Enhanced Dechlorination of Chlorinated Methanes and Ethenes by Chloride Green Rust in the Presence of Copper(II)

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The enhanced removal of carbon tetrachloride (CCl$_4$), tetrachloroethene (C$_2$Cl$_4$), and trichloroethene (C$_2$HCl$_3$) by chloride green rust (GR(Cl)) in the presence of copper ions was investigated. X-ray powder diffraction (XRPD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the crystallization and chemical speciation, respectively, of the secondary mineral phases produced in the GR(Cl)–Cu(II) system. The addition of Cu(II) to GR(Cl) suspensions resulted in enhanced dechlorination of the chlorinated hydrocarbons examined in this study. The degradation reactions followed pseudo-first-order kinetics and the pseudo-first-order rate constant (k_{obs}) for CCl$_4$ (20 μM) removal by GR(Cl) at pH 7.2 was 0.0808 h^{-1}. Addition of 0.5 mM Cu(II) completely dechlorinated CCl$_4$ within 35 min, and the k_{obs} was 84 times greater than that in the absence of Cu(II). Chloroform (CHCl$_3$), the major chlorinated product in CCl$_4$ dechlorination, accumulated at a concentration up to 13 μM in the GR(Cl) system alone, but was completely dechlorinated within 9 h in the GR(Cl)–Cu(II) suspension. Also, rapid removal of C$_2$Cl$_4$ and C$_2$HCl$_3$ by GR(Cl) was observed when Cu(II) was added. The k_{obs} values for the removal of chlorinated ethenes were 4.7–7 times higher than that obtained in the absence of Cu(II). In addition, the k_{obs} for PCE removal increased linearly with respect to Cu(II) concentrations in the range from 0.1 to 1.0 mM. Addition of Cu(II) at a concentration higher than 1.0 mM decreased the k_{obs} for the removal of both C$_2$Cl$_4$ and C$_2$HCl$_3$ due to the decrease in structural Fe(II) concentration in GR(Cl) and the changes in redox potentials and pH values. Moreover, the highest removal efficiency and rate of C$_2$Cl$_4$ was obtained at near-neutral pH when Cu(II) was added into the GR(Cl) suspension. XPS and XRPD results showed that the Fe(II) in the GR(Cl) suspension could reduce Cu(II) to both Cu(I) and metallic Cu. These findings are relevant to the better understanding of the role of abiotic removal of chlorinated hydrocarbons during remediation and/or natural attenuation in iron-reducing environments.

Introduction

The reduction of environmentally hazardous chemicals by ferrous ions has recently received great attention as a potential means for natural attenuation. Surface-bound Fe(II) species have been reported to be more reactive compared to dissolved Fe(II) species. Moreover, mixed-valence iron minerals such as magnetite and green rust (GR) also contain a large portion of Fe(II) in their structures (*1*) and may contribute to the natural attenuation and treatment of reducible contaminants in soil and groundwater. Green rust is a double-layered hydroxide built upon Fe(OH)$_2$-like sheets that have anionic interlayers (*2–4*). The characteristics of GR depend on the type of anion present within these interlayers. According to the interlayer anion, GR can be divided into two types: type I contains halogen ions (e.g., Cl$^-$) or planar molecules (e.g., CO$_3^{2-}$), whereas type II contains three-dimensional molecules (e.g., SO$_4^{2-}$) (*5–7*). GR(Cl) is usually rhombic, and GR(SO$_4$) and GR(CO$_3$) are hexagonal in their crystal shapes. However, McGill et al. (*3, 4*) also observed the formation of hexagonal GR(Cl) by corrosion of cast iron in water containing NaCl, K$_2$SO$_4$, and Na$_2$CO$_3$ under various degrees of aeration. This compound is remarkably stable and coexists with magnetite and γ-FeOOH.

Laboratory experimental results suggest that GRs are naturally produced by both abiotic and biotic reactions under alkaline and neutral suboxic conditions. Abiotically, GRs are identified as intermediates in the formation of iron oxides during the oxidation of iron(II) under neutral and weakly alkaline conditions (*8*) and the transformation of poorly crystalline hydrous ferric oxides by Fe(II) sorption (*8–10*). Biological formation of GR has been observed in microbial oxidation of Fe(II) (*11, 12*) and in the reduction of Fe(III) minerals by dissimilatory iron-reducing bacteria (DIRB) (*13–17*). The frequent availability of GRs in anoxic hydromorphic soils, where DIRB are among the most metabolically active bacterial species, is direct evidence of GR formation by biological Fe(III) reduction (*5, 18*). GR is also formed in both microbial- and abiotic-induced corrosion processes of steels (*7, 19*). Depending on the environmental conditions, such as the pH, the availability and concentration of anions or cations, and the oxidation conditions, GR can be further oxidized to other minerals (*20*); magnetite (Fe$_3$O$_4$) is usually found as the major oxidation product of GR under suboxic condition at near-neutral or alkaline pH (*3, 17*).

GRs are potentially strong sorbents because of their interlayer regions, which hold and exchange anions. GRs also have been reported to reduce cations, such as U(VI) (*21*), and anions, such as Se(VI) (*22, 23*), Cr(VI) (*24, 25*), and nitrate (*9, 26*). Owing to the possible availability of GR in natural environments (*18, 27, 28*) and its strong reduction potential, GRs have been used as natural reductants in laboratory studies to reduce different classes of chemical compounds, such as chlorinated methanes (*29, 30*), chlorinated ethanes (*31*), chloronitrobenzene (*32*), and chlorinated ethenes (*33, 34*). In contrast to the surface-bound Fe(II) species, GRs have the ability to dechlorinate both chlorinated methanes and ethenes and to produce low concentrations of their chlorinated intermediates (*34*). Recently, O'Loughlin et al. (*30, 31*) reported that chlorinated methanes and ethanes can be effectively dechlorinated by GR(SO$_4$) in the presence of transition metal ions including Ag(I), Au(III), Cu(II), and Hg(II). A possible mechanism for the dechlorination of CCl$_4$ in the presence of metal ions was also proposed. Presumably, the dechlorination mediated by GR(SO$_4$) was much faster and produced lower amounts of chlorinated products when it occurred in the presence of metal ions because of the formation of nanosized zerovalent metal particles (*30*). This finding suggests that GR may be one of the most promising materials for the engineered remediation of chlorinated compounds and heavy metals. However, the effects of

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environmental conditions on the removal of chlorinated hydrocarbon by GR in the presence of metal ions have received less attention. Refait et al. (7) reported that GR(Cl) was formed in the aqueous corrosion of iron metals in the presence of chloride ions. During the removal of chlorinated compounds by zerovalent iron, the release of chloride ion could promote the formation of GR(Cl). However, most studies have focused only on the reactivity of GR(SO_4) for the removal. Although GR(Cl) has been used for the reduction of other inorganic species such as Cr(VI) (24) and nitrate (26), the reactivity of GR(Cl) has not been studied for dechlorination processes.

In this study, the reactivity of GR(Cl) for the reduction of chlorinated methanes and ethenes including carbon tetrachloride (CCl_4), trichloroethylene (C_2HCl_3), and tetrachloroethylene (C_2Cl_4) with the addition of Cu(II) ion was investigated. The effects of environmental parameters including the pH and the concentrations of GR(Cl) and Cu(II) on the removal rate and efficiency of target compounds were also studied. Control experiments in the absence of GR were performed to assess the magnitude of the loss of chlorinated hydrocarbons due to volatilization and sorption. X-ray powder diffraction (XRPD) and X-ray photoelectron spectroscopy (XPS) were used to identify the crystalline properties and the changes in the chemical species in the solid phase of the GR(Cl) suspensions. In addition, the changes in morphologies of the solids were examined by transmission electron microscopy (TEM).

Materials and Methods

Chemicals. The following chemicals were used as received without further treatment. Carbon tetrachloride (CCl_4, >99.8%, GC grade), chloroform ($CHCl_3$, > 99.8%, GC grade), $CuCl_2 \cdot 2H_2O$, and tris(hydroxymethyl)aminomethane (Tris buffer) were purchased from Merck Co. (Darmstadt, Germany). Trichloroethylene (C_2HCl_3, >99.8%, GC grade), tetrachloroethylene (C_2Cl_4, >99.8%, GC grade), $FeCl_2 \cdot 4H_2O$ (99%), N-(2-hydroxyethyl)piperazine-N-2-ethanosulfonic acid (HEPES, 99.5%), 2-(N-morpholine)ethanosulfonic acid (MES, >99.5%), hydrochloric acid (HCl) (37%), and sodium hydroxide (NaOH, >98%) were obtained from Sigma-Aldrich Co. (Milwaukee, WI). Bathocuproinedisulfonic acid disodium salt ($C_{26}H_{18}N_2Na_2O_6S_2$, 90%) was purchased from Fluka (Buchs, Switzerland). All chemical solutions were prepared with high-purity deoxygenated deionized water (Millipore, 18.3 Ω cm) using a vacuum and a N_2 (>99.9995%) purging system (35−38).

Synthesis and Characterization of GR(Cl). GR(Cl) was synthesized by partial oxidation of ferrous chloride solution at neutral pH (1). Briefly, $FeCl_2 \cdot 4H_2O$ (49.7 g) was dissolved in 1 L of deionized water with magnetic stirring under ambient conditions. After the complete dissolution of the ferrous salt, 1 M NaOH was added to the solution dropwise through a stopcock funnel until the pH was maintained at 7.0. The suspension of the dark blue-green precipitate was then transferred into a 1-L screw-capped bottle. The bottle was vacuumed (6.7 Pa) for 30 min and then purge with N_2 for 15 min. This process was repeated at least five times while the suspension stirred continuously. The suspension was maintained under anoxic conditions for 1 week and the pH was adjusted to 7.0 by the use of a NaOH solution. Once the pH was stable, 50-mL aliquots of the suspension were transferred from the sealed bottle into a centrifuge tube using a 100-mL N_2-purged plastic syringe. The supernatant was removed by centrifugation at 7000g for 10 min under N_2 atmosphere. The pellets in the centrifuge tubes were washed five times using deoxygenated deionized water to remove the residual Fe(II) in the solution. After washing, the GR(Cl) suspension was transferred anaerobically into a 500-mL serum bottle under a N_2 purge. The bottle was

capped with a rubber septum followed by vacuuming and N_2 purging for several times before being stored under a N_2 atmosphere.

The Fe(II)/Fe(III) ratio of the prepared solids was determined to quantify the concentration of chloride GR. The dissolved and HCl-extractable Fe(II) concentrations were determined using the ferrozine method (35−38). The total iron concentration in the GR(Cl) suspension was also determined by adding 10% hydroxylamine solution to reduce Fe(III) to Fe(II) (34). The concentration of Fe(III) was calculated by the difference in HCl-extractable Fe(II) concentration of the suspension before and after the reduction. The dissolved and HCl-extractable Fe(II) concentrations were 3.8 and 16.7 mM, respectively, which implies that the Fe(II) concentration in the GR(Cl) suspension was 12.9 mM. After reducing the Fe(III) in the suspension, the HCl-extractable Fe(II) concentration was 20.7 mM. Since the solubility of Fe(III) is quite low at neutral pH, the Fe(III) concentration in GR(Cl) was calculated to be 4.0 mM. Therefore, the molar ratio of Fe(II)/Fe(III) in GR(Cl) is 3.2, which is in a good agreement with the reported value of 3 (28).

Reduction Experiments. The degradation of chlorinated hydrocarbons by GR(Cl) was studied under anoxic conditions by using 70-mL serum bottles containing 50 mL of deoxygenated buffer solutions. Anoxic solutions were prepared by purging with N_2 (99.9995%) at a flow rate of 42 L min^{-1} in vacuum-sealed bottles. This process was repeated four or five times to remove trace amounts of oxygen in solution (35, 36). An aliquot of GR(Cl) from the stock suspension (1 mL) was delivered into the serum bottle through a N_2-purged plastic syringe. The stock solution of Cu(II) (50 mM) was prepared by dissolving $CuCl_2$ in deoxygenated deionized water in sealed serum bottles. The concentration effect of GR(Cl) was examined by introducing various volumes of GR(Cl) stock suspensions (0.25−4 mL) and 0.5 mL Cu(II) stock solution into the deoxygenated buffer solutions to obtain final concentrations ranging between 0.37 and 9 g of GR(Cl) L^{-1}. For the experiments examining pH effects, 50 mM MES solutions were used for pH 5.5 and 6.0, HEPES buffer was selected to maintain the pH at 7.2 and 8.0, and Tris buffer was used for pH 9. All of the serum bottles were sealed with Teflon-lined rubber septa and aluminum crimp caps. The total liquid volumes were maintained at 50 mL, resulting in a 20-mL headspace for headspace analysis. The headspace of the bottles was maintained under anoxic conditions by filling with a mixture of N_2 and Ar (80/20, v/v). After equilibrating for 20 h, an aliquot of a stock solution of a target compound (CCl_4, C_2HCl_3, or C_2Cl_4) dissolved in degassed methanol was injected into the serum bottle using a gastight glass syringe. Serum bottles were then incubated at 25 ± 1 °C in the dark using an orbital shaker at 150 rpm. Control experiments were also performed by using 50 mL of buffer solution only. All experiments were run in duplicate or triplicate.

Analytical Methods. The headspace analytical technique was used for the determination of chlorinated and non-chlorinated hydrocarbons. The concentrations of CCl_4 and the byproducts in the headspace of the test bottles were monitored by withdrawing 50 μL of gas in the headspace using a 100-μL gastight syringe. For C_2Cl_4 and C_2HCl_3 analyses, 60 μL of headspace gas was withdrawn. The headspace sample was immediately injected into a gas chromatograph (GC) equipped with an electron capture detector (ECD) and a flame ionization detector (FID) (Perkin-Elmer, Autosystem, Norwark, CT). A 60-m VOCOL fused-silica megabore capillary column (0.545 mm × 3.0 μm, Supelco Co.) was used to separate the organic compounds, and the column was connected to both the ECD and FID simultaneously through a Y-splitter. The column temperature was maintained at 90 °C and N_2 was used as the carrier gas. The injector
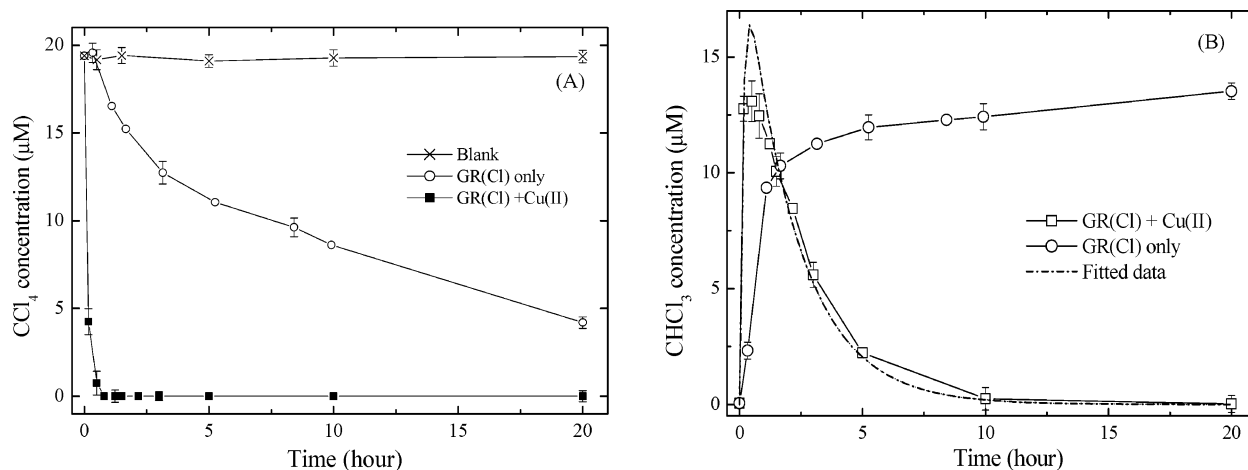
FIGURE 1. (a) Dechlorination of 20 μM carbon tetrachloride (CCl$_4$) by (GR(Cl)) (1.5 g L^{-1}) and (b) the production of chloroform (CHCl$_3$) at pH 7.2 in the presence and absence of 0.5 mM Cu(II).

temperature was 250 °C, and the temperatures of the ECD and FID were maintained at 350 and 250 °C, respectively. The relative standard deviations of ECD analyses were within 10% and those for FID analyses were within 5%. Control samples were also used to check the possible leakage of target compounds during the incubation process. 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.

Mineral phases were characterized by XRPD by using an X-ray diffractometer (Regaku D/max-II B) with a Cu Kα radiation source ($\lambda = 1.54056$ Å) operating at 30 kV voltage and 20 mA current. The precipitates in the serum bottles were left to settle after the termination of reaction, and the supernatants were removed carefully from the sealed bottles using a N$_2$-purged syringe. The solid phase remaining in the bottle was dried with a stream of N$_2$ gas (Figure S1, Supporting Information). After drying the precipitate, samples were mounted on a glass sample holder using small amounts of grease. A drop of glycerol was added immediately on the mounted powder layer to minimize the reaction with oxygen. The scan range for all samples was between 5 and 90° (2θ) at a scanning speed of 4° min^{-1}. Samples for transmission electron microscopy (TEM) analyses of the morphology of the solid phase in the GR(Cl)−Cu(II) suspension were prepared in the same way as they were for the XRD studies. The XPS measurements were performed by an ESCA PHI 1600 photoelectron spectrometer (Physical Electronics, Eden Prairie, MN) using Al Kα X-ray source (1486.6 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 (*35*).

Concentrations of HCl-extractable Fe(II) in the serum bottles were monitored by withdrawing 0.5 mL of the suspensions using N$_2$-purged syringes, and aliquots were immediately acidified with 1 mL of 1 M HCl. The acidified samples were centrifuged at 10 000g for 10 min to remove particles, and the Fe(II) contents were determined by the ferrozine method at 562 nm using a UV−visible spectrophotometer (Hitachi, U3010). 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. After dissolving GR(Cl) in 1M HCl, the total concentration of iron species in the HCl-extractable fraction was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer, Optima 3000XL). The sorbed

Fe(II) was calculated from the difference between the acid extractable and dissolved concentrations of Fe(II).

The concentration of extractable Cu(I) was determined using the bathocuproinedisulfonic acid method with minor modifications (*39*). A 1-mL aliquot was withdrawn by a 1-mL N$_2$-purged plastic syringe and immediately added into the mixture containing 1 mL of 10% tartrate solution and 0.5 mL of 1% bathocuproinedisulfonic acid solution. After 30 min of reaction, the mixture was centrifuged at 10 000g for 5 min. The Cu(I) concentration in the supernatant was then determined by the colorimetric method at 483 nm. Standard solutions of Cu(I) were prepared using 10% hydroxylamine as a reductant to reduce the CuCl$_2$ solutions.

When the reactions were terminated, the pH and oxidation−reduction potentials (ORP) in the bottles were measured after opening bottles under a gentle purge of N$_2$ at 25 °C. The pH and ORP were measured using a Microprocessor pH meter equipped with a pH electrode and an ORP combination electrode, respectively.

Results and Discussion

Reduction of Chlorinated Methanes by GR(Cl). Figure 1 shows the removal of CCl$_4$ by GR(Cl) suspensions in the presence and absence of 0.5 mM Cu(II) and the production of CHCl$_3$ at pH 7.2. Approximately 80% of the initial CCl$_4$ was removed by GR(Cl) within 20 h in the absence of Cu(II). Chloroform (CHCl$_3$) was identified as the major product of CCl$_4$ dechlorination and the maximum detected CHCl$_3$ concentration was 13.5 μM after 20 h of incubation. In addition, the CCl$_4$ concentrations in the control sample were in the range of 19.2−19.4 μM, showing that the possible leakage of CCl$_4$ during the experimental course can be neglected.

The addition of Cu(II) greatly enhanced the removal of CCl$_4$. Nearly complete removal of CCl$_4$ by GR(Cl) suspensions was observed within 35 min when 0.5 mM Cu(II) was added to the system. The maximum CHCl$_3$ concentration of 13 μM was observed after 30 min, with complete degradation of CHCl$_3$ after 10 h of incubation. However, no chlorinated product in the headspace was detected using GC-ECD analysis, presumably due to the formation of only nonchlorinated products. To further understand the distribution of final products, another independent experiment using high concentrations of chlorinated hydrocarbons (65−70 μM) was performed. Table 1 shows the product distribution and carbon recovery of CCl$_4$, C$_2$Cl$_4$, and C$_2$HCl$_3$ by GR(Cl) in the presence and absence Cu(II). In the absence of Cu(II), the carbon recovery of CCl$_4$ was 78.1% with CHCl$_3$ as the major

TABLE 1. Comparison of the Product Distribution and Carbon Recovery of CCl₄, C₂Cl₄, and C₂HCl₃ Dechlorination by GR(Cl) in the Presence and Absence Cu(II)[a,b]

target compds	products	GR(Cl) alone reported value	GR(Cl) alone this study	GR(Cl) with Cu(II) reported value	GR(Cl) with Cu(II) this study
CCl_4	CCl_4	17.0[c]	3.3	nd[c]	nd
	$CHCl_3$	45.00[c]	65.5	nd[c]	nd
	CH_4	4.0[c]	8.7	26.0[c]	24.0
	C_2H_4	nd[c]	nd	4.0[c]	7.8
	C_2H_6	nd[c]	0.6	1.0[c]	1.4
	total carbon recovery		78.1		33.2
C_2Cl_4	C_2Cl_4	64.7[d]	66.6		12.4
	C_2HCl_3	nd[d]	9.6		16.6
	C_2H_2	5.1	nd		nd
	C_2H_4	0.7[d]	0.6		31.9
	C_2H_6	nd[d]	0.1		0.1
	total carbon recovery		76.9		61
C_2HCl_3	C_2HCl_3	60.0[d]	79.0		51.0
	C_2H_4	1.2[d]	0.2		11.0
	C_2H_6	nd[d]	0.1		1.0
	total carbon recovery		79.3		63.0

[a] nd = not determined. [b] The incubation time was 20 d for CCl₄ and 35 d for C₂Cl₄ and C₂HCl₃. [c] See ref 30. [d] See ref 33.

product (65.5%). However, only 33.2% of carbon was recovered after 20 d when 0.5 mM Cu(II) was added to the suspensions. This low carbon recovery may be due to the formation of nonchlorinated compounds that cannot be detected by the headspace method coupled with GC-FID. A recent study (30) showed that carbon monoxide, methane, ethane, and ethylene were the final products of CCl₄ dechlorination by GR amended with Cu(II). In addition, a previous study showed that CCl₄ could be transformed to carbon monoxide (CO) and formate (HCOO⁻) via reductive hydrolysis (32). These results indicate that the reduction of chlorinated methanes by GR(Cl) in the presence of Cu(II) involves other processes in addition to reductive dechlorination, and the loss of CCl₄ may be due to the formation of formate and carbon monoxide.

The removal of the chlorinated methanes by sequential reductive dechlorination can be described as follows (40):

$$\frac{dC_A}{dt} = -k_1 Fe(II)_{GR} C_A \tag{1}$$

$$\frac{dC_B}{dt} = k_1 Fe(II)_{GR} C_A - k_2 Fe(II)_{GR} C_B \tag{2}$$

where C_A and C_B are the concentrations of CCl₄ and CHCl₃, respectively, k is the reaction rate constant, and $Fe(II)_{GR}$ is the Fe(II) concentration in GR(Cl). For a high initial concentration of Fe(II) in GR(Cl) (12.9 mM), eqs 1 and 2 can be treated as a pseudo-first-order reaction:

$$C_A = C_A^0 e^{-k_{obsA} t} \tag{3}$$

$$C_B = k_{obsA} C_A^0 / k_{obsB} - k_{obsA}(e^{-k_{obsA} t} - e^{-k_{obsB} t}) + C_B^0 e^{-k_{obsB} t} \tag{4}$$

where k_{obs} is the pseudo-first-order rate constant ($k_{obs} = kFe(II)_{GR}$), C_A^0 and C_B^0 are the initial concentrations of CCl₄ and CHCl₃, respectively, and t is time. A good linear relationship between $\ln(C_A/C_A^0)$ and time (t) was observed. The k_{obs} for CCl₄ reduction was 0.0808 ± 0.0047 h⁻¹ (($2.24 \pm 0.13) \times 10^{-5}$ s⁻¹), which agrees with the reported values for GR(SO₄) that fall in the range between 0.47×10^{-5} and 2.18

$\times 10^{-5}$ s⁻¹ (29, 30). When 0.5 mM Cu(II) was added, the k_{obs} for CCl₄ reduction was 6.779 ± 0.644 h⁻¹ (($1.88 \pm 0.18) \times 10^{-3}$ s⁻¹), which was 84 times higher than that for the GR(Cl) system alone. Moreover, the rate constant for CHCl₃ reduction by GR(Cl) in the presence of 0.5 mM Cu(II) is calculated to be 0.471 h⁻¹, which is much slower than that for CCl₄ removal.

Reduction of Chlorinated Ethenes by GR(Cl). Figure 2 shows the removal of 18 μM C₂Cl₄ by the GR(Cl) suspension at pH 7.2 in the absence and presence of Cu(II) ions. C₂Cl₄ was dechlorinated rapidly during the first 12 d and then a slow removal was observed. In the suspensions without addition of Cu(II), a removal efficiency of 33% for C₂Cl₄ removal was observed after the incubation of 40 d. The k_{obs} for C₂Cl₄ reduction during the first 12 d was 0.0182 ± 0.0013 d⁻¹. Similar to the degradation of CCl₄ by GR(Cl), the removal efficiency and rate of C₂Cl₄ were both enhanced significantly when Cu(II) ions were added to the mixture. Within 40 d, 89% of the initial C₂Cl₄ was removed in the GR(Cl) suspension with the addition of 0.5 mM Cu(II). The reduction followed pseudo-first-order kinetics, and the k_{obs} for PCE removal was 0.0735 ± 0.0095 d⁻¹. The product distribution shown in Table 1 shows that C₂HCl₃ was the major chlorinated byproduct, and reductive dechlorination could be the major pathway for C₂Cl₄ dechlorination in the absence of Cu(II). Also, trace amounts of ethene (0.6%) and ethane (0.1%) were identified as the end products for C₂Cl₄ dechlorination after 35 d of incubation. Lee and Batchelor (33) used GR(SO₄) to dechlorinate C₂Cl₄ in batch reactors under anaerobic conditions. Acethylene (C₂H₂) and ethene (C₂H₄) were found as the major end products, while no C₂HCl₃ was detected in their study. The carbon recovery was 70.5%, which is in good agreement with our results (76.9%). In the presence of 0.5 mM Cu(II), however, the maximal concentration of C₂HCl₃ at 4.75 μM was observed after 12 d followed by a gradual decrease to 2.75 μM after an incubation of 40 d. Ethene (31.9%) and ethane (0.1%) were found to be the end products. These results indicate that Cu(II)−GR(Cl) is a good reducing agent for the dechlorination of chlorinated methanes in engineered systems. In addition, Cu(II)-amended GR(Cl) system significantly accelerated the dechlorination of chlorinated ethenes when compared to the system containing GR(Cl) alone.

Concentration Effect of GR(Cl) on C₂Cl₄ Reduction. Because the structural Fe(II) in GR(Cl) plays a pivotal role in the reduction of chlorinated hydrocarbons, the effect of GR-(Cl) concentration on the removal of C₂Cl₄ was studied. The concentrations of GR(Cl) were in the range of 0.37−9 g L⁻¹. Moreover, the effect of GR(Cl) concentration on the removal of C₂Cl₄ in Cu(II)-amended suspension was also studied. In the absence of Cu(II), the removal efficiency of C₂Cl₄ increased slightly upon increasing GR(Cl) concentration, and only 18−21% of the initial C₂Cl₄ was removed after 66 d (Figure S2, Supporting Information). In contrast, the removal efficiency increased from 17% at 0.37 g of GR(Cl) L⁻¹ to 92% at 9 g of GR(Cl) L⁻¹ when 0.5 mM Cu(II) was added. Figure 3 shows the k_{obs} for C₂Cl₄ reduction as a function of GR(Cl) concentration. With the addition of Cu(II), the k_{obs} for PCE removal increased rapidly from 0.003 d⁻¹ at 0.37 g of GR(Cl) L⁻¹ to 0.0712 ± 0.0103 d⁻¹ at 1.5 g of GR(Cl) L⁻¹ and then leveled off to 0.0761 ± 0.0023 d⁻¹ at 9 g of GR(Cl) L⁻¹. Similar relationships between GR(Cl) concentration and rate constant were observed for GR(Cl) suspensions in the absence of Cu(II). It is noted that these reaction rate constants with respect to GR(Cl) concentration plateau quite quickly, which indicates that low concentrations of GR can significantly enhance the removal efficiency of C₂Cl₄. O'Loughlin et al. (30) first reported that addition of Cu(II) into GR(SO₄) formed zerovalent Cu particles and suggested that the enhanced dechlorination of chlorinated methanes in Cu(II)-amended GR(SO₄) suspension was due to the galvanic activity between
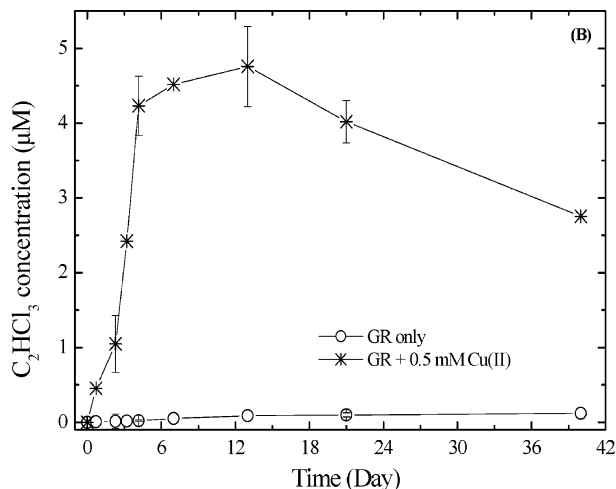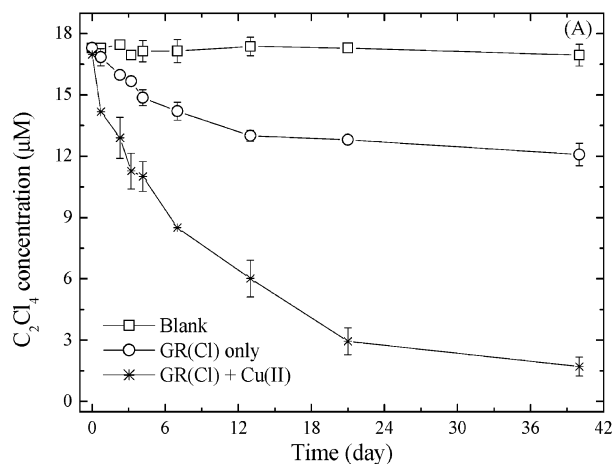
FIGURE 2. Dechlorination of C_2Cl_4 (17.8 μM) by GR(Cl) (1.5 g L^{-1}) in the presence and absence of 0.5 mM Cu(II). The pH of the system was maintained at 7.2 by using 50 mM HEPES. (a) C_2Cl_4 concentration profile. (b) The formation of C_2HCl_3 as the major chlorinated product.
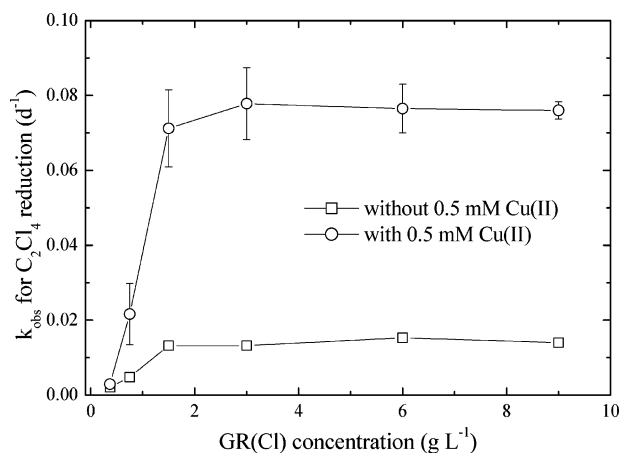

FIGURE 3. The k_{obs} for C_2Cl_4 removal as a function of GR(Cl) concentration in the presence and absence of 0.5 mM Cu(II) at pH 7.2.

GR(SO$_4$) and zerovalent Cu particles. Previous studies also depicted that the Cu(II) could be reduced to Cu(I) by the oxidation of Fe(II) and subsequently enhanced the dechlorination rate of CCl$_4$ (35, 36). In addition, Fe(II) concentration is a crucial parameter influencing the reduction rate of chlorinated methanes, and the dechlorination rate of CCl$_4$ increases with increasing surface-bound Fe(II) concentration in the Fe(II)-amended goethite suspensions (35). These results suggest that the added Cu(II) can be reduced to the catalytic Cu(I) or Cu(0) ion by the structural Fe(II) in GR(Cl) and then accelerates the rate and efficiency of C$_2$Cl$_4$ removal. Also, high concentrations of GR(Cl) provide higher amount of Fe(II) as bulk reductant to accelerate the reduction of C$_2$Cl$_4$. To further understand the role of Cu(II) in the removal efficiency and reaction mechanism, the concentration effect of Cu(II) on C$_2$HCl$_3$ or C$_2$Cl$_4$ reduction by GR(Cl) was examined.

Effect of Cu(II) Concentration. Figure 4 shows the reduction of chlorinated ethenes (C$_2$HCl$_3$ and C$_2$Cl$_4$) by GR(Cl) at pH 7.2 in the presence of various concentrations of Cu(II). No obvious decrease in C$_2$HCl$_3$ was observed in the control experiments without the addition of GR(Cl), which implies that possible leakage of C$_2$HCl$_3$ due to volatilization and sorption during the incubation period can be neglected (Figure 4a). Addition of GR(Cl) alone slightly increased the removal efficiency of C$_2$HCl$_3$ and only 18% of the initial C$_2$HCl$_3$ concentration was removed within 35 d. With the addition of Cu(II), however, the removal efficiency and rate of C$_2$HCl$_3$ increased significantly. After incubation for 35 d,

the removal efficiency of C$_2$HCl$_3$ by GR(Cl) increased from 50% at 0.5 mM Cu(II) to 62% at 1 mM Cu(II). A linear relationship between the k_{obs} and the concentration of added Cu(II) ranging between 0 and 1.0 mM was observed (Figure S3, Supporting Information). The removal efficiency and rate of C$_2$HCl$_3$ decreased as the Cu(II) concentration further increased to 2 mM, which clearly indicates that the addition of high concentrations of Cu(II) inhibits the reduction of C$_2$HCl$_3$ by GR(Cl).

The relationship between the Cu(II) concentration and the removal ability of GR(Cl) was further investigated over a wide Cu(II) concentration range of 0.1−5 mM by using C$_2$Cl$_4$ as the target compound. In addition, a relative high concentration (3 g L^{-1}) of GR(Cl) was used. Similar to that of C$_2$HCl$_3$, the removal efficiency of C$_2$Cl$_4$ increased from 41% at 0.2 mM to 92% at 1 mM within 40 d (Figure 4b). Further increase in Cu(II) concentration decreased the rate and efficiency of C$_2$Cl$_4$ removal. The k_{obs} was proportional to the Cu(II) concentration and increased linearly from 0.0184 d^{-1} in the absence of Cu(II) to 0.139 d^{-1} at 1 mM Cu(II) (R^2 = 0.949, $n = 7$) (Figure S4, Supporting Information). The oxidation of Fe(II) to Fe(III) in GR(Cl) suspension and the decrease in pH of the system may be the possible reasons for the decrease in rate constants after addition of a high concentration of Cu(II). A previous study (35) demonstrated that Cu(II) can react with Fe(II) to form ferrihydrite (Fe$_5$HO$_8$·4H$_2$O) and cuprous oxide (Cu$_2$O) in the Fe(II)−goethite suspensions. Also, 4 mol of proton is released into the solution to decrease the solution pH. It can be postulated that the addition of Cu(II) into the GR(Cl) suspensions decreases the reducing capacity of GR(Cl) due to the decrease in Fe(II) concentration and pH. Therefore, the changes in concentration and chemical species of metal ions and the effect of pH on the removal of chlorinated hydrocarbons were further examined.

Table 2 illustrates the concentrations of total Fe(II) and Cu(I) in the GR(Cl) systems upon the addition of various concentrations of Cu(II). The total Fe(II) concentrations decreased upon increasing the Cu(II) concentration, suggesting that Fe(II) was oxidized to Fe(III) by Cu(II). It is noted that a slight decrease in Fe(II) concentration (1.0 mM) occurred in the absence of Cu(II), presumably due to the oxidation of GR(Cl) at neutral pH under strictly anaerobic condition (32). In addition, the Cu(I) concentration increased substantially from 0.07 mM at 0.1 mM Cu(II) to 0.19 mM at 1 mM Cu(II) and then leveled off to 0.25 mM when the Cu(II) concentration was further increased to 5 mM. However, the yield of Cu(I) decreased with the addition of increasing
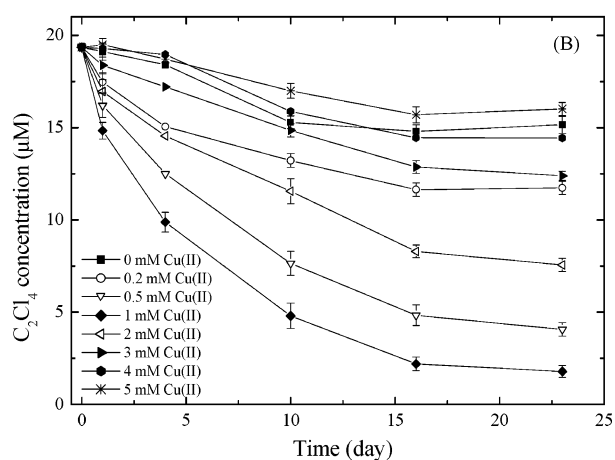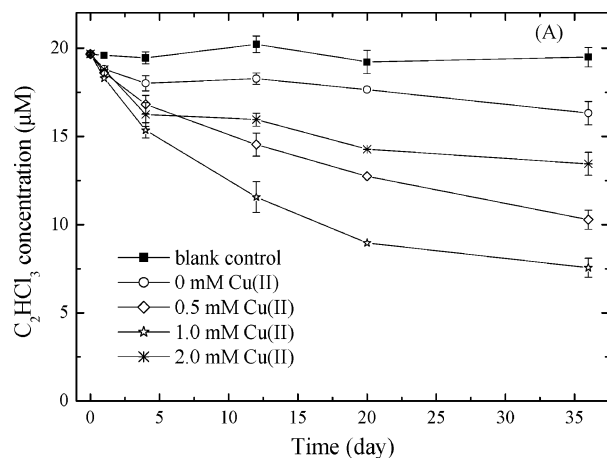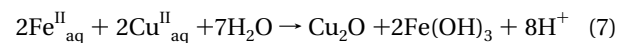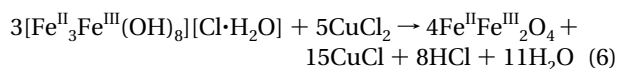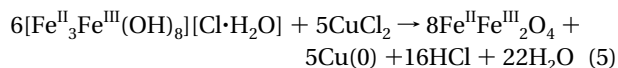
FIGURE 4. Effects of Cu(II) concentration on the removal of (a) C_2HCl_3 and (b) C_2Cl_4 at pH 7.2 in the GR(Cl) suspension systems.

TABLE 2. Total Fe(II) Concentrations and Extractable Cu(I) Concentration in GR Suspension (3 g L^{-1}) at Various Concentrations of Cu(II) after the Equilibrium of 30 h

| added Cu(II) concn (mM) | total Fe(II) concentration (mM) | | | extractable Cu(I) concn (mM) |
	initial	after 30 h	decreased amount	
0	15.9	14.9	1.0	0
0.1	15.9	14.7	1.2	0.069
0.2	15.9	14.8	1.1	0.11
0.3	15.9	14.6	1.3	0.091
0.4	15.9	14.4	1.5	0.13
0.5	15.9	14.1	1.8	0.13
1.0	15.9	13.5	2.3	0.18
2.0	15.9	13.1	2.8	0.19
3.0	15.9	11.9	4.0	0.24
4.0	15.9	11.3	4.6	0.25
5.0	15.9	10.4	5.5	0.25

FIGURE 5. XPS spectra for the identification of Cu species in the solid-phase of the suspension of GR(Cl) in the presence of 0.5mM Cu(II).

amounts of Cu(II) when normalized to the Cu(II) concentration. O'Loughlin et al. (30) found that Cu(II) could be reduced to its zerovalent state by the oxidation of Fe(II) in GR(SO$_4$) to accelerate the removal of CCl$_4$, but no Cu(I) was identified in their study. In addition, our previous study demonstrated that Cu(II) can be reduced to Cu(I) by the oxidation of Fe(II) in the surface-bound Fe(II) system (35). These observations imply that Cu(II) could be reduced by Fe(II) to form both Cu(I) and Cu(0) under suitable conditions. In this study, a good linear relationship between the decreased total Fe(II) concentration and the added Cu(II) concentration was established ($R^2 = 0.989$, $n = 11$) (Figure S5, Supporting Information), which suggests that the generation of Cu(I) occurs mainly from the reaction of Cu(II) with Fe(II). In addition, the decrease in the Fe(II) concentration is much higher than the increase in the Cu(I) concentration. The slope of 1.8 shown in Figure S5 implies that Fe(II) in the GR(Cl) suspension could reduce Cu(II) to both Cu(I) and metallic Cu:

$$6[Fe^{II}_3Fe^{III}(OH)_8][Cl \cdot H_2O] + 5CuCl_2 \rightarrow 8Fe^{II}Fe^{III}_2O_4 + 5Cu(0) + 16HCl + 22H_2O \quad (5)$$

$$3[Fe^{II}_3Fe^{III}(OH)_8][Cl \cdot H_2O] + 5CuCl_2 \rightarrow 4Fe^{II}Fe^{III}_2O_4 + 15CuCl + 8HCl + 11H_2O \quad (6)$$

$$2Fe^{II}_{aq} + 2Cu^{II}_{aq} + 7H_2O \rightarrow Cu_2O + 2Fe(OH)_3 + 8H^+ \quad (7)$$

Analysis of the Solid-Phase of the GR(Cl)−Cu(II) Suspension. To further characterize the possible change in Fe and Cu sp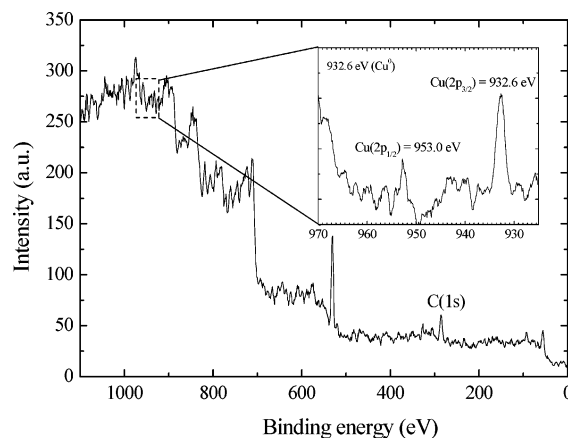ecies, XRPD and XPS were used to identify the crystal phases and chemical species of the solids in the GR(Cl) systems. Figure 5 shows the XPS spectra of the solid phase obtained in the GR(Cl) suspensions. Two peaks centered at 932.6 and 953 eV clearly appeared in the XPS spectra, which could be assigned as Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively. This observation implies that the major copper species in the Cu(II)-amended GR(Cl) system should be Cu(0). To understand the crystalline properties of Cu and Fe in the heterogeneous system, the solid phases were further characterized by XRPD. Figure 6 shows the XRPD patterns of the solid phases in the GR suspensions in the presence of various concentrations of Cu(II). Two GR peaks at 12.08° and 23.59° (2θ) appeared clearly in the XRPD patterns in the absence of Cu(II). Addition of Cu(II) changed the crystalline properties of GR(Cl). Peaks at 35.46°, 43.31°, 56.96°, and 62.79° (2θ), which represent magnetite (Fe$_3$O$_4$) or maghemite (γ-Fe$_2$O$_3$), were observed when various concentrations of Cu(II) were added to the suspensions. In addition, the major peaks for elemental Cu at 43.47°, 50.37°, and 73.99° (2θ) were observed. However, no Cu$_2$O peaks at 36.42°, 42.22°, and 61.3° 2θ were identified in the XRPD patterns, presumably due to the amorphous form of Cu$_2$O or sorbed Cu(I) species. TEM images of GR(Cl) in the absence and presence of 0.5 mM Cu(II) were also recorded (Figure S6, Supporting Information). In the absence of Cu(II), GR(Cl) could be observed in rhomboid form. However, hexagonal GR(Cl) particles also appeared. McGill et al. (4) depicted that a flat rhombohedral crystal with a ($\bar{5}\,\bar{6}\,\bar{6}$) habit plane may have hexagonal geometry. In contrast, some additional particles, having diameters in the range 10−20 nm appeared when 0.5 mM Cu(II) was added. The EDS analysis clearly showed
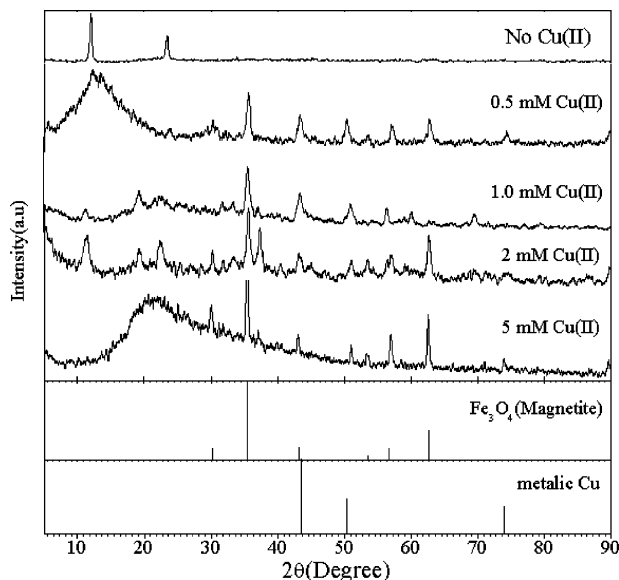
FIGURE 6. XRD patterns of the solid phase of the GR(Cl) suspension in the presence of various Cu(II) concentrations.

FIGURE 7. The k_{obs} for C_2Cl_4 removal by GR(Cl) (1.5 g L^{-1}) suspension as a function of pH in the presence and absence of 0.5 mM Cu(II).

the peak of Cu, which indicates the formation of Cu(0)- or Cu(I)-containing mineral species attached to the surface of GR(Cl).

In addition to the oxidation of Fe(II), another plausible reason for the decrease in rate constant at high Cu(II) concentration is the changes in pH and redox potentials in the GR(Cl) system (Figure S7, Supporting Information). The initial pH values were all at pH 7.2 and decreased as the Cu(II) concentrations increased. The pH values decreased from 7.2 in the absence of Cu(II) to 7.0 at 1 mM Cu(II). Meanwhile, the measured redox potential increased gradually from −555 to −500 mV. Further increase in Cu(II) concentration to 5 mM decreased the pH to below 7.0 and increased the redox potential to −380 mV, which is attributed to the release of large amounts of proton (eqs 5−7). These results are similar to those in the aqueous solution containing Cu(II) and Fe(II) ions (*36*). Maithreepala and Doong (*35*) used anoxic NaOH solution to adjust the pH value of the solution to pH 7 after the addition of Cu(II) ions to understand the effect of Cu(II) concentration on the dechlorination of CCl$_4$ in Fe(II)−goethite suspensions. The measured redox potential increased from − 320 mV to + 100 mV and the rate constant for CCl$_4$ dechlorination decreased rapidly when the Cu(II) concentration was higher than 2 mM, presumably due to the decrease in Fe(II) concentration. Although the reactivity of Fe(II)/Fe(III) systems cannot be predicted only by the values of redox potentials, these findings reflect the fact that the decrease in the efficiency and rate of C$_2$Cl$_4$ reduction by GR(Cl) at high concentration of Cu(II) may be due to the decrease in the available GR(Cl) concentration and the changes in the pH and ORP values.

Effect of pH on C$_2$Cl$_4$ Reduction. GR is a metastable iron mineral, and the hydrated GR bears hydroxide functional groups, which can be protonated or deprotonated upon changes in pH. In addition, the stability of green rust is also affected by pH, especially under acidic conditions (*28*, *41*). Therefore, the effect of pH on the reduction of C$_2$Cl$_4$ by GR(Cl) in the presence and absence of 0.5 mM Cu(II) was studied (Figure S8, Supporting Information). In the absence of Cu(II), the removal efficiency of C$_2$Cl$_4$ by 1.5 g of GR(Cl) L^{-1} slightly increased from 18% at pH 5.5 to 29% at pH 9.0 within 31 d. Trace amounts of C$_2$HCl$_3$ in the concentration range 0.04−0.12 μM were obtained after termination of the experiments (Table S1, Supporting Information). The removal efficiency and rate of C$_2$Cl$_4$ increased from 20% to 74% as the
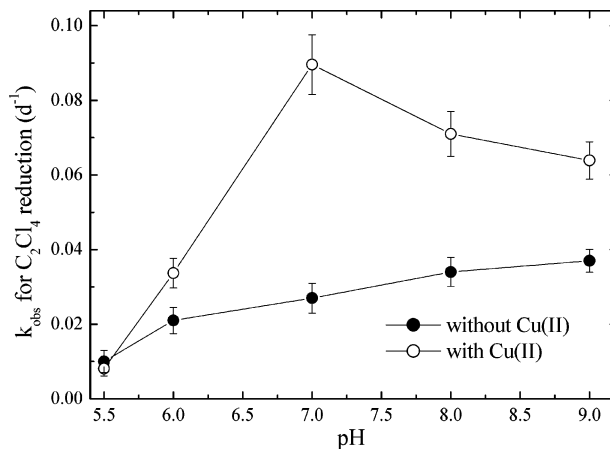
pH values increased from 5.5 to 7.2. A Further increase in pH, however, decreased the removal efficiency from 66% at pH 7.2 to 36% at pH 9. The C$_2$HCl$_4$ concentrations ranged between 2 and 5.2 μM in the presence of Cu(II) after 31 days, which were 40−86 times higher than those obtained in the absence of Cu(II).

The removal of C$_2$Cl$_4$ by GR(Cl) at various pH values followed pseudo-first-order kinetics. Figure 7 shows the k_{obs} for C$_2$Cl$_4$ removal as a function of pH in the presence and absence of 0.5 mM Cu(II). In the absence of Cu(II), the k_{obs} for C$_2$Cl$_4$ removal increased slightly from 0.01 ± 0.002 d^{-1} at pH 5.5 to 0.037 ± 0.005 d^{-1} at pH 9.0. A previous study demonstrated that the rate constant for C$_2$HCl$_3$ removal could increase 3-fold when the pH increased from 6.8 to 9.2 in GR(SO$_4$) suspension (*33*), which was similar to the result obtained in this study using GR(Cl). In contrast to the GR(Cl) suspension alone, the k_{obs} for C$_2$Cl$_4$ removal increased from 0.0081 ± 0.002 to 0.0896 ± 0.008 d^{-1} when the pH increased from 5.5 to 7.2 and then slightly decreased to 0.0639 ± 0.005 d^{-1} at pH 9.0 when 0.5 mM Cu(II) was added into the suspensions. These results clearly indicate that the maximum reactivity of GR(Cl) for C$_2$Cl$_4$ reduction occurs at near-neutral pH with the addition of Cu(II).

Environmental Significance

GR is a mixed-valence metastable iron oxide mineral containing a high concentration of Fe(II) (*1*, *25*) and can be formed abiotically by partial oxidation of Fe(II), interactions of Fe(II) ions with Fe(III) minerals, and reduction of Fe(III) or oxidation of Fe(II) by bacterial activity (*8*, *10*, *11*, *13*). GR may play an important role in the biogeochemistry of subsurface environments with respect to iron cycling, as well as the fate and transport of environmental contaminants under subsurface environments (because of its reducing power to reductively transform various kinds of priority pollutants including chlorinated hydrocarbons (*29*, *33*) and metal ions (*22−25*, *42*)). The removal of chlorinated methanes and ethenes by GR has, however, not been addressed systematically through an evaluation of the effects of environmental parameters on the degradation. A recent study reported that the rate and efficiency of the dechlorination of chlorinated alkanes was enhanced by the presence of Ag(I), Cu(II), and Au(III) species (*31*). In this study we demonstrate that, with the addition of Cu(II), GR(Cl) can effectively dechlorinate carbon tetrachloride, chloroform, tetrachloroethene, and trichloroethene under various environmental conditions. Our results indicate that GR(Cl) can reduce Cu(II) to both Cu(I) and Cu(0), thus enhancing the removal efficiency and rate of chlorinated methanes and ethenes. It is noted that GR can be formed from the biotic

and abiotic corrosion of metallic iron (*7, 19*), which is the dominant material that has been used in the innovative permeable reactive barrier (PRB) technique for the in-situ remediation of contaminated groundwater. GR has also been observed as a corrosion product both in a laboratory Fe(0) column (*43*) and in PRBs with zerovalent iron as the packing material (*44, 45*). A recent report described the effects of transition metal ions including Cu(II) on the reactivity of PRBs (*46*). Because both the metal ions and the chlorinated compounds coexist in contaminated sites, the reactive surfaces on the iron particles may form metal−GR complexes, which catalyze the dechlorination reactions and accelerate the efficiency and rate of dechlorination processes. Therefore, the results obtained in this study may be important for evaluating the enhanced reactivity in both the natural attenuation of contaminants by GR that may be present in the subsurface conditions and in the enhanced reactivity and long-term performance of iron permeable reactive barriers.

Acknowledgments

Supporting Information Available

Illustration of the drying procedure of GR(Cl) (Figure S1), removal of C_2Cl_4 by various concentrations of GR(Cl) ranging from 0.37 to 9 g/L^{-1} in the presence and absence of 0.5 mM Cu(II) (Figure S2), the k_{obs} for C_2HCl_3 removal as a function of Cu(II) concentration at pH 7.2 (Figure S3), the k_{obs} for C_2Cl_4 reduction as a function of Cu(II) concentration at pH 7.2 (Figure S4), effect of the concentration of Cu(II) (0−5.0 mM) on the decreased amounts of Fe(II) (Figure S5), TEM image of the solid phases of the GR(Cl) suspensions in the presence and absence of 0.5 mM Cu(II) (Figure S6), the changes in the pHs and redox potentials of the aqueous solutions at various concentrations of Cu(II) (Figure S7), effect of pH on the dechlorination of PCE by GR(Cl) in the absence and presence of Cu(II) (Figure S8), and effect of pH on the production of trichloroethene (C_2HCl_3) in the GR(Cl) suspension at pH 7.2 (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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