Enhanced remediation of carbon tetrachloride by Fe(II)-Fe(III) systems in the presence of copper ions

R.A. Maithreepala and R.-A. Doong

Department of Atomic Science, National Tsing Hua University, 101, Sec 2, Kuang Fu Road, Hsinchu, 30013, Taiwan (E-mail: *radoong@mx.nthu.edu.tw*)

Abstract The effect of Cu(II) ion on the dechlorination of carbon tetrachloride (CT) by Fe(II) associated with various iron oxides was investigated. Iron oxides including goethite, hematite, ferrihydrite and magnetite were selected as the model compounds. CT was dechlorinated to chloroform (CF) by 3 mM Fe(II) in iron oxide suspensions at pH 7.2. The dechlorination followed pseudo first-order kinetics and the pseudo first-order rate constants (k_{obs}) were 0.048 h^{-1}, 0.0836 h^{-1}, 0.0609 h^{-1} and 0.0144 h^{-1} in goethite-, hematite-, ferrihydrite- and magnetite-amended systems, respectively. Addition of Cu(II) into systems increased the k_{obs} for CT dechlorination significantly. A 3- to 120-fold increase in k_{obs} relative to the systems without Cu(II) was observed when 0.5 mM Cu(II) was added to the Fe(II)-Fe(III) suspensions. The pH of the system is an important factor controlling the dechlorination rate of CT. The increase in concentrations of Fe(II) and iron oxides also enhanced the dechlorination efficiency and rate of CT. Moreover, a linear relationship between the k_{obs} and Cu(II) concentration ranging between 0 and 0.4 mM was observed. Results obtained demonstrate the feasibility of using surface-bound iron species with Cu(II) for the detoxification of chlorinated solvents in the contaminated aquifers.

Keywords Cu(II) ions; dechlorination; enhanced remediation; Fe(II) ions; iron oxides; surface-bound Fe(II)

Introduction

The contamination of groundwaters with chlorinated hydrocarbons is a widespread environmental problem. The environmental and health impacts of chlorinated hydrocarbons have prompted investigations regarding their removal from natural environments. A number of chlorinated solvents in contaminated aquifers are relatively susceptible to abiotically reductive transformation under anoxic conditions. Recently, laboratory and field studies have focused on the significance of Fe(II) ions in reductive transformation of halogenated compounds in soil and groundwater. The Fe(II) ion has been shown to reduce chlorinated hydrocarbons under anoxic conditions (Doong and Wu, 1992). More recently, Fe(II) species associated with iron oxides have been demonstrated to be more reactive than dissolved ferrous ions in reductive transformation of pollutants (Maithreepala and Doong, 2004).

The utilization of iron species to reduce chlorinated hydrocarbons is of economically great advantage because iron oxides bound to aqueous and solid-phase Fe(II) species are natural reductants and are abundant in soils and sediments. Basically, oxygen supply is limited under subsurface conditions and Fe(II) species associated with iron minerals can act as alternative electron acceptors. The high reactivity of the surface-bound Fe(II) species can be maintained over a long period of time because of the continuous generation of surface-bound Fe(II) either by the uptake of Fe(II) from the aqueous solution or by the reduction of Fe(III) oxides by dissimilatory iron-reducing bacteria (DIRB) (Amonette *et al*., 2000; Pecher *et al*., 2002). Moreover, surface-bound Fe(II) species generated by metal iron corrosion play a pivotal role in the long-term reactivity of permeable reactive barriers. Transition metal ions often coexist with chlorinated organic compounds in the contaminated sites. Also, certain transition metal ions such as Ni(II) and Cu(II) have been used as catalysts to

increase the rates of dechlorination reactions in the presence of bulk reductants (O'Loughlin *et al.*, 2003). Although the reductive dechlorination of chlorinated methanes by the surface-bound Fe(II) species has been investigated under anoxic conditions, the influence of transition metal ions on the dechlorination of chlorinated hydrocarbons is not well-understood. Goethite (GT, α-FeOOH), hematite (HM, α-Fe$_2$O$_3$), ferrihydrite (FH, Fe(OH)$_3$), and magnetite (MG, Fe$_3$O$_4$) are the most abundant iron oxide minerals. Cu(II) is one of the common environmental pollutants in contaminated aquifers. Therefore, the objective of this work was to investigate the effect of Cu(II) ion on the dechlorination of carbon tetrachloride (CT) by Fe(II) associated with goethite, hematite, ferrihydrite and magnetite. Effects of pH, Fe(II) concentration and iron oxide surface areas on the dechlorination efficiency of CT were investigated to elucidate the catalytic effect of Cu species. Pseudo first-order kinetics was also used to calculate the rate constants for CT dechlorination.

Materials and methods

Dechlorination experiments

Batch experiments were conducted using 70 mL serum bottles filled with 50 mL of deoxygenated buffer solution under N$_2$ atmosphere. Iron oxide minerals including GT, HM, FH and MG were synthesized according to the procedures described by Schwertman and Cornell (1991) and were characterized by the X-ray powder diffraction (XRPD) technique. Iron oxide was withdrawn from anoxic stock slurry using a N$_2$-purged syringe and was delivered into serum bottles to get the final concentration of 10 mM. Fe(II) solutions were prepared in deoxygenated buffer solution in sealed bottles and were introduced into the serum bottles. The final concentration of Fe(II) was 3 mM. HEPES (50 mM) buffer solutions were used to control pH at 7.1 ± 0.1. A 50 mM stock solution of CuCl$_2$·2H$_2$O was prepared using deoxygenated water in sealed bottles. Appropriate amounts of stock Cu(II) solution were introduced into the serum bottles to get a final concentration of 0.5 mM using N$_2$-purged plastic syringes. Bottles were then sealed with Teflon-lined rubber septa and aluminum crimp caps, and were incubated in an orbital shaker at 150 rpm (25 ± 1°C) in the dark. After 20 h of equilibrium, an aliquot of the CT stock solution dissolved in methanol was delivered into the serum bottles by a N$_2$-purged gas-tight glass syringe to obtain the concentration of 20 μM. The total volume of the liquid phase in the serum bottles was maintained at 50 mL, resulting in 20 mL left for headspace analysis. Parallel experiments were also carried out without the addition of Fe(II). To study the combined effect of Fe(II) and Cu(II) on the dechlorination of CT, experiments were carried out according to the procedures described above except for the addition of iron oxides. Concentrations of Cu(II) and Fe(II) in the systems were in the range of 0–3 mM. All the experiments were run in duplicate or triplicate.

Analytical methods

The headspace analytical technique was used in this study for the determination of chlorinated hydrocarbons. Concentrations of CT and the products in the headspace of the test bottles were monitored by withdrawing 50 μL gas in the headspace using a 100 μL gas-tight syringe. The mixture was immediately 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 $\times$ 3.0 μm, Supelco Co.) was used to separate the chlorinated compounds. The GC-column temperature was maintained at 90°C isothermally using nitrogen (N$_2$) as the carrier gas. The external calibration method was used to determine the concentrations of CT and the chlorinated products (Doong *et al.*, 2003). After the termination of the experimental course, serum bottles were opened under N$_2$ atmosphere to measure the pH and OPR in the

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suspensions. The Fe(II) concentrations in the serum bottles were determined colorimetrically at 562 nm using the ferrozine method (Doong and Schink, 2002).

Results and discussion

Dechlorination of CT by surface bound Fe system

In order to compare the reductive capacity of dissolved and surface-bound Fe(II), CT was incubated with 3 mM Fe(II) at pH 7.2 in the absence and presence of iron oxide minerals. Figure 1 illustrates the dechlorination of CT and the production of chloroform (CF) in Fe(II)-amended solution with and without the addition of iron oxides. No obvious change in CT concentration was observed during the experimental course in solutions containing Fe(II) only. Addition of iron oxides increased the efficiency and rate of CT dechlorination. A nearly complete dechlorination of CT was observed within 48 h when suspensions contained 10 mM HM and 3 mM Fe(II). Good removal efficiencies of CT were also observed in FH-Fe(II) and GT-Fe(II) suspensions. MG-Fe(II) suspension showed least reductive capacity and only 43% of the initial CT was dechlorinated within 48 h. Chloroform (CF) was found to be the major product in the surface-bound iron systems and the maximum concentrations were in the range of 10.5–12 μM. Trace amount of dichloromethane (DCM) was determined after 10 d of incubation. The carbon mass balance was 72%, 60%, 73% and 10.3% in GT-, HM-, FH- and MG-amended systems, respectively.

The CT dechlorination in surface-bound Fe(II) systems followed the pseudo first-order kinetics

$$\ln [C_t/C_0] = k_{obs}t \tag{1}$$

where C_0 and C_t are the concentrations of CT at the initial time and at time t, respectively. A good linearity was found in the plot of $\ln(C_t/C_0)$ vs time during the first 10–20 h followed by a slight decrease due to the possible consumption of more reactive Fe(II) species on the mineral surfaces. Table 1 shows the pseudo first-order rate constant (k_{obs}) and the normalized surface area rate constant (k_{sa}) for CT dechlorination by 3 mM Fe(II) associated with various iron oxides at pH 7.2. The k_{obs} for CT dechlorination followed the order of HM > FH > GT > MG. When the rate constant was normalized to the surface area concentration, the k_{sa} followed the order of GT > HM > MG > FH. Since the dechlorination in the Fe(II)-Fe(III) system is a surface-mediated reaction, it is reasonable to use k_{sa} to elucidate the dechlorination kinetics of CT. It is also noted that goethite and hematite, the most stable crystalline iron oxides, had high k_{sa} values, while ferrihydrite, the amorphous iron mineral with high specific surface area, had the smallest k_{sa} for CT dechlorination. This means that

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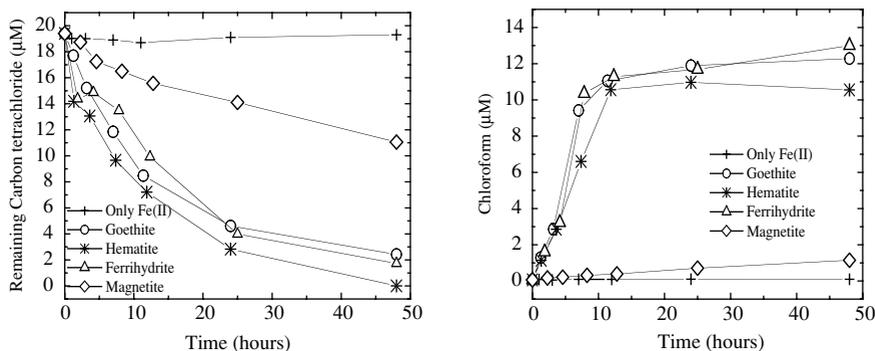
Figure 1 Reductive dechlorination of 20 μM carbon tetrachloride (CT) by 3 mM Fe(II) solution in the absence and presence of 10 mM iron oxides under anoxic conditions

Table 1 The pseudo-first-order rate constant (k_{obs}) and the normalized surface area rate constant (k_{sa}) for the dechlorination of CT by 3 mM Fe(II) amended with 10 mM iron oxides
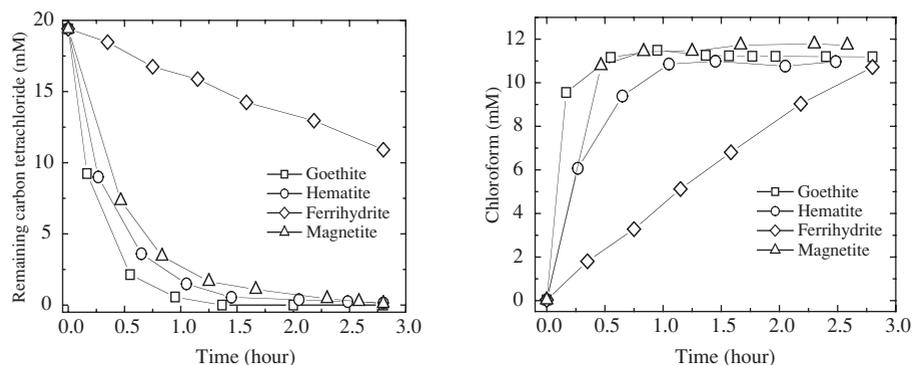
Mineral type	Abbreviation	Specific surface area (m^2g^{-1})	Rate constant for CT dechlorination	
			k_{obs} (h^{-1})	k_{sa} ($h^{-1}m^{-2}$)*
Goethite	GT	28.80	0.0480	0.0019
Hematite	HM	39.40	0.0836	0.0013
Ferrihydrite	FH	222	0.0609	0.0002
Magnetite	MG	11.67	0.0144	0.0005

* k_{sa} = (k_{obs}/surface area concentration of added iron oxides)

crystallization of the iron minerals is one of the factors influencing the dechlorination efficiency of CT. Since goethite suspensions had the highest capability for CT dechlorination, it was selected as the model iron oxide in the later experiments.

Dechlorination of CT by surface-bound Fe(II) species in the presence of Cu(II) ion

Addition of Cu(II) significantly enhanced the dechlorination efficiency and rate of CT in surface-bound iron systems. As shown in Figure 2, the addition of 0.5 mM Cu(II) into Fe(II)-Fe(III) suspensions completely dechlorinated CT within 1–3 h. No obvious dechlorination of CT was observed when Cu(II) was added to the iron oxide suspensions in the absence of Fe(II). Also, the amendment of Cu(II) had different enhancement effects on the dechlorination of CT in various iron oxide systems. GT-Fe(II) suspensions showed the highest capability for CT dechlorination. A complete degradation of CT with k_{sa} of 0.149 $h^{-1}m^{-2}$ was observed within 1.5 h in the presence of 0.5 mM Cu(II), whereas only 50% of the initial CT was dechlorinated within 3 h in FH-Fe(II) suspensions with 0.5 mM Cu(II), depicting that addition of Cu(II) influences the dechlorination efficiency of CT by surface-bound iron species. The dechlorination still followed the pseudo first-order kinetics in the presence of Cu(II). Table 2 shows the pseudo first-order rate constant (k_{obs}) and the normalized surface area rate constants (k_{sa}) for CT dechlorination by surface-bound iron species with 0.5 mM Cu(II). The k_{sa} for CT dechlorination were 0.0005, 0.041, 0.064 and 0.149 h^{-1} m^{-2} in FH-, HM-, MG-, and GT-amended suspensions, respectively, which corresponds to 3–120 times increase in k_{sa} relative to the suspensions without Cu(II). The highest enhancement effect in the MG system may be due to the existence of mixed-valence Fe species. A recent study showed that Cu(II) could be reduced to Cu(I) by Fe(II), and thus acts as an electron mediator for the enhancement of the dechlorination efficiency of CT (Maithreepala and Doong, 2004). This suggests that the high enhancement effect of

Figure 2 Reductive dechlorination of 20 µM carbon tetrachloride by 3mM Fe(II) in the iron oxide suspensions containing 0.5 mM Cu(II) at pH 7.2

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Table 2 The pseudo first-order rate constants for CT dechlorination by surface-bound iron species in the presence of 0.5 mM Cu(II) at pH 7.2.

| Mineral type	Abbreviation	Rate constant for CT dechlorination	
		k_{obs} (h^{-1})	k_{sa} (h^{-1}m^{-2})
Goethite	GT	3.807	0.149
Hematite	HM	2.476	0.041
Ferrihydrite	FH	0.196	0.0005
Magnetite	MG	1.722	0.064

k_{sa}= (k_{obs}/surface area concentration of added iron oxides)

magnetite on the dechlorination of chlorinated hydrocarbons in the presence of Cu(II) may probably be due to the reduction of Cu(II) by structural Fe(II) in addition to that by surface-bound Fe(II).

Similar to the systems without Cu(II), the production of CF increased with the decrease in CT concentrations in Cu(II)-amended systems, clearly showing that the reductive dechlorination is still the major pathway for CT dechlorination. The maximum concentrations of CF in the Fe(II)-Fe(III) systems containing 0.5 mM Cu(II) were in the range of 10.7–11.7 µM, which corresponds to 55–60% loss of CT. It is noted that the carbon mass balance for CF in the FH-Fe(II)-Cu(II) system can reach 95%, which is quite a bit higher than those in the other iron oxide-amended suspensions. This suggests that the dechlorination mechanism in the amorphous iron oxide system may be slightly different from the other crystalline iron oxide systems.

Effect of pH on dechlorination

The pH value plays a pivotal role in determining the reducing power of the surface-bound Fe(II) species. Because the uptake of the dissolved Fe(II) ions onto iron mineral surfaces significantly depends on the pH value, the formation of reactive sites of surface-bound iron species is pH-dependent. Figure 3 illustrates the rate constants for CT dechlorination as a function of pH in the GT-Fe(II) system. The k_{obs} for CT dechlorination increased positively with increasing pH in the presence and absence of Cu(II). When pH increased from 4 to 8.5, the k_{obs} increased from 0.0078 to 15.143 h^{-1} and from 0.001 to 1.861 h^{-1} in 0.5 mM
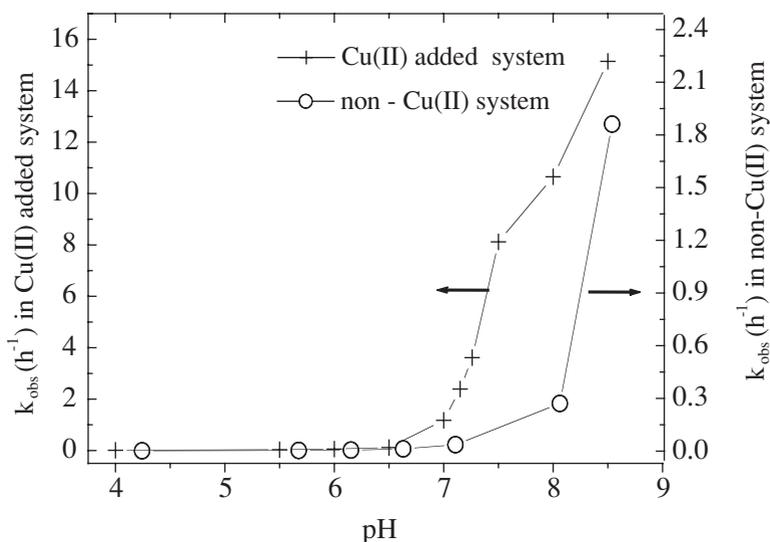
Figure 3 Effect of pH on the rate constant (k_{obs}) for the dechlorination of 20 µM CT by 3 mM Fe(II) associated with goethite in the absence and presence of 0.5 mM Cu(II)

Cu(II)-amended and -unamended suspensions, respectively. This depicts that the pH is an important factor in the Cu(II)-amended system because not only the Fe(II) species but also the Cu species can easily precipitate at high pH to form much more reactive sites over the goethite surface.

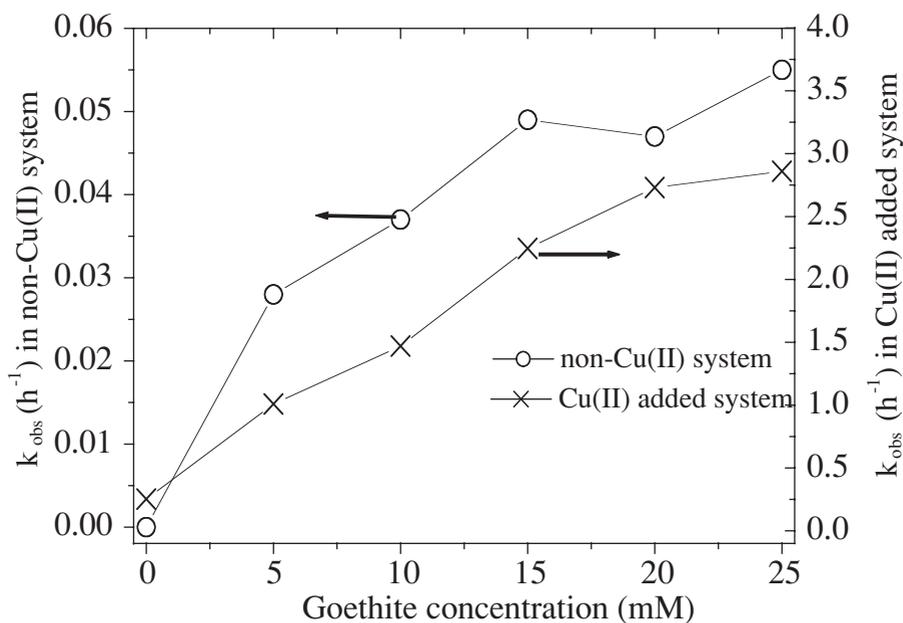### The effect of the concentration of Fe(II) on dechlorination

Fe(II) is an essential bulk reductant for the dechlorination reaction in Fe(II)-iron oxide systems. Figure 4 shows the rate constant (k_{obs}) for CT dechlorination as a function of initial Fe(II) concentration in the presence and absence of Cu(II) ions. No CT was dechlorinated in GT and GT-Cu(II) suspensions under anoxic conditions in the absence of Fe(II). However, the k_{obs} increased rapidly when low concentrations of Fe(II) ranging from 0.1 to 0.75 mM were added into the solution. Further increase in Fe(II) concentration did not show rapid increase in k_{obs} for dechlorination due to the saturation of the surface active sites with Fe(II) species. Since the goethite concentration was constant (10 mM) in the system, the surface area may be the limiting factor to form surface-bound Fe(II) species. Therefore, the effect of goethite concentration on the CT dechlorination was investigated.

Effect of goethite concentration on dechlorination

The effect of goethite concentration on CT dechlorination by 3 mM Fe(II) in the presence and absence of 0.5 mM Cu(II) is shown in Figure 5. When 3 mM Fe(II) was mixed with 0.5 mM Cu(II) without the addition of goethite, the k_{obs} for CT dechlorination was 0.252 h^{-1}, presumably due to the reaction of Fe(II) with Cu(II) to form the reactive surface-bound iron species and Cu(I) ions (Maithreepala and Doong, 2004). The increase in goethite concentration also enhanced the dechlorination efficiency of CT and the k_{obs} increased from 0.252 h^{-1} in the absence of goethite to 2.86 h^{-1} in the presence of 25 mM goethite in the solutions containing 0.5 mM Cu(II) and 3 mM Fe(II). Similar degradation patterns but less extents were observed in Fe(II)-Fe(III) solutions in the absence of Cu(II). The k_{obs} for CT dechlorination increased from 0 to 0.055 h^{-1} when the goethite concentration increased from 0 to 25 mM, proving that goethite provides a surface to form reactive sites for CT dechlorination.
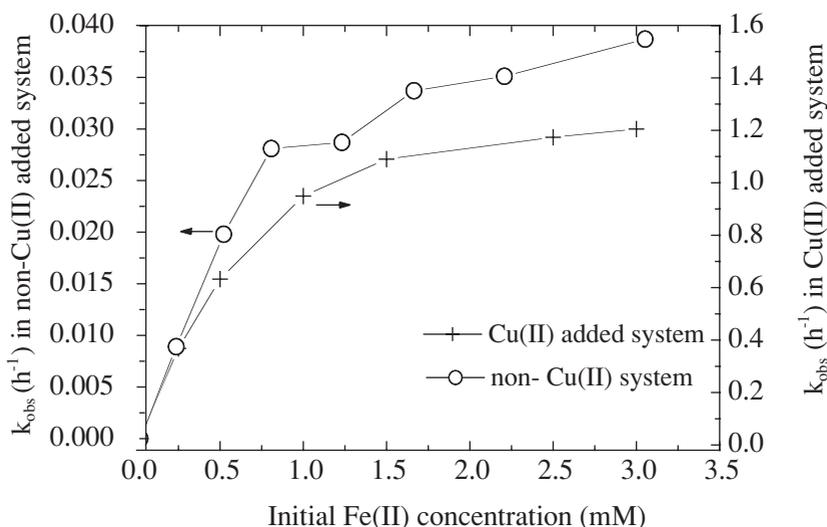
Figure 4 The rate constant (k_{obs}) for CT dechlorination as a function of initial Fe(II) concentration in 10 mM goethite suspensions with and without the addition of 0.5 mM Cu(II) ions at pH 7.2

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Figure 5 Effect of goethite concentration on CT dechlorination by 3 mM Fe(II) in the absence and presence of 0.5 mM Cu(II) at pH 7.0

Table 3 The effect of Cu(II) concentration on the rate constant $(k_{obs})(h^{-1})$ for CT dechlorination and the pH and Fe(II) concentration in the system in 3 mM Fe(II) with 10 mM goethite system

Concentration of Cu(II) (mM)	$k_{obs}(h^{-1})$	The physicochemical parameters in the system		
		pH	Total Fe(II) (mM)	Redox potential (mV)
0	0.035	7.07	3.08	–334
0.1	0.362	7.03	3.07	–380
0.2	0.761	7.01	2.93	–419
0.3	1.123	7.00	2.89	–358
0.4	1.293	6.99	2.72	–234
0.5	1.175	6.93	2.46	–224
1	1.142	6.73	1.91	–156
2	0.603	6.34	1.20	–100
3	0.036	6.01	0.76	–75

Effect of Cu(II) ion concentration

The effect of Cu(II) concentration on the dechlorination of CT was investigated by adding various concentrations (0–3 mM) of Cu(II) into suspensions containing 3 mM Fe(II) and 10 mM goethite at pH 7.1. The increase in Cu(II) concentration up to 0.4 mM linearly increased the k_{obs} from 0.035 to 1.293 h^{-1}. Further increase in Cu(II) concentration, however, decreased the dechlorination rate constant, mainly attributed to the decrease in the pH and Fe(II) concentration. As depicted in Table 3, both the pH values and total Fe(II) concentration decreased rapidly when the Cu(II) concentration exceeded 0.5 mM. The measured ORP values in the system increased from –334 mV to –75 mV as the Cu(II) concentration increased from 0 to 3 mM. These results clearly show that Cu(II) does not increase the reducing power but acts as a catalyst for CT dechlorination in the Fe(II)-iron oxide systems. The catalytic effect of Cu species is due to the formation of Cu(I) ions generated from the reduction of Cu(II) by Fe(II).

Conclusions

Fe(II) species associated with iron oxide minerals can reduce CT effectively. Addition of low concentrations of Cu(II) in the range of 0–0.5 mM significantly increased the efficiency and rate of CT dechlorination. The dechlorination followed pseudo first-order kinetics and the k_{obs} for CT dechlorination were in the range of 0.196–3.807 h^{-1} in the presence of 0.5 mM Cu(II). Goethite has the highest dechlorination capability, while ferrihydrite has the lowest capability for CT dechlorination. Moreover, the increase in pH value, Fe(II) concentration and iron oxide surface can increase the dechlorination rate of CT by surface-bound Fe(II) species. Results obtained clearly demonstrate that the surface-bound iron species with low concentration of Cu(II) accelerates the dechlorination rate of chlorinated hydrocarbons and gives impetus to the degradation of heavy metals and chlorinated hydrocarbons under iron-reducing conditions.

References

Amonette, J.E., Workman, D.J., Kennedy, D.W., Fruchter, J.S. and Gorby, Y.A. (2000). Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environ. Sci. Technol.*, **34**, 4606–4613.

Doong, R.A. and Wu, S.C. (1992). Reductive dechlorination of chlorinated hydrocarbons in aqueous solutions containing ferrous and sulfide ions. *Chemosphere*, **24**, 1063–1075.

Doong, R.A. and Schink, B. (2002). Cysteine-mediated reductive dissolution of poorly crystalline iron(III) oxides by *Geobacter sulfurreducens*. *Environ. Sci. Technol.*, **36**, 2939–2945.

Doong, R.A., Chen, K.T. and Tsai, H.C. (2003). Reductive dechlorination of carbon tetrachloride and tetrachloroethylene by zerovalent silicon-iron reductants. *Environ. Sci. Technol.*, **37**, 2575–2581.

Maithreepala, R.A. and Doong, R.A. (2004). Synergistic effect of copper ion on the reductive dechlorination of carbon tetrachloride by surface-bound Fe(II) associated with goethite. *Environ. Sci. Technol.*, **38**, 260–268.

O'Loughlin, E.J., Kemner, K.M. and Burris, D.R. (2003). Effects of Ag(I), Au(III), and Cu(II) on the reductive dechlorination of carbon tetrachloride by green rust. *Environ. Sci. Technol.*, **37**, 2905–2912.

Pecher, K., Haderlein, S.B. and Schwarzenbach, R.P. (2002). Reduction of polyhalogenated methanes by surface-bound Fe(II) in aqueous suspension of iron oxides. *Environ. Sci. Technol.*, **36**, 1734–1741.

Schwertman, U. and Cornell, R.M. (1991). *Iron Oxides in the Laboratory, Preparation and Characterization*, VCH Publishing Co., Weinheim, Germany, pp. 61–114.

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