

Dechlorination of carbon tetrachloride by ferrous ion associated with iron oxide nano particles

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Abstract

Dechlorination of carbon tetrachloride (CT) by Fe(II) ion in suspensions of crystalline iron oxide minerals including goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (Fe₃O₄), and amorphous ferrihydrite (Fe(OH)₃) in Fe(II) ion solution was investigated. Experiments were performed in sealed vials using 10 mM iron oxides and 3 mM Fe(II) to form surface-bound Fe(II)- iron mineral complexes in the suspension at pH 7.2 under anoxic condition. To understand the effect of Cu(II) for the dechlorination by Fe(II) associated with iron minerals, 0.5 mM Cu(II) was added to certain batches of mixtures. Dechlorination followed pseudo first-order kinetics. The rate constants (k_{obs}) were 0.380 h⁻¹ and 0.836 h⁻¹ in goethite and hematite suspensions, respectively. Whereas the k_{obs} was 0.061 h⁻¹ for magnetite and 0.014 h⁻¹ for ferrihydrite, which were lower than those in the highly crystalline Fe (III) oxide suspensions. The major product of CT dechlorination was chloroform (CF,) and the ratio of CT conversion to CF was within the range of 14 – 57 % during 2.8 h of incubation, depending on the type of iron oxides. The rate and efficiency of dechlorination also depend on the concentration of Fe(II) and a linear relationship between surface concentration and k_{obs} was established. The pH of the surface-bound Fe (II) system strongly influenced the rate and efficiency of dechlorination and both k_{obs} and sorbed Fe(II) concentrations exponentially increased with the increase in pH within the range of 4 - 8.5 showing that the increase in k_{obs} with the increase in pH is mainly attributed to the increase in the surface-bound Fe(II) concentration. Dechlorination of CT was significantly enhanced by the addition of 0.5 mM Cu(II) into the suspension of iron oxide mineral mixed with Fe(II). The k_{obs} values for CT dechlorination were 119, 100, 30 and 3 times greater than those in the absence of Cu(II) in the magnetite, goethite, hematite and ferrihydrite suspensions, respectively. Previously we have reported that CF also could be dechlorinated in the Cu(II)-amended iron, which was not observed without Cu(II) addition, indicating that the addition of Cu(II) into Fe(II)/Fe(III) systems enhances the dechlorination efficiency of highly chlorinated compounds (Maithreepala and Doong 2004). This method can be used to make environmentally benign compounds from highly chlorinated organic compounds.

Introduction

Groundwater contamination with persistent xenobiotic compounds such as chlorinated hydrocarbons is a widespread environmental problem. The impact of chlorinated hydrocarbons on the environment and human health has prompted scientific investigations to develop applicable technologies for the removal of such compounds from natural environments. A number of chlorinated solvents found in contaminated aquifers are relatively susceptible to undergo transformation reactions through reductive pathways under anoxic conditions.

Fe (II) ion has been identified as a naturally available reductant for possible application in reducing chlorinated hydrocarbons under anoxic conditions by abiotic natural attenuation. Recently, laboratory and field studies have focused on the significance of Fe (II) ions in reductive transformation of halogenated compounds in soil and groundwater (Klausen et al. 1995, Heijman et al. 1995). Also, laboratory and field studies

have focused on the significance of Fe (II) ions in reductive transformation of halogenated compounds in soil and groundwater (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 ubiquitous 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. 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), the high reactivity of the surface-bound Fe(II) species can be maintained over a long period of time (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 contaminated sites (Riley et al. 1992). Some transition metal ions such as Ni(II) and Cu(II) have been identified as catalysts to increase the rates of dechlorination reactions in the presence of bulk reductants (O'Loughlin et al., 2003). 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 effect of transition metals on the reactivity of Fe(III)-containing minerals for the dechlorination of chlorinated hydrocarbons. Also it is important to compare the reactivity of Fe(II) species associated with various "iron oxide minerals" in their aqueous suspensions in the presence of Fe(II) ions .

Goethite (GT, α -FeOOH), hematite (HM, α -Fe₂O₃), ferrihydrite (FH, Fe(OH)₃), and magnetite (MG, Fe₃O₄) are the most abundant iron oxide minerals. They all contain only Fe (III) iron and 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 were used to calculate the rate constants for CT dechlorination.

Experimental section

Synthesis and characterization of nanocrystalline iron oxides

Iron oxide minerals were synthesized according to the method described by Schwertmann and Cornell (1991) and stored in slurry form in sealed bottles with N₂ filled headspace. Dried samples of ironoxide minerals under anoxic conditions following previously described method (Maithreepala and Doong 2005) were characterized by XRPD using x-ray diffractometer (Regaku D/max-II B) with a Cu K α radiation source operating at 30 kV voltage and 20 mA current. The scan range for all samples was between 5 and 90° (2 θ) at a scanning speed of 4° min⁻¹. According to the peak pattern at characteristic 2 θ and d-spacing, the synthesized iron oxide minerals were identified. The morphology of the iron oxides was studied by using scanning electron microscope (Topcon ABT-150s). Specific surface areas of synthesized iron oxide minerals were measured using BET surface area analyzer (Micrometrics, ASAP 2020) using N₂ as the adsorbate.

Dechlorination experiments

Batch experiments were conducted using 70mL serum bottles. Required aliquots of the slurry of iron oxide were withdrawn from stock anoxic slurry and were delivered into serum bottles containing 50 mM HEPES buffer solutions (pH 7.2) under anoxic conditions

to get the final concentration of 10 mM. The required volume of stock solution of Fe(II) was introduced into the serum bottles to obtain a concentration of 3 mM under continuous flush of N₂. 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 CCl₄ (CT) stock solution dissolved in degassed methanol was delivered into the serum bottles by a N₂-purged gastight micro glass syringe to obtain the final concentration of 20 μM of CT. The total liquid volume in serum bottles were maintained at 50 mL, and a 20-mL headspace was left for headspace analysis. Parallel experiments were also carried out without the addition of Fe(II).

Analytical techniques

The headspace analytical technique was used for the determination of chlorinated hydrocarbons. The concentrations of carbon tetrachloride (CT) and their products in the headspace of the test bottles were monitored by withdrawing 50 μL of gas in the headspace using a 100 μL gas-tight syringe. The withdrawn gas sample 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 × 3.0 μm, Supelco Co.) was used to separate the chlorinated compound. The GC-column temperature was maintained at 90 °C isothermally with the nitrogen (N₂) as the carrier gas. The concentrations of Fe (II) in the serum bottles were monitored using ferrozine method. 0.5 mL of ferrozine solution was added into 1 mL of acidified sample solution in 2 mL vial and after 10 min the mixture was analyzed by UV-visible spectrometer at 562 nm.

Results and discussion

Characterization of iron oxide minerals

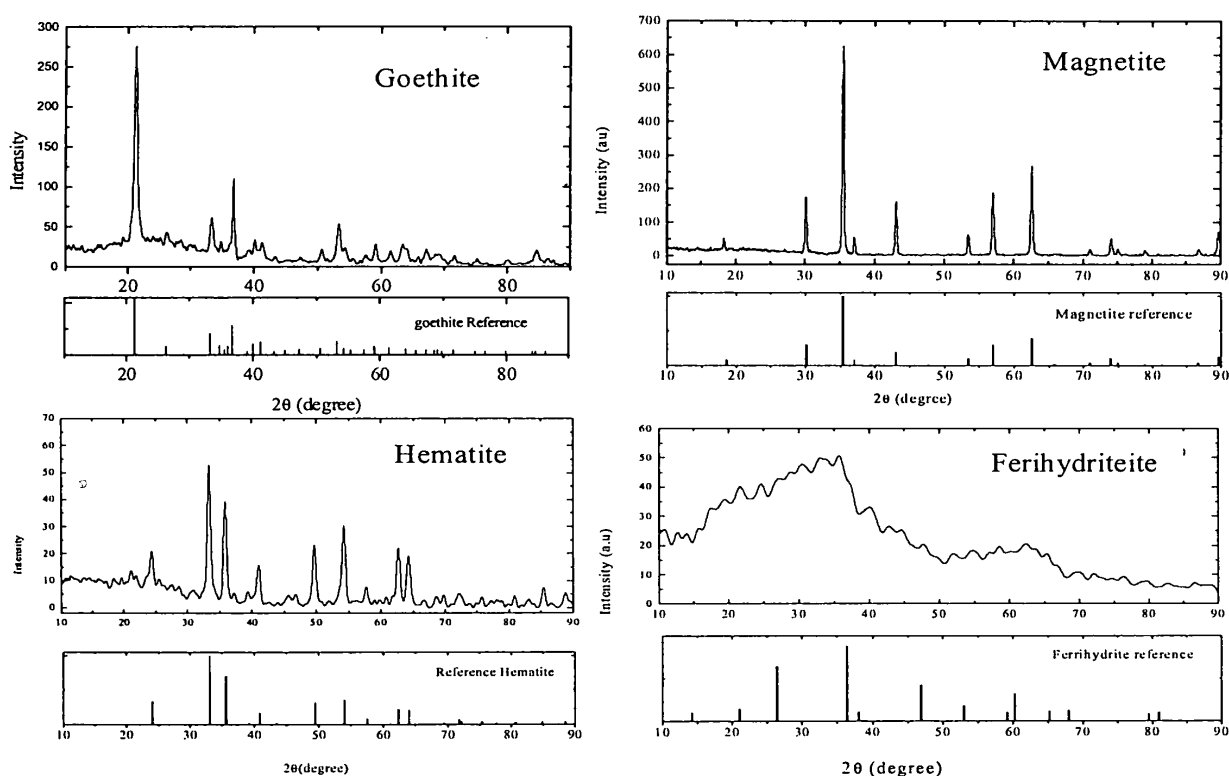


Figure 1. XRD patterns of synthesized iron oxide minerals and the standard reference XRD patterns for the same minerals.

As shown in Figure 1, the XRD pattern of synthesized products were similar to the standard XRD patterns of those iron oxide minerals and the color of the products were also similar as indicated in literature as dark yellow for goethite, brick red for hematite, dark brown for ferrihydrite and black for magnetite. Moreover, the black powder also had magnetic sensitivity proving that it is magnetite. The surface morphology of synthesized particles observed by SEM is shown in Figure 2, which indicates that goethite is rod shaped and all other types of iron oxides are spherical shaped particles and all are aggregated during the drying process. However, all the particles in each mineral phase are characteristic with the mineral type, and purity is good enough for utilization in dechlorination experiments.

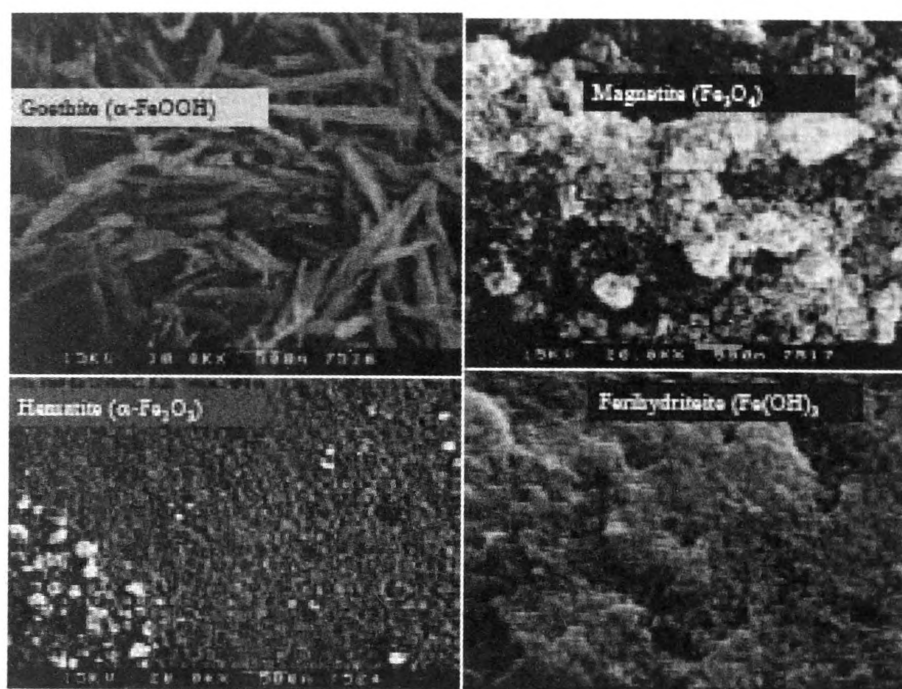


Figure 2. SEM images of iron oxide minerals synthesized

Dechlorination of carbon tetrachloride by surface-bound Fe (II)

Reductive capacity of dissolved and surface-bound Fe(II) was studied by injecting CT into serum bottles with 3 mM Fe(II) at pH 7.2 in the absence and presence of iron oxide minerals. As shown in Figure 3, the dechlorination of CT and the production of chloroform (CF) were not observed in the absence of Fe(II) by any of iron oxide minerals. Also no obvious change in CT concentration was found during the experimental course in solutions containing Fe(II) only. Addition of iron oxides increased the efficiency and rate of CT dechlorination. Almost complete dechlorination of CT was observed within 48 h when suspensions contained 10 mM hematite 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 10.5–13 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.

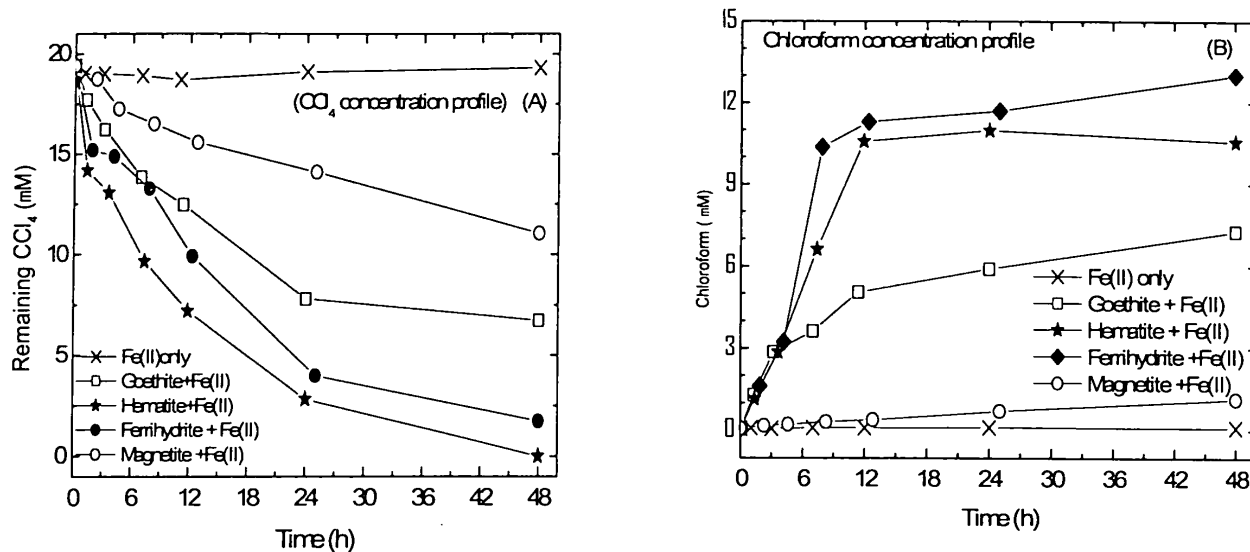


Figure 3. Dechlorination of carbon tetrachloride (CT) in the reactor bottles during incubated time. (a) CT concentration profile (b) Chloroform concentration. The initial concentration of Fe (II) ion and the concentration of iron oxide were 3 and 10 mM respectively. The pH of the system was maintained at 7.2 using 50 mM HEPES buffer.

Previous studies (Maithreepala and Doong 2004, and 2005) have shown that dechlorination in surface-bound Fe (II) systems followed the pseudo first-order kinetics and it can be explained as

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

where C_0 and C_t are the concentrations of CT at the initial time and at time t , respectively. 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 in the suspension of 3 mM Fe(II) associated with various iron oxides at pH 7.2. The magnitude of k_{obs} for CT dechlorination followed the sequence of HM > FH > GT > MG. Rate constant was normalized to the surface area concentration using the specific surface area of the iron oxide measured by surface area analyzer. The values were 28.8 ± 0.1 , 39.4 ± 0.2 , 222.00 ± 0.3 and $11.7 \pm 0.1 \text{ m}^2\text{g}^{-1}$ in GT, HM, FH and MG samples respectively. It is also noted that goethite and hematite, the most stable crystalline iron oxides, had higher k_{sa} values, while ferrihydrite, the amorphous iron mineral with high specific surface area, had the smallest k_{sa} for CT dechlorination.

Effect of pH

The pH of the iron oxide-Fe(II) system plays a pivotal role in determining the reducing power of the surface-bound Fe(II) species. A parallel series of serum bottles were prepared by following the similar procedures with the exception of CT amendments to determine the concentrations of surface-bound Fe(II).

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	Rate constant for CT dechlorination	
		k_{obs} (h^{-1})	k_{sa} ($h^{-1}m^{-2}$)*
Goethite	GT	0.0380	0.0296
Hematite	HM	0.0836	0.0265
Ferrihydrite	FH	0.0609	0.0051
Magnetite	MG	0.0144	0.0106

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

Figure 4(a) indicates that rate constant (k_{obs}) increases exponentially with the increase in pH. Similar trend in the relationship between k_{obs} and pH with surface-bound Fe (II) concentration has been observed in the reduction of fluorotribromomethane (CFBr₃) by Fe (II)-goethite suspension (Pecher et al., 2002). Several studies also have reported the increase in k_{obs} at high pH and it may be because the pH controls some factors directly responsible for the reactivity of the system (Pecher et al, 2002, Haderline et al, 1998). For example, the uptake of dissolved Fe (II) ions onto the surface of iron mineral significantly depends on the pH. The precipitation of dissolved Fe (II), mainly as hydroxide, can actively participate in the reducing reaction at high pH (Haderline et al, 1998, Jeon et al, 2002). Figure 4(a) also shows that similarly with k_{obs} , surface-bound Fe (II) also increased with increase in pH. Moreover, Figure 4(b) shows that there is a linear relationship between surface-bound Fe (II) concentration on goethite surface and k_{obs} for dechlorination of CCl₄. As a minor factor, the oxidation-reduction potentials (REDOX) of reactions may depend on the pH and may serve as another factor influencing the change in k_{obs} for the dechlorination with variable pH.

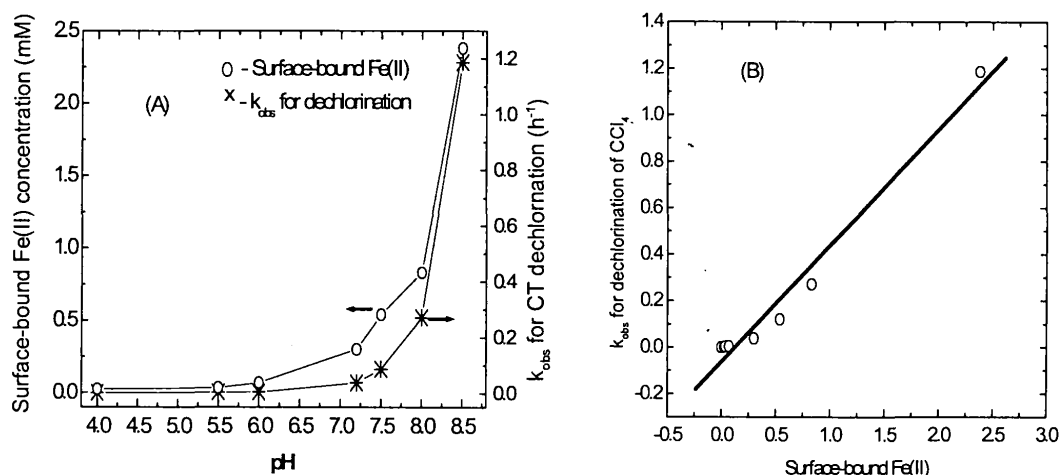


Figure 4. (a) The variance of k_{obs} and surface-bound Fe(II) concentration associated with goethite due to the change in pH and (b) the relationship between surface bound Fe(II) concentration and rate constant (k_{obs}) of the dechlorination of CCl₄.

Effect of copper ions on the dechlorination

The effect of inorganic ions on the reactivity of surface-bound Fe(II) systems is not well-known. Cu(II) ions made complexes with Fe(II) species associated with goethite have been shown to catalyze dechlorination reactions (Maithreepala and Doong 2004). Therefore, the effect of Cu(II) ions on the dechlorination of CT by Fe(II) with various iron

oxides was further studied. The concentrations of Fe(II) and iron oxide were 3mM and 10 mM respectively.

As shown in Figure 5, addition of Cu(II) enhanced the rate and efficiency of CT dechlorination. Also, the amendment of 0.5 mM Cu(II) had different enhancement effects on the dechlorination of CT in various Fe(II)-iron oxide systems. The Fe(II)-goethite suspensions showed the highest efficiency for CT dechlorination and a nearly complete CT dechlorination was observed during 1.5 h. The dechlorination efficiency with 0.5 mM Cu(II) is 90 times greater than that without Cu(II) in Fe(II)-goethite suspension. Similar degradation patterns were observed in magnetite-Fe(II) and hematite-Fe(II) systems and the degradation efficiency of CT were enhanced nearly 25 and 30 times respectively, in comparison with the suspensions without Cu(II). The CT degradation pattern in amorphous ferrihydrite-Fe(II) system was different from those in crystalline Fe(III) oxide systems and only 50% of the initial CT was dechlorinated within 2.8 h. This proves again that Fe(II) bound to crystal surfaces may be more effective than amorphous Fe(III) oxide systems in the presence of Cu(II).

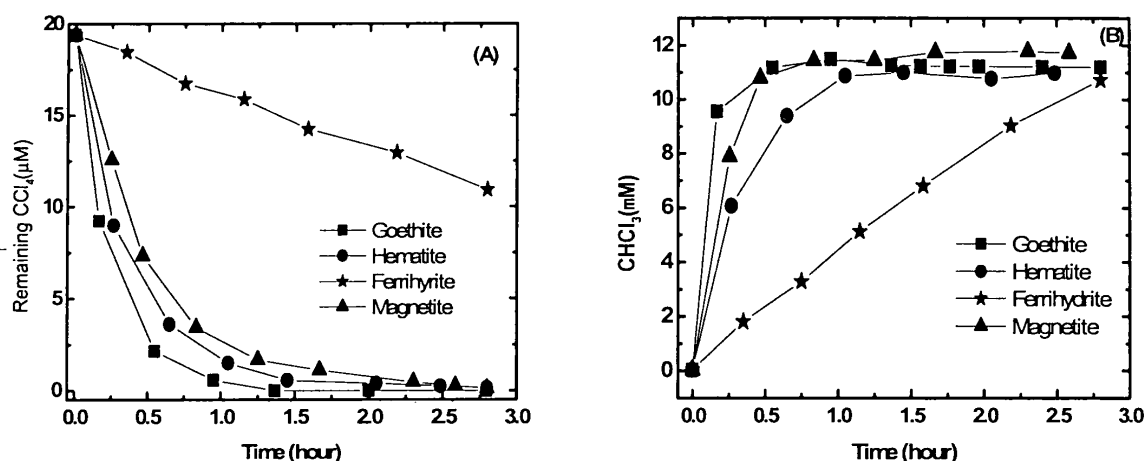


Figure 5. Dechlorination of CCl_4 in the suspension of 10 mM iron oxide and 3mM Fe (II) in the presence of 0.5 mM Cu (II) at pH 7.2. (a) CCl_4 concentration profile and (b) The concentration profile of CHCl_3 as the major product in the dechlorination process.

Chloroform (CF) was found as the major chlorinated byproduct (Figure 5). The production of CF increased with the decrease in CT concentrations in Cu(II)-amended systems, clearly showing that reductive dechlorination is still the major pathway for CT degradation in the presence of Cu(II). The maximum concentrations of CF were in the range of 10.7 - 11.7 μM , which accounted for 55 - 60% of the degraded CT concentration. It was found that the maximum concentration of CF in the ferrihydrite-Fe(II)-Cu(II) system corresponded to around 95 % of the dechlorinated CT. This value is quite higher than that in the other iron oxide-Fe(II)-Cu(II) suspensions, further suggesting that the dechlorination mechanisms in amorphous iron oxide system could be different from those in crystalline iron oxide systems. Even in the presence of Cu(II) ions the surface-bound Fe(II) systems show pseudo-first order reaction kinetics for CCl_4 dechlorination. Table 2 includes the rate constant for CCl_4 dechlorination (k_{obs}) in each of iron oxide systems in the presence of Cu(II) ions.

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

Mineral type	Rate constant for CT dechlorination
	k_{obs} (h^{-1})
Goethite	
Hematite	2.476
Ferrihydrite	0.196
Magnetite	1.722

According to the magnitude of k_{obs} for CT dechlorination surface-bound Fe(II) systems were in the order of goethite > hematite > magnetite > ferrihydrite, which is a little different from that for the Fe(II)-iron oxide suspensions without Cu(II). Addition of Cu(II) ion enhanced the k_{obs} values up to 100, 29.6, 3.2 and 120 times in goethite, hematite, ferrihydrite and magnetite suspensions, respectively. The highest enhancement effect on the CT dechlorination was found in magnetite suspension, while low enhancement effect was observed in the amorphous ferrihydrite system.

During 90 days incubation of iron oxide suspensions with Fe(II) and Cu(II) using $CHCl_3$ as target compound, it was found that $CHCl_3$ was further degraded. The initial rates for the dechlorination of CF in iron oxide suspension were $0.27 \mu M d^{-1}$ for ferrihydrite, $0.29 \mu M d^{-1}$ for hematite and $0.31 \mu M d^{-1}$ for goethite. However, only a trace amount of dichloromethane (DCM) as chlorinated product in the headspace of bottles was detected by GC-ECD. Generally, the Fe(II)-iron oxide systems need a very long time for possible degrading of $CHCl_3$ but this study shows that more persistent compounds can also be degraded by Cu(II) amended iron oxide-Fe(II) systems.

Conclusions

Surface-bound Fe(II) associated with iron oxides can dechlorinate CCl_4 and addition of Cu(II) into the system significantly increased the dechlorination reaction rates. Moreover, the product chloroform was further dechlorinated by Cu(II) amended iron oxide-Fe(II) systems which were not observed in the systems without Cu(II). The findings of this study show that Cu(II) combined surface-bound Fe(II) systems can be utilized for transformation of persistent toxic compounds to environmentally benign compounds.

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