural environments, the oxygen supply is limited, but iron oxides are present as alternative electron acceptors. The use of iron species to reduce chlorinated hydrocarbons is of great advantage because iron oxides bind with aqueous and solid-phase Fe(II) species and are natural reductants in many hydro-morphic soils and subsurface environments (3).

Laboratory and field studies have demonstrated the importance of iron species in the reductive transformation of organic and inorganic compounds (4–14). Minerals that contain structural Fe(II) such as green rust and magnetite have been found to reduce several classes of priority pollutants, including halogenated hydrocarbons (5–10), nitroaromatic compounds (11, 12), and inorganic ions (13, 14). Moreover, the systems containing dissolved Fe(II) and various iron oxides have also shown high reactivity with respect to chlorinated hydrocarbons under anoxic conditions (4, 15–17). It is generally believed that ferrous iron associated with iron oxides is much more reactive than dissolved Fe(II) (4, 11, 12, 15). The high reactivity of the heterogeneous Fe(II)/Fe(III) system can be maintained over a long period of time because of the continuous generation of surface-bound Fe(II) species by the uptake of Fe(II) from the aqueous phase (4). Several factors including the pH value, surface density of Fe(II), available surface area of iron minerals, and contact time of Fe(II) with minerals have been shown to influence the reactivity of Fe(II) species bound with iron oxides (4, 16, 17). Amonette et al. (17) dechlorinated carbon tetrachloride (CT) in an Fe(II)-amended goethite system and found that the density of sorbed Fe(II) over goethite surface was the major factor on which the rate of dechlorination was dependent. More recently, Hofstetter et al. (18) showed that the types of Fe(II) species on clay minerals influenced the reducing efficiency and rate of nitroaromatic compounds. Both structural Fe(II) and Fe(II) complexed by surface hydroxyl groups of clay minerals reduced nitroaromatics to aniline effectively, whereas Fe(II) bound by ion exchange did not contribute to the reductive transformation.

Iron minerals are also potentially strong sorbents that have often been used to remove a variety of metal ions from aqueous solutions and soils (19, 20). The sorption of metal ions, including Fe(II), Zn(II), Cu(II), Ni(II), and Co(II), from aqueous solutions to a goethite surface have been observed (21–24). Metal ions sorb to the active adsorption sites on the surface of iron oxides at the first stage and then complex with surface hydroxyl groups to form reactive sites, leading to the occurrence of redox reactions on the solid phase (25). Moreover, the heterogeneous redox reactions involving electron transfer between Fe(II) and Fe-containing minerals have been demonstrated (14, 26). White and Peterson (14) systematically investigated the reduction of the first row of transition metal species on the surface of magnetite and illmenite and found that the surfaces of structural Fe(II) minerals could effectively reduce Fe(III), Cu(II), Cr(VI), and V(V) in solutions. This implies that the redox reactions controlled by solid-state Fe(II), either structural or surface associated, might be a useful reductant for transition metals in aqueous solution.

Transition metals are often found with chlorinated organic compounds in contaminated groundwaters (27). Although the reactivity of various surface-bound iron species are commonly considered in the dechlorination of chlorinated hydrocarbons, much less emphasis has been placed on the synergistic effect of transition metals with Fe(III)-containing minerals on dechlorination. Certain transition metals, such

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as nickel and copper, also can act as mediators to enhance the dechlorination efficiency of chlorinated hydrocarbons (28–30). Therefore, the objective of the present study was to investigate the synergistic effect of transition metal ions with surface-bound Fe(II) species on the dechlorination of CT. Goethite was selected as the model iron oxide because it is one of the most abundant crystalline iron oxyhydroxide minerals in the natural environment and is widely used to remove trace organics and metal ions (22, 31). Transition metals including Co(II), Ni(II), Cu(II), and Zn(II) were selected because of their availability and abundance in both natural and contaminated environments. The chemical states of transition metals and crystal phase of precipitate on iron oxides were characterized using X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD) techniques. The effects of pH and concentrations of Fe(II) and Cu(II) on the dechlorination efficiency were also examined to understand the role of transition metal ions in the dechlorination reaction under iron-reducing conditions.

Materials and Methods

Chemicals. All chemicals were used as received without further treatment. Carbon tetrachloride (CT, > 99.8%, GC grade), chloroform (CF, > 99.8%, GC grade), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (99%), and ZnCl_2 (98%) were purchased from Merck Co. (Darmstadt, Germany). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), *N*-(2-hydroxyethyl)-piperazine-*N'*-(2-ethanesulfonic acid) (HEPES) (99.5%), and 2-(*N*-morpholino)ethanesulfonic acid (MES) (>99.5%) were purchased from Sigma-Aldrich Co. (Milwaukee, WI). Methylene chloride (DCM, >99.8%, GC grade) and ethanol (HPLC grade) were obtained from J. T. Baker Co. (Phillipsburg, NJ). Bathocuproinedisulfonic acid disodium salt ($\text{C}_{26}\text{H}_{18}\text{N}_2\text{Na}_2\text{O}_6\text{S}_2$, 90%) was purchased from Fluka (Buchs, Switzerland). Goethite was synthesized according to the method of Schwertmann and Cornell (32) and was characterized by XRPD. The XRPD pattern showed major peaks at 21.25° , 33.3° , 36.65° , and 53.3° 2θ , which proved that this preparation was goethite and contained no other Fe(III) oxides (Figure S1, Supporting Information). The surface area of goethite was determined by a BET N_2 adsorption surface area analyzer (Micromeritics, ASAP 2000). The powder sample of goethite was degassed with N_2 (99.9995%) and vacuumed (5×10^{-3} mmHg) repeatedly in a sealed vacuumed desiccator. The surface area was then determined by one-point measurement, and a value of $28.8 \text{ m}^2/\text{g}$ was obtained.

Dechlorination Experiments. Batch experiments were conducted using 70-mL serum bottles filled with 50 mL of deoxygenated buffer solution under anoxic conditions (33, 34). A high purity of N_2 (>99.9995%) at a flow rate of 42 L/min was used to maintain the anoxic conditions during the experimental processes. Goethite was withdrawn using an N_2 -purged syringe and was delivered into serum bottles to a final concentration of 10 mM ($25.6 \text{ m}^2 \text{ L}^{-1}$). Fe(II) solutions were prepared in deoxygenated buffer solutions in sealed bottles and were introduced into the serum bottles to a concentration of 3 mM. HEPES (50 mM) buffer solutions were used to control pH at 7.0 ± 0.1 . The stock solutions of divalent ions of transition metals (Cu, Zn, Co, and Ni) were prepared using deoxygenated water in sealed bottles. Appropriate amounts of stock solutions were introduced into the serum bottles to a final concentration of 0.5 mM using N_2 -purged plastic syringes. Equilibrium calculations showed that Cu(II), Zn(II), and Co(II) were mainly in their dissolved forms, while 30% of Cu(II) was precipitated onto the surface of the goethite. Bottles were then sealed with Teflon-lined rubber septa and aluminum crimp caps and were incubated in an orbital shaker at 150 rpm and at $25 \pm 1^\circ \text{C}$ in the dark. After 20 h of equilibrium, 25 μL of the CT stock solution dissolved in methanol was delivered into the serum bottle

by a gastight glass syringe to obtain the final concentration of 20 μM . The total volume of the liquid phase in the serum bottle was maintained at 50 mL, which resulted in a 20-mL headspace left for headspace analysis. Parallel experiments were also carried out without the addition of Fe(II). All the experiments were run in duplicate or triplicate.

The combined effect of Fe(II) and Cu(II) on the dechlorination of CT without the addition of goethite was also performed according to the above procedures to understand the role of Cu(II) in the dechlorination of CT. The concentrations of Cu(II) and Fe(II) in the aqueous solutions were in the range of 0.1–4 and 0.2–3 mM, respectively. After the addition of Cu(II) into the Fe(II) containing solution, a precipitate was observed that was harvested for species identification. The suspension was transferred into a 50-mL centrifuge tube using N_2 -purged syringe and was centrifuged at $8000 \times g$ for 10 min. After the supernatants were removed, the residue was dried with nitrogen gas and transferred to a 4-mL glass vial anaerobically. The glass vial was stored under nitrogen atmosphere in a tightly sealed vacuum desiccator until analysis.

Analytical Methods. The headspace analytical technique was used to determine the chlorinated hydrocarbons. The concentrations of CT and the byproducts of the test bottles were monitored by withdrawing 50 μL of headspace using a 100- μL gastight glass syringe. The mixture was then immediately injected into a gas chromatograph (GC) equipped with a flame ionization detector (FID) and an electron capture detector (ECD) (Perkin-Elmer, Autosystem, Norwalk, CT). A 60-m VOCOL fused-silica megabore capillary column (0.545 mm \times 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^{-1}) going to the ECD for better identification and quantification of the chlorinated hydrocarbons. The column temperature was maintained at 50°C isothermally with nitrogen (N_2) as the carrier gas. Concentrations of chlorinated hydrocarbons in aqueous solutions were then calculated using the external standard method by preparing the known concentrations of chlorinated hydrocarbons in aqueous solutions. The relative standard deviation for GC analysis was controlled within 10%. The serum bottles were opened after the headspace analysis and pH was measured using a microprocessor pH meter.

The non-chlorinated products after the termination of the dechlorination experiment were monitored by using a Varian 3800 GC equipped with a mass spectrometer (MS) (Saturn 2000) and an FID. This automated system can analyze 56 volatile organic compounds in gaseous samples (35). Two capillary columns, a PLOT (Chrompack, 50 m \times 0.32 mm \times 5.0 μm) and a DB-1 (J&W, 60 m \times 0.32 mm \times 1.0 μm), were connected in parallel by a Y-splitter with approximately one-third of the flow going to the PLOT column. The PLOT column was coupled to an FID, and the DB-1 column was connected to the MS for the separation and detection of hydrocarbons. Four internal standards including bromochloromethane, chlorobenzene, 1,4-difluorobenzene, and 1-bromo-4-fluorobenzene were spiked into the samples on-line to accurately monitor the stability of retention times of the analyzed compounds in MS spectra.

XRPD and XPS were used to identify the crystal phases and chemical states of transition metals on the solid residues, respectively. XRPD was performed using an X-ray diffractometer (Regaku D/max-II B) and a $\text{Cu K}\alpha$ -radiation source with 30 kV voltage and 20 mA current. Samples were mounted on a glass sample holder using small amounts of grease. A drop of glycerol was immediately added on the mounted powder layer to minimize the reaction with oxygen. The scan range for all samples was between 10 and 90° (2θ) at a

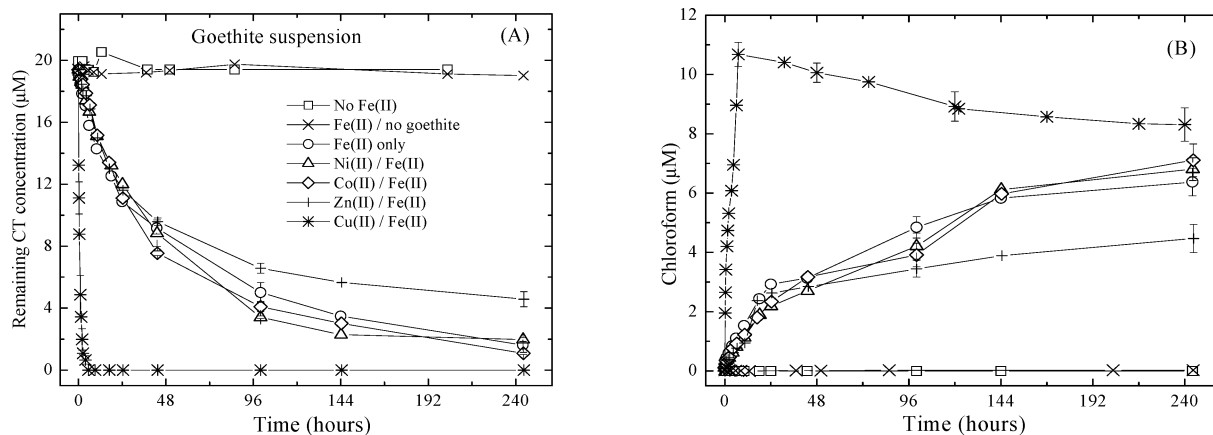


FIGURE 1. Dechlorination of 20 μM CT in the anoxic suspensions containing 10 mM goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$) and 3 mM Fe(II) in the presence of 0.5 mM of transition metals. 50 mM HEPES buffer was used to control pH at 7.0 ± 0.1 : (A) concentration profile of CT and (B) formation of chloroform. Error bars indicate ± 1 SD of triplicate runs ($n = 3$).

scanning speed of $4^\circ/\text{min}$. The XPS measurements were performed with an ESCA PHI 1600 photoelectron spectrometer (Physical Electronics, Eden Prairie, MN) using a Mg $K\alpha$ X-ray source (1253.6 eV photon energy). The spherical capacitor analyzer with a multichannel detector had a takeoff angle of 70° related to the horizontal of the sample plane. The binding energies of the photoelectrons were determined under the assumption that carbon has a binding energy of 284.8 eV. The data were recorded digitally, and all peak scans were signal-averaged until an acceptable signal-to-noise ratio was obtained. During the data acquisition, the pressure in the sample chamber did not exceed 2.5×10^{-9} Torr. The binding energies of Fe and Cu species were calibrated with reference to the binding energy of adventitious carbon 1s electron (284.8 eV). Although some probable errors may occur during the identification of chemical species, this technique is generally accepted for insulating samples (36).

Concentrations of total HCl extractable Fe(II) in the serum bottles were monitored by withdrawing 0.5 mL of suspension using N_2 -purged syringes and were immediately acidified with 1 M HCl. After mixing vigorously, the acidified samples were centrifuged at $8000 \times g$ for 10 min to remove particles and Fe(II) contents were determined with ferrozine at 562 nm (33). The dissolved fraction of Fe(II) was determined in the filtrates (0.2- μm cellulose acetate filter) acidified with 0.5 mL of 1 M HCl.

The concentration of Cu(I) was determined using the bathocuproinedisulfonic acid method with minor modifications (37). The aliquot was withdrawn by a 1 mL N_2 -purged plastic syringe and filtered through a 0.2- μm membrane filter. Then, 0.2 mL of supernatants was added into a 1.5-mL vial that contained 0.5 mL of 1% bathocuproinedisulfonic acid solution. The total volume was adjusted to 1 mL and centrifuged at $8000 \times g$ for 5 min. The aqueous Cu(I) concentration was then determined at 483 nm. Standard solutions of Cu(I) were prepared using 10% hydroxylammonium chloride as a reductant to reduce CuCl_2 solutions. Dissolved and total concentrations of copper species were determined using inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer, Optima 3000XL). The concentrations of copper ions attached to the solid-phase were calculated from the difference between total and dissolved concentrations.

Results and Discussion

Effect of Transition Metal Ions on CT Degradation. Figure 1 illustrates the dechlorination of CT and the production of

CF by surface-bound iron species in the presence of 0.5 mM of metal ions. Ferrous iron species attached to solid surfaces have been reported to be more reactive in dechlorination reactions than the dissolved form (4, 11, 12, 15–17). Our results showed a similar trend. Although the Fe(II) ion is thermodynamically capable of dechlorinating CT (38), no obvious degradation of CT by 3 mM Fe(II) was observed within 10 days at neutral pH. In the presence of goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$) and 3 mM Fe(II), however, 92% of CT degradation with a concomitant increase in CF concentration was observed. Chloroform was identified as the major product. Trace amounts of DCM were also identified after the experimental course of 30 days.

Different effects of transition metals on the dechlorination of CT by Fe(II)-bound goethite were observed. An obvious difference between CT reduction by Fe(II) in the presence and absence of metal ions was observed after 48 h when the *F*-test was applied ($p < 0.05$). As depicted in Figure 1, the addition of 0.5 mM Zn(II) into the heterogeneous Fe(II)/Fe(III) system decreased the dechlorination efficiency of CT, and only 76% of CT was removed within 10 days. The maximum concentration of CF was $4.5 \mu\text{M}$. The addition of Ni(II) and Co(II) decreased the dechlorination of CT at the first stage, but the dechlorination efficiency and production of CF were slightly enhanced after 96 h. Of interest, CT was rapidly dechlorinated to CF in the presence of Cu(II). Nearly complete removal of CT with a rapid accumulation of CF was observed within 6 h. The maximum concentration of CF was $10.8 \mu\text{M}$ and then it slightly decreased to $8.5 \mu\text{M}$, followed by the increase of DCM and methane in trace amounts. The concentration of DCM increased very slowly, and a maximum concentration of $1.35 \mu\text{M}$ was obtained during the incubation of 10 days. The low carbon recovery may be due to the formation of non-chlorinated compounds that cannot be detected by GC-ECD. When GC-MS was employed to identify the intermediates during the dechlorination experiment using a high concentration of CT (1 mM), methane, acetylene, ethane, ethylene, and tetrachloroethylene were identified. A recent study (39) also showed that carbon monoxide, methane, ethane, and ethylene were the final products in CT dechlorination by green rust amended with Cu(II). This implies that processes other than reductive dechlorination are also involved in CT dechlorination in the Cu(II)-amended Fe(II)/Fe(III) system. Moreover, no obvious degradation of CT was observed when the goethite suspension contained only Cu(II), showing that Cu(II)-associated goethite without Fe(II) ions has little effect on the dechlorination of CT.

TABLE 1. Rate Constants (k_{obs} , h^{-1}) for CT Dechlorination in the Anoxic Suspension of Goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$), 3 mM Fe(II) and 0.5 mM Transition Metal Ions^a

experimental system	k_{obs} (h^{-1})	number of replicates
goethite + Fe(II)	0.036 ± 0.005	4
goethite + Fe(II) + Ni(II)	0.026 ± 0.004	4
goethite + Fe(II) + Co(II)	0.020 ± 0.007	4
goethite + Fe(II) + Zn(II)	0.023 ± 0.004	4
goethite + Fe(II) + Cu(II)	1.175 ± 0.189	5
only Fe(II) + Cu(II)	0.252 ± 0.011	3

^a 50 mM HEPES buffer was used to control pH at 7.0 ± 0.1 .

The dechlorination of CT by surface-bound Fe(II) oxidation can be explained by a pseudo-first-order reaction kinetics (4, 15–17)

$$\ln(C_t/C_0) = -k_{\text{obs}}t \quad (1)$$

where C_0 and C_t are the concentrations of CT at the initial time and at time t , respectively, and k_{obs} is the first-order rate constant for CT dechlorination. A good linear relationship between $\ln(C_t/C_0)$ and time was observed within the first 10 h. Table 1 shows the k_{obs} for CT dechlorination by surface-bound iron species in the presence of different metal ions. The k_{obs} for CT dechlorination in the absence of transition metal ions was 0.036 h^{-1} and decreased to 0.020 – 0.026 h^{-1} with amended Ni(II), Co(II), and Zn(II). On the contrary, a 33-fold increase in k_{obs} relative to the unamended system was obtained in the Cu(II)-amended suspension, which shows that the addition of Cu(II) can significantly enhance the dechlorination rate of CT.

The effect of metal ions complexed with macromolecules acting as active electron transfer mediators in the presence of various bulk reductants has been recently studied in both heterogeneous and homogeneous systems (31, 40–42). A common result shows that the degradation efficiency and the rate of chlorinated compounds increase with the addition of certain transition metal ions into systems containing bulk reductants and macromolecules. Recent studies observed that the dechlorination rate of hexachloroethane in heterogeneous systems of sulfur-containing iron minerals (mackinawite) increased in the presence of Cu(II) (43, 44). White and Peterson (14) reported that the structural Fe(II) in Fe(II)-bearing minerals can be oxidized by soluble Cu(II) species. However, the role of Cu(II) in the dechlorination of chlorinated hydrocarbon under iron-reducing conditions is not well-understood. In the present study, the efficiency and rate of CT dechlorination by a surface-mediated goethite system increased greatly when Cu(II) was presented. To further elucidate the possible mechanisms of Cu(II) on CT dechlorination, the effect of pH and the surface characterization of the solid phase were tested.

Effect of pH on CT Dechlorination. The pH value plays an important role in the dechlorination of chlorinated compounds in heterogeneous Fe(II)/Fe(III) systems. Figure 2 illustrates the effect of pH on the dechlorination of CT in the presence of surface-bound iron species with 0.5 mM Cu(II). The pH values were in the range of 4.0–7.0. MES buffer was selected to control the pH at pH 5.5–6.5, and HEPES buffer was used at pH 7. In the unbuffered system, the initial pH was 4.0, and the rate constant (k_{obs}) for CT degradation was 0.008 h^{-1} . The increase in pH value enhanced both the efficiency and the rate of CT dechlorination. The k_{obs} for CT dechlorination increased from 0.031 to 1.175 h^{-1} when the pH increased from 5.5 to 7.0, which is 4–146 times higher than the values obtained in the unbuffered system. This relationship is similar to that shown in previous reports

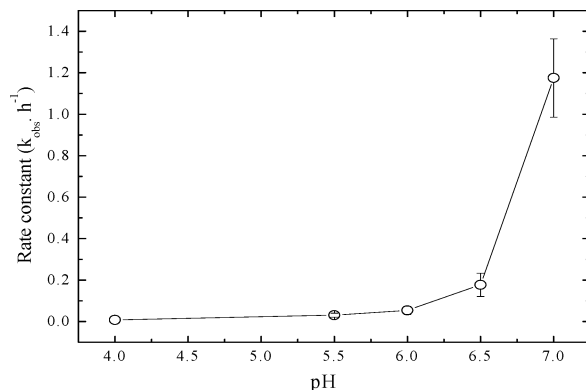
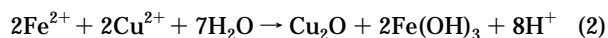


FIGURE 2. The rate constant (k_{obs}) for the dechlorination of CT as a function of pH value in a 10 mM goethite suspension to which 0.5 mM Cu(II) and 3 mM Fe(II) were added. Error bars indicate ± 1 SD of triplicate runs ($n = 3$). Bars not visible are smaller than symbol.

for the dehalogenation of halogenated methanes by surface-bound Fe(II) species without the amendment of Cu(II) (16, 17). This increase in the dechlorination rate of chlorinated compounds at high pH values may be attributed to the increase in the sorbed Fe(II) density on the surface of iron oxyhydroxide particles. The formation of precipitates with different types of surface active sites at the solid surface is another possibility. When Cu(II) was added into the heterogeneous Fe(II)/goethite buffered suspensions at pH 7, the color changed from bright yellow to yellowish blue-green. However, the color remained its original bright yellow at low pH in the unbuffered suspension (pH 4). Similar results were observed in the homogeneous solution when 0.5 mM Cu(II) was added into 3 mM Fe(II) buffered solution without goethite. Nearly complete removal of CT with the production of precipitate was observed within 10 h, and the k_{obs} for CT dechlorination was 0.252 h^{-1} in the solution at neutral pH. However, a small quantity of precipitate with little dechlorination of CT was observed in the homogeneous solution at pH 4. When the precipitate of 0.5 mM Cu(II) and 3 mM Fe(II) ions was filtered through a $0.2\text{-}\mu\text{m}$ membrane under N_2 atmosphere and the filtrate was reinjected into another sealed serum bottle, no CT was dechlorinated within 10 h. This implies that the reactivity of Cu(II)-amended goethite system might be mainly from the surface-bound species on solid. To further understand the characteristics of the precipitate generated in the absence of goethite in the buffered system at pH 7, XRPD and XPS were used to identify the crystal phases and chemical structures of the precipitate. As shown in Figure 3, the XRPD pattern showed clear peaks at 36.42° , 42.22° , and $61.30^\circ 2\theta$ and the XPS spectra also showed a peak at 932.0 eV (Cu $2p_{3/2}$). These results clearly show that cuprous oxide (Cu_2O) was formed in the precipitate. The Fe $2p_{3/2}$ spectrum showed a peak at 710.8 eV, indicating that Fe(III)OFe(III) is substantial. However, no XRD peak of iron oxide was observed, which suggests that a poorly crystalline ferric oxide, ferrihydrite ($\text{Fe}(\text{OH})_3$), could be formed. This means that the aqueous CuCl_2 reacts with FeCl_2 to form Cu_2O and ferrihydrite at neutral pH according to the following relationship:



According to eq 2, 1 mol of Cu(II) can react with 1 mol of Fe(II) to form catalytic Cu(I) ion. Also, 4 mol of proton are released into the solution. At high concentrations of Cu(II), the release of a large amount of protons lowers the pH value of the solution and subsequently decreases the extent and rate of CT dechlorination.

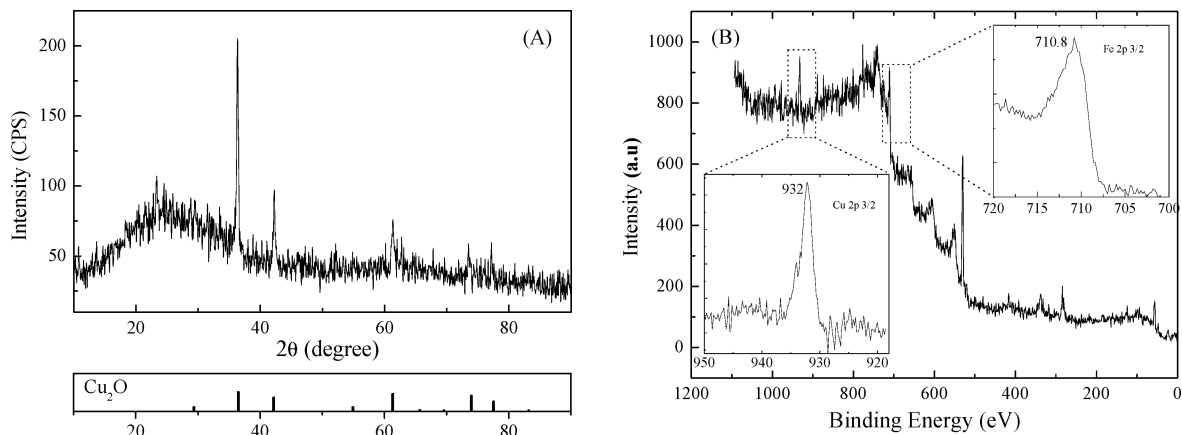


FIGURE 3. (A) XRD pattern and (B) XPS spectra of the precipitate in buffer solutions containing Fe(II) and Cu(II) at neutral pH.

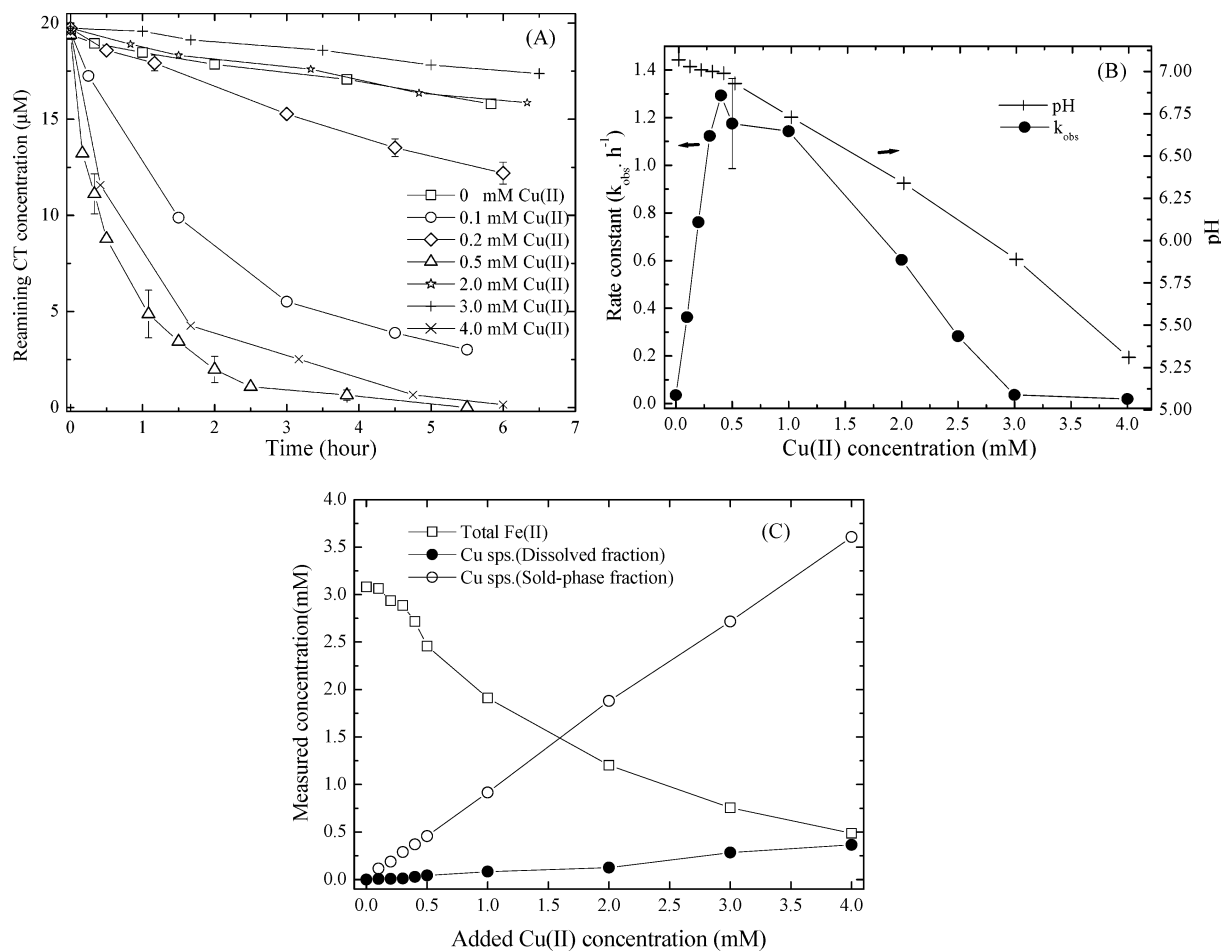


FIGURE 4. Effect of the Cu(II) concentration on the dechlorination of CT in buffered solutions containing 3 mM Fe(II) and 10 mM goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$): (A) concentration profile of CT, (B) first-order rate constant (k_{obs}) for CT dechlorination and pH of the solution, and (C) total Fe(II) and Cu concentrations in the aqueous and solid phases.

Effect of Cu(II) Concentration on CT Dechlorination. To further understand the effect of Cu(II) concentration on the efficiency and rate of CT dechlorination and the change in solution pH, various concentrations of Cu(II) ranging from 0.1 to 4 mM were added to solutions that contained 3 mM Fe(II) and 10 mM goethite at pH 7. Figure 4 illustrates the dechlorination efficiency and rate constants of CT by surface-bound Fe(II) species in the presence of various concentrations of Cu(II). The addition of low concentrations of Cu(II) ranging between 0.1 and 0.5 mM greatly enhanced the efficiency and rate of CT dechlorination. The k_{obs} increased rapidly from 0.363 h^{-1} at 0.1 mM Cu(II) to 1.294 h^{-1} at 0.4 mM and then slightly decreased to 1.143 h^{-1} when Cu(II) was at 1 mM.

This shows that the addition of low concentrations of Cu(II) enhances the dechlorination of CT effectively in Fe(II)-amended goethite suspensions. Further increasing the Cu(II) concentration, however, lowered the dechlorination efficiency, and only 20% of CT was dechlorinated when the Cu(II) concentration was increased up to 3 mM. Little degradation of CT was observed as Cu(II) concentration increased to 4 mM. The decrease in dechlorination efficiency at high Cu(II) concentrations may be attributed to the change in pH value of the solution. As shown in Figure 4(b), the pH value was maintained at $\text{pH } 7.0 \pm 0.1$ when Cu(II) concentrations were in the range of 0.1–0.5 mM. However, the pH value of the solution decreased linearly from 7.0 to 5.3 when

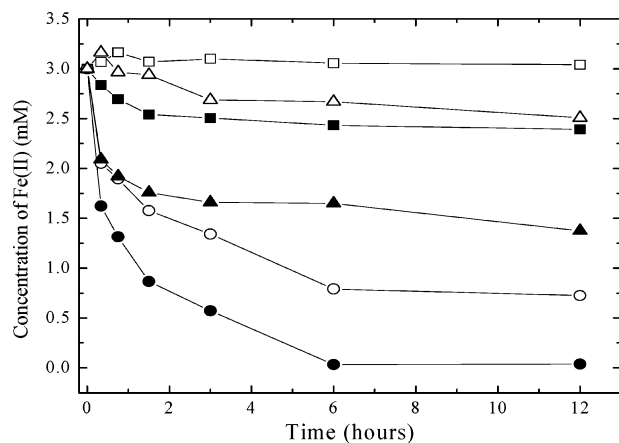


FIGURE 5. The Fe(II) concentration profile during the first 12 h when various concentrations (0, 0.5, and 3.0 mM) of Cu(II) were added to the 3 mM Fe(II)-amended goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$) suspension: (□) total (1 M HCl extractable) Fe(II) in the absence of Cu(II), (■) dissolved Fe(II) in the absence of Cu(II), (△) total (1 M HCl extractable) Fe(II) in the suspension with 0.5 mM Cu(II), (▲) dissolved Fe(II) in the suspension with 0.5 mM Cu(II), (○) total (1 M HCl extractable) Fe(II) in the suspension with 3 mM Cu(II), and (●) dissolved (1 M HCl extractable) Fe(II) in the suspension with 3 mM Cu(II).

the Cu(II) concentration was higher than 0.5 mM. The decrease in pH may be due to the hydrolysis of CuCl_2 in water or the release of protons during the reduction of Cu(II) by Fe(II). Only 0.2 unit of pH was decreased when 4 mM Cu(II) was added into the goethite suspension in the absence of Fe(II), which demonstrates that the release of protons by the hydrolysis of CuCl_2 is not the main reason for the decrease in pH.

It is noted that the k_{obs} for CT dechlorination with the addition of 4 mM Cu(II) is similar to that with 0.5 mM Cu(II) at pH 5.5 (Figure 2). This result also implies that the oxidation of Fe(II) to Fe(III) coupled with the reduction of Cu(II) to Cu(I) could be another possible reason for the decrease in the rate constant of dechlorination at high concentrations of Cu(II). The Fe(II) concentrations at various Cu(II) concentrations in Fe(II)-amended goethite systems were measured after the termination of the dechlorination experiment. The total concentration of Fe(II) decreased when the Cu(II) concentration increased, which indicates that Fe(II) was oxidized by Cu(II) (Figure 4(c)). Also, the fraction of solid-phase Cu species increased with increasing Cu(II) concentrations and was much higher than that of dissolved species, suggesting that Cu(II) was mainly sorbed onto the surface of goethite or was converted to Cu_2O . Moreover, the sorbed Cu(II) concentration was higher than the consumed Fe(II) concentrations when the added concentration of Cu(II) was higher than 2 mM, presumably because of the precipitation of Cu(II) onto the surface of goethite.

To further study the oxidation of Fe(II) by Cu(II), total and dissolved Fe(II) concentrations in Fe(II)/Fe(III) suspensions amended with various concentrations of Cu(II) were measured. As depicted in Figure 5, the dissolved Fe(II) decreased from 3 to 1.5 mM within 12 h with the addition of 0.5 mM Cu(II), whereas only 0.03 mM of Fe(II) was detected in the 3 mM Cu(II)-amended suspension. This decrease in Fe(II) is due to both the sorption of Fe(II) onto the surfaces of goethite and the oxidation of Fe(II) by Cu(II). In the absence of Cu(II), the dissolved Fe(II) decreased from 3 to 2.4 mM within 12 h, while the total Fe(II) concentration maintained a nearly constant value (3 mM). This suggests that about 20% of Fe(II) was sorbed onto the surface of goethite, which is in agreement with the results of previous reports of the dehalogenation of polyhalogenated methanes by surface-

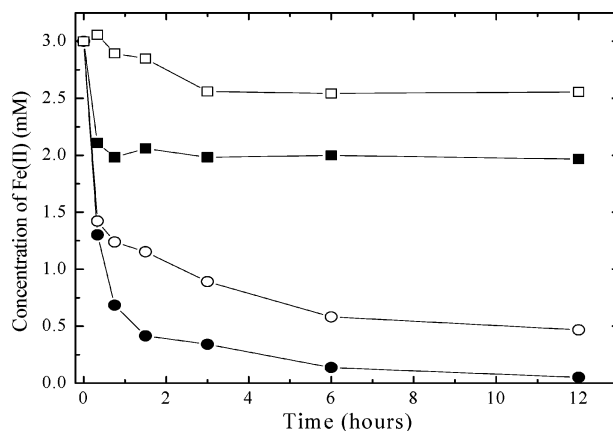


FIGURE 6. The Fe(II) concentration profile during first 12 h when 0.5 and 3.0 mM of Cu(II) were added to the solution containing 3 mM Fe(II) and 50 mM HEPES buffer at pH 7: (□) total (1 M HCl extractable) Fe(II) in the suspension with 0.5 mM Cu(II), (■) dissolved Fe(II) in the solution with 0.5 mM Cu(II), (○) total Fe(II) in the solution with 3 mM Cu(II), and (●) dissolved Fe(II) in solution with 3 mM Cu(II).

bound Fe(II) in goethite suspensions without Cu(II) (16). In contrast, the total concentration of Fe(II) decreased from 3 to 2.5 mM and 0.7 mM within 12 h in the presence of 0.5 and 3 mM Cu(II), respectively. This means that a large fraction of Fe(II) was oxidized by Cu(II). The difference between the total and dissolved Fe(II) concentrations in suspensions with 0.5 and 3 mM Cu(II) added were 1.0 and 0.7 mM, respectively, which are higher than that of sorbed Fe(II) in blank controls (without Cu(II)). This indicates that the sorbed amounts of Fe(II) onto goethite increased slightly in the presence of Cu(II). The increase in the surface density of Fe(II) may also enhance the dechlorination efficiency and the rate of CT.

The oxidation of Fe(II) by Cu(II) was further evaluated in the absence of goethite. Figure 6 illustrates the aqueous Fe(II) concentration at various concentrations of Cu(II) without goethite. A reddish-yellow precipitate was formed when Cu(II) was mixed with 3 mM Fe(II). Therefore, the total and dissolved Fe(II) concentrations were determined. Similar to the concentration profile of Fe(II) in the goethite-amended system, the dissolved Fe(II) concentration decreased rapidly during the first 2 h and then decreased slowly within 12 h. This decrease was more rapid than that in the presence of goethite, suggesting that the oxidation of Fe(II) by Cu(II) in the absence of goethite is more rapid than that in its presence. This may be due to the sorption of both Cu(II) and Fe(II) onto the goethite surface. Cu(II) has a high sorption affinity onto goethite (45). The added Cu(II) would sorb onto the surface of goethite, leading to a decrease in the dissolved concentration and oxidation capability of Cu(II). To elucidate the relationship of Cu(II) and Fe(II) concentrations on CT dechlorination, another independent experiment was performed. Various concentration of Cu(II) ranging from 0.1 to 4 mM were added to homogeneous solution containing 3 mM Fe(II) without goethite. The pH values of solutions were adjusted to pH 7 by using anoxic solution of NaOH under N_2 atmosphere. After 20 h of equilibrium, 20 μM of CT was injected to start the dechlorination reaction. Results showed that the k_{obs} for CT dechlorination increased linearly with increasing Cu(II) concentration. However, the k_{obs} decreased rapidly when the Cu(II) concentration was higher than 2 mM (Figure S2, Supporting Information). Also, the measured redox potentials increased from -320 to $+100$ mV when the Cu(II) concentrations increased from 0 to 4 mM. These results depict that Cu(II) has great effect on the dechlorination of CT when solutions contain large excess of Fe(II) and the low reactivity at high Cu(II) concentration may be due to the consumption of Fe(II) reductant and the decrease in pH.

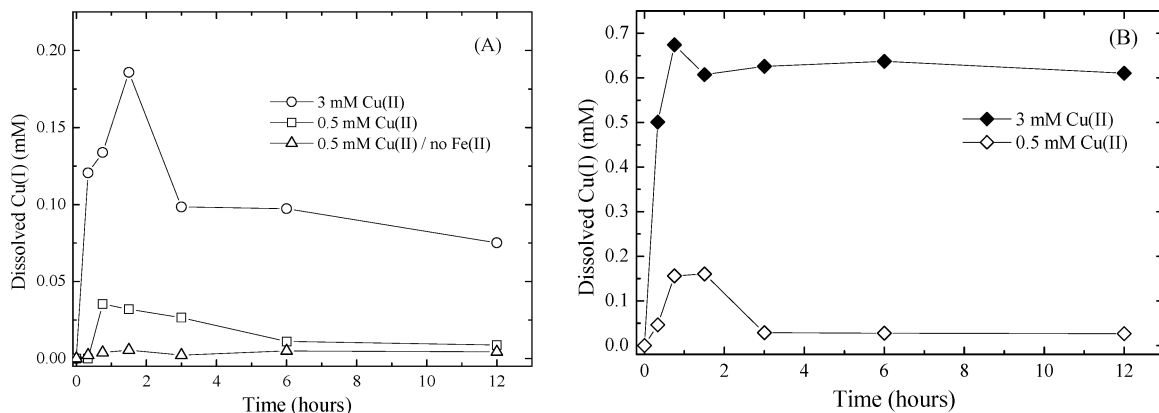


FIGURE 7. Concentration profile of dissolved Cu(I) at various concentrations of Cu(II) in (A) 3 mM Fe(II)-amended goethite ($25.6 \text{ m}^2 \text{ L}^{-1}$) suspension and (B) 3 mM Fe(II) solution.

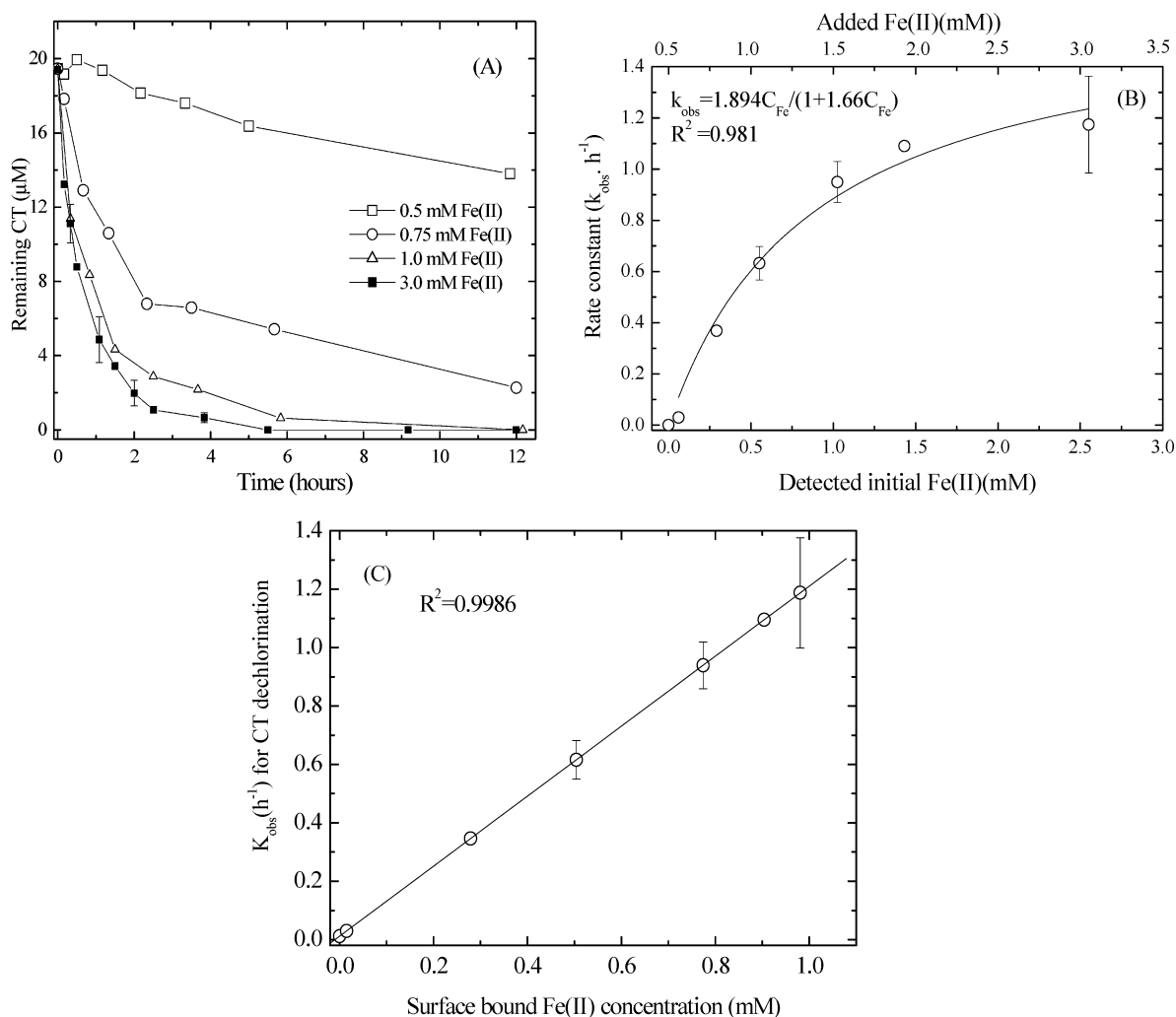


FIGURE 8. The effect of total Fe(II) for the dechlorination of CT in the goethite system with 0.5 mM Cu(II) and at neutral pH: (A) the concentration profile of CT, (B) the pseudo-first-order rate constant (k_{obs}), and (C) the relationship of surface-bound Fe(II) concentrations k_{obs} for CT dechlorination.

Figure 7 shows the dissolved aqueous Cu(I) concentration in the presence and absence of goethite. The Cu(I) concentration in the presence of goethite was lower than that without the addition of goethite, which is in good agreement with the concentration profile of Fe(II). To further understand the possibility of a freshly formed Cu(I) precipitate acting as an additional reductant, 3 mM Cu_2O was amended into the Fe(II)-goethite suspensions at pH 7. A nearly complete dechlorination of CT within 10 h was observed, which shows

that Cu_2O is an active reductant for the dechlorination of CT (data not shown). The k_{obs} for CT dechlorination was 5 times higher than that without Cu(I), proving that Cu(I) is an effective species for the dechlorination of CT.

Effect of Fe(II) on CT Dechlorination. The dechlorination rates of CT in the Fe(II)/Fe(III) suspensions were found to be influenced both by Cu(II) and Fe(II) concentrations. Therefore, various concentrations of Fe(II) were added into the goethite system containing 0.5 mM Cu(II) to understand

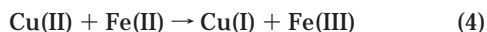
the influence of Fe(II) concentration on CT dechlorination. Figure 8 shows the degradation efficiency and the rate constant of CT with the amendment of various concentrations of Fe(II). The dechlorination efficiency of CT increased with increasing Fe(II) concentration. Only 27% of CT was dechlorinated within 12 h in the 0.5 mM Fe(II)-amended system, whereas a nearly complete degradation of CT was observed when the Fe(II) concentration was higher than 1 mM. Also, the k_{obs} for CT dechlorination increased from 0.029 h⁻¹ at 0.5 mM to 0.949 h⁻¹ at 1.5 mM and then leveled off to 1.175 h⁻¹ at 3.0 mM, reflecting that the addition of 1.5 mM of Fe(II) is sufficient for CT dechlorination in Fe(II)/goethite suspensions with 0.5 mM Cu(II).

Because the dechlorination of CT on a surface-bound Fe(II) system is a surface-mediated reaction, a Langmuir–Hinshelwood kinetics can be used to describe the relationship between the Fe(II) concentration and the reaction rate

$$k_{\text{obs}} = k_{\text{app}} \frac{K_{\text{Fe}} C_{\text{Fe}}}{1 + K_{\text{Fe}} C_{\text{Fe}}} \quad (3)$$

where k_{obs} is the rate constant of the dechlorination reaction, k_{app} is the apparent reaction rate constant, K_{Fe} is the equilibrium constant for the adsorption of Fe(II) to goethite, and C_{Fe} is the initial aqueous concentration of Fe(II). In this study, the added Fe(II) reacted with Cu(II), and the initial concentration of Fe(II) decreased before the injection of CT. Therefore, the measured Fe(II) concentrations were used as the initial aqueous concentration of Fe(II). A good fit between the Fe(II) concentration and the k_{obs} with k_{app} and K_{Fe} of 1.141 h⁻¹ and 1.66 mM⁻¹, respectively, was obtained ($r^2 = 0.981$, $n = 6$), which indicates that Fe(II) serves as the bulk reductant for CT dechlorination. Moreover, the rate constant (k_{obs}) for CT dechlorination was linearly correlated with the concentration of surface-bound Fe(II), showing that the sorption density of Fe(II) at the surface of iron oxide is a crucial factor when evaluating the transformation rate of CT by surface-bound Fe(II) species (16, 17).

Environmental Implication. Although the reductive dechlorination of chlorinated methanes by the surface-mediated Fe(II) species under anoxic conditions has been investigated for several years, the influence of transition metals on the dechlorination reaction under natural iron-reducing conditions is not well-understood. Copper species have been used as catalysts for dechlorination reactions in laboratory studies as well as in the pilot plants (46). Previous studies (39, 47, 48) have shown that the addition of Cu²⁺ greatly enhanced the dechlorination rate of CT and CF by green rust. The transformation of dichloroacetylene to chloroacetylene and then to acetylene in solutions containing cuprous chlorides (CuCl) was also observed at temperatures of 67–87 °C (30). Recently, Chien et al. (49) observed that CT degradation was catalyzed by Cu(II) at temperatures higher than 300 °C. In the present study, we demonstrate that the addition of Cu(II) in concentrations of 0.1–0.5 mM can significantly enhance the dechlorination efficiency and the rate of CT by surface-bound Fe(II) species in goethite suspensions at pH 7. Fe(II) serves as a reductant and reacts with the available Cu(II) to form Cu(I). Moreover, Cu(I) may also be reoxidized to Cu(II) by providing electrons to CT. Therefore, copper species may act as the electron mediator in the surface-bound iron system.



Unlike the structural Fe(II) present in certain minerals such as green rust and magnetite, the high reactivity of Fe(II) bound iron oxide species can be maintained over long periods

of time, because such Fe(II) species may constantly be regenerated, either by the sorption of Fe(II) from aqueous solution or the microbial Fe(III) oxide reduction (12, 16, 33). Therefore, surface-bound Fe(II) species are thought to be one of the promising materials that can be used for long-term application to the remediation of groundwater contaminated with chlorinated hydrocarbons (16). Cu(II) is a common environmental pollutant in contaminated aquifers and wastewater. In contaminated aquifers where metal ions and chlorinated solvents coexist, surface-bound iron species can sorb Cu(II) first and then convert to Cu(I) using Fe(II). This process significantly accelerates the dechlorination rate of chlorinated hydrocarbons and gives great impetus to the coupled degradation of heavy metals and chlorinated hydrocarbons under anoxic conditions. In conclusion, our results clearly show the influence of Cu(II) on the dechlorination of chlorinated methanes by surface-bound Fe(II) species in goethite suspensions. Although the concentrations of Cu(II) used in this study were higher than those naturally available Cu(II), results shown in this study will be helpful in facilitating the development of processes that could be useful for the coupled degradation of mixed contaminants and the detoxification of chlorinated solvents and metal ions.

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Supporting Information Available

XRD patterns of the synthesized goethite (Figure S1) and the rate constant for CT dechlorination as a function of Cu(II) concentration in solutions containing 3 mM Fe(II) with and without the pH adjustment (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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