

Coupled Transformation of Carbon Tetrachloride and Copper Ion by Nanocrystalline Ferric Oxides and Ferrous Ions

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Abstract: The transformation of carbon tetrachloride (CT) and copper ions by Fe(II) ions associated with nanocrystalline iron oxides minerals including hematite (α -Fe₂O₃) and ferrihydrite (Fe(OH)₃) was investigated. Experiments were performed using 10 mM iron oxides and 3 mM Fe(II) to form surface-bound iron suspensions at pH 7.2 under anoxic condition. X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM) showed that the particle sizes of synthesized iron oxides were in the range of 30 – 100 nm. In addition, the specific surface areas of nanocrystalline hematite and ferrihydrite were 39.4 and 222 m²/g, respectively. The sorption of Fe(II) ions onto hematite followed Langmuir sorption equation, while sorption of Fe(II) ions onto ferrihydrite obeyed Freundlich isotherm kinetics, presumably due to the high specific surface area of ferrihydrite. In addition, the sorption of Cu(II) ion onto iron oxides also followed Langmuir isotherm. The dechlorination of CT by surface-bound iron species followed pseudo first-order kinetics. The rate constants (k_{obs}) for CT dechlorination were 0.0836 and 0.0609 h⁻¹ in hematite and ferrihydrite suspensions, respectively. The produced chloroform ranged 7.3 – 13 μ M, depicting that reductive dechlorination is the major pathway for CT dechlorination in surface-bound iron system. Addition of 0.5 mM Cu(II) greatly enhance the dechlorination efficiency and rate of CT. The k_{obs} for CT dechlorination were 3 and 30 times greater than those in the absence of Cu(II) in the ferrihydrite and hematite systems, respectively. These results show that the Cu(II) plays a positive role in enhancing the dechlorination efficiency and rate of CT by Fe(II) associated with nanocrystalline iron oxides.

Keywords: Carbon tetrachloride (CT), Nanocrystalline iron oxides, Surface-bound iron species, Dechlorination, Copper ion

1. INTRODUCTION

The contamination of groundwater with chlorinated hydrocarbons is a widespread environmental problem. The environmental and health impacts of chlorinated hydrocarbons have

prompted investigations regarding to their attenuation in natural environments [1, 2]. Several chlorinated solvents including carbon tetrachloride (CT), chloroform (CF) and tetrachloroethylene (PCE) are rather persistent

under aerobic conditions, but they may undergo reductive dehalogenation under reducing environments [3]. Recently, the dechlorination of chlorinated compounds under iron-reducing conditions has become an important issue with respect to the remediation of the contaminated groundwater.

Fe (II) is one of the natural reductants available in various forms including dissolved, mineral-bound, and surface-bound. In both pristine and contaminated subsurface environments, oxygen concentration is usually limited and iron species will become a dominant species to control the redox reactions in the subsurface environments. Laboratory and field studies have focused on the significance of Fe (II) ions in the abiotic reductive transformation of halogenated compounds in soils and groundwaters [4-6]. Fe (II) ion complexes in dissolved forms have shown to reduce different kinds of organic compounds including polyhalogenated methanes, halogenated ethanes and nitroaromatic compounds under anoxic conditions [4-7]. Several studies have reported the high reactivity of Fe (II) ion when bound to Fe (III)-bearing minerals [4, 5]. The high reactivity of Fe(II) species attached to solid Fe(III) minerals is rationalized within the framework of surface complexation theory [7]. It is generally believed that during the contact of Fe (II) ions with the surface of iron oxide minerals, the protons in the surface hydroxyl groups are replaced by Fe(OH)₂ to form $\equiv\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH}$, and the concentration of the species is proportional to the initial rates of reduction reaction [5]. Recent field studies demonstrated that even in geochemically complex polluted aquifers, surface-bound Fe (II) was the predominant

reductant for nitroaromatic compounds [6]. It means that surface-bound Fe (II) systems play a pivotal role as natural mediators in the *in-situ* reduction of contaminants.

Large fractions of iron in the subsurface exist in the form of Fe (III) and are available as iron oxides. The most abundant available iron oxides in the nature are goethite, hematite, magnetite and ferrihydrite. Ferrihydrite is a poorly crystalline oxide mineral and is easily converted to nanocrystalline iron minerals such as magnetite and siderite by dissimilatory iron-reducing bacteria (DIRB) under anaerobic conditions [8, 9]. In addition, nanocrystalline iron minerals are potentially strong sorbents that have been used to remove a variety of metal ions from aqueous solutions and soils [10, 11]. The sorption of metal ions, including Fe (II), Zn (II), Cu (II), Ni (II), and Co (II), from aqueous solutions to a goethite surface have been observed [12-14]. White and Peterson [15] systematically investigated the reduction of the first row of transition metal species on the surface of magnetite and illmenite and found that the surfaces of structural Fe (II) minerals could effectively reduce Fe (III), Cu (II), Cr (VI), and V (V) in solutions. Transition metals are often found with chlorinated organic compounds in contaminated groundwaters. Although the reactivity of surface-bound iron species are commonly considered in the dechlorination of chlorinated hydrocarbons, much less attention has been paid on the synergistic effect of transition metals with nanocrystalline iron oxide minerals on dechlorination.

In this study, the dechlorination of carbon tetrachloride (CT) by Fe (II) ions associated with nanocrystalline iron oxides in the presence of Cu

(II) ions was investigated. Nanocrystalline hematite and ferrihydrite were selected as the model minerals because hematite is one of the most stable oxides in the natural environments, while ferrihydrite is a precursor to form other nanocrystalline iron oxides by biological reactions. Cu (II) ion was selected because it shows a catalytic characteristic in the reduction of chlorinated compounds and is a common environmental pollutant in wastewater. The sorption experiments of Fe (II) and Cu (II) onto iron oxides were also performed to verify the reactivity of such systems for the reductive transformation of CT.

2. MATERIALS AND METHODS

2.1 Synthesis and characterization of nanocrystalline iron oxides

Hematite and ferrihydrite were synthesized following the methods by Schwertman and Cornell [17]. In order to prepare dry samples of iron oxide for the mineralogical characterization and surface morphology studies, dry powder samples were prepared in sealed vials by continuous purging with N₂. A 50-mL serum bottle was first sealed using rubber septum and aluminum crimp cap. Then the bottle was purged with N₂ using syringe needle and 1 mL of the stock suspension of iron oxide was withdrawn using N₂-purged 1mL plastic syringe and injected into the serum bottle. Nitrogen gas was purged continuously until the suspension was transformed to dry powder.

2.2 Dechlorination Experiments

Batch experiments were conducted with 70 mL serum bottles. The buffer solutions were delivered to serum bottles using 60 mL air-tight

plastic syringe under gentle flow of N₂ (42 L min⁻¹). Hematite or ferrihydrite was withdrawn from stock anoxic slurry and were delivered into serum bottles 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. 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 glass syringe to obtain the final concentration of 20 μM. The total liquid volume was 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).

2.3 Analytical Methods.

The headspace analytical technique was used for the determination of chlorinated hydrocarbons. The concentrations of chlorinated hydrocarbons 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 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 × 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.

Samples for specific surface area analyses were measured using BET surface area analyzer (Micrometrics, ASAP 2020) using N₂ as the adsorbate. Single point surface area was determined following the standard procedure. The measured specific surface areas of ferrihydrite and hematite were 222 ± 0.3 and 39.4 ± 0.2 m²/g, respectively, which are generally in a good agreement with those reported values [17]. For XRPD analysis, powder samples were mounted on a glass sample holder using small amounts of grease. XRPD was performed using an X-ray diffractometer (Regaku D/max-II B) and a Cu K α -radiation source ($\lambda = 1.54056$ Å) with 30 kV voltage and 20 mA current. The peak pattern for relevant iron oxides was compared with the standard peak pattern of pure iron oxide minerals available in the JCPDF database.

3. RESULTS AND DISCUSSION

3.1 Characterization of iron oxide minerals

Figure 1 shows the XRPD patterns and SEM images of the synthesized iron oxide minerals. The iron oxide that was synthesized following the hematite preparation procedure had dominant peaks at 33.11° , 35.61° , 54.0° and 24.12° 2θ with intensities of 100, 70, 36 and 24 %, respectively, which are well-fitted with the standard XRPD patterns of hematite in the JCPDF database. The SEM image indicates that the synthesized hematite is a well-crystallized fine particle with particle sizes of 30 - 50 nm.

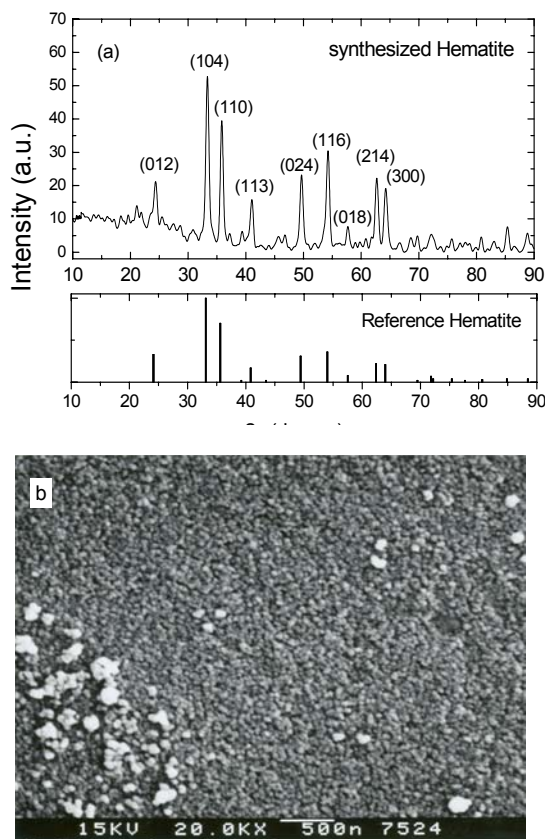


Figure 1. The (a) XRPD patterns and (b) SEM image of the synthesized hematite.

In contrast to the crystalline iron oxide minerals, ferrihydrite, also known as amorphous ferric oxide, is a poorly crystalline mineral. Since XRPD only shows peaks for crystalline materials, the XRD pattern of ferrihydrite does not show sharp peaks. As shown in Figure 2, the synthesized ferrihydrite has two broad peaks at around 36.4° and 60.2° 2θ . This sort of ferrihydrite is referred to as two-line ferrihydrite. The SEM image also showed the poor crystalline property. The particle sizes of the synthesized ferrihydrite were in the range of 60 – 100 nm.

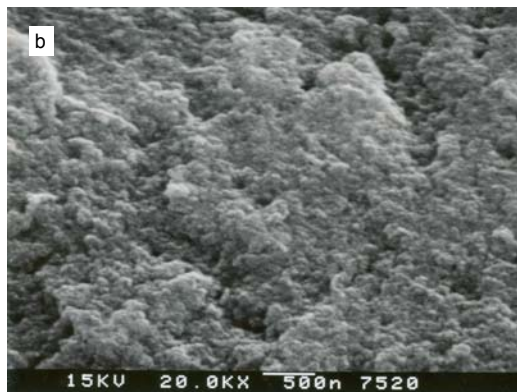
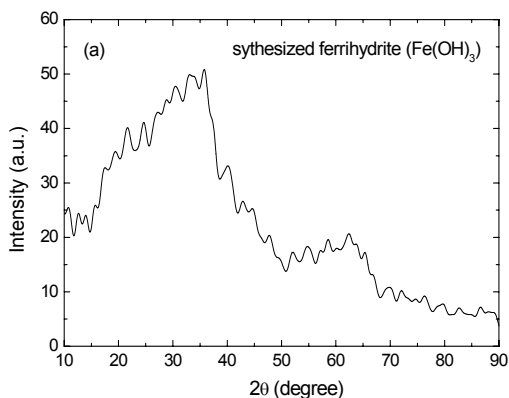


Figure 2. The (a) XRD patterns and (b) SEM images of the synthesized ferrihydrite.

3.2 Sorption of Fe (II) onto iron oxides.

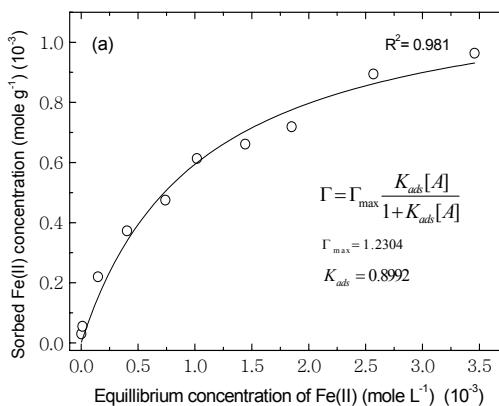
The sorption of heavy metal ions onto iron oxide minerals has been carried out by numerous studies with the objective of possible removal of metal ions from the aqueous solutions [19]. However, only few studies have focused on the sorption of Fe (II) species onto iron minerals, probably because Fe (II) ions are easily oxidized to Fe (III) in the presence of trace amounts of oxygen. Since sorbed Fe (II) ions on the Fe (III) oxides form Fe (II)/Fe (III) oxide redox couple which often buffers the oxidation-reduction potential of anoxic systems, the sorption behavior of Fe (II) onto Fe (III) minerals may be

compatible with the dechlorination behaviors of chlorinated hydrocarbons by surface-bound Fe (II) systems.

The Fe (II) sorption on hematite followed Langmuir isotherm equation, which gives the relationship of the sorbed concentration on the surface of hematite and the equilibrium concentration:

$$\Gamma = \Gamma_{\max} \frac{K_{ads} [A]}{1 + K_{ads} [A]} \quad (1)$$

where Γ is the density of adsorbate on the surface, Γ_{\max} is the maximum density of the adsorbate, and $[A]$ represents the aqueous concentration of adsorbate at equilibrium. As shown in Figure 3, the sorption of Fe (II) on hematite can be fitted with equation (1), suggesting that Fe (II) sorption follows Langmuir isotherm. The sorption behavior of Fe (II) onto ferrihydrite was different from that in hematite system. An exponential increase in sorbed Fe (II) density upon increasing Fe (II) concentration in the solution was observed, which can be assigned as a Freundlich isotherm. This may be attributed to that ferrihydrite is a poorly crystalline Fe (III) mineral which has high specific surface area and amorphous characteristics.



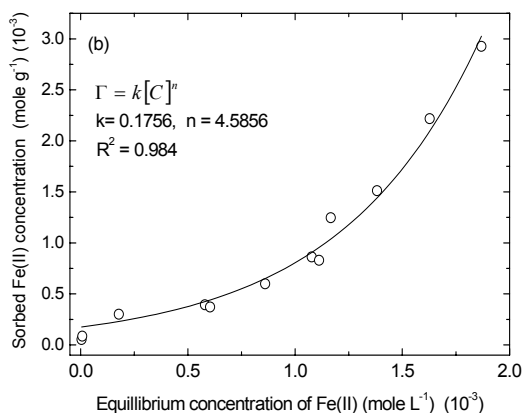


Figure 3. The sorption isotherm of Fe(II) onto (a) hematite and (b) ferrihydrite at 25 °C.

3.3. Sorption of Cu (II) onto iron oxides

Cu (II) ion also can be sorbed onto the surface of iron oxides in the surface-bound iron systems. The sorption isotherms of Cu (II) on iron oxide surfaces are shown in Figure 4. Cu (II) has very high affinity on hematite and obeys Langmuir isotherm equation. Iron oxide surfaces can form irreversible chemical bonds by inner-sphere surface complexation with iron oxide surfaces [20]. It is noted that the affinity of Cu (II) onto hematite is higher than that for Fe (II) on iron oxides [21]. This also can be evidenced by the result obtained in this study. The adsorption constant (K_{ads}) for Cu (II) is several hundreds times higher than that for Fe (II) on hematite under the experimental conditions, showing that Cu (II) has higher sorption affinity than Fe (II) onto iron oxides.

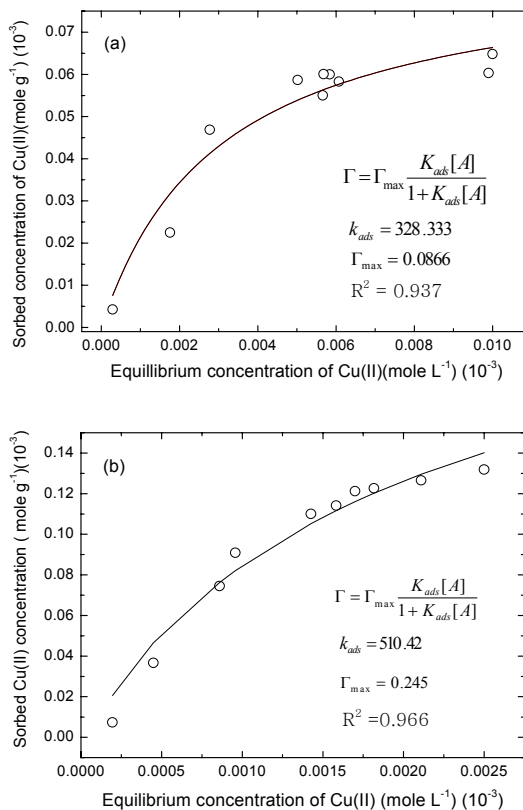


Figure 4. The sorption isotherm of Cu(II) onto (a) hematite and (b) ferrihydrite at 25 °C.

The adsorption capability of Cu (II) by ferrihydrite has been studied by several studies [22, 23]. The general conclusion is that ferrihydrite has very high sorption capacity for Cu (II) ions. However, this capability is mainly influenced by pH and the existence of other metal ions. At low pH, large fraction of sorbed Cu (II) was desorbed [24]. It also has been reported that the sorption of Cu (II) onto ferrihydrite occurs simultaneously with chemisorption in which Cu (II) ions infiltrated into the lattice of the ferrihydrite structure [25]. Also, coincidental sorption and precipitation of Cu (II) on ferrihydrite was observed at a concentration of

0.06 mM [19]. In this study, however, only dissolved Cu (II) existed in the solution because the equilibrium concentration of Cu (II) were all lower than 0.1 mM. This means that the threshold value for the dissolved Cu (II) in solution and the sorption of Cu (II) onto ferrihydrite could be fitted with Langmuir isotherm, which is consistent with the reported result [23].

3.4 Dechlorination of CT by surface-bound Fe (II)

In order to compare the reductive capacities 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 nanocrystalline iron oxide minerals. Figure 5 illustrates the dechlorination of 20 μ M CT and the production of chloroform (CF) in Fe (II)-amended iron oxides systems. No obvious change in CT concentration was observed during the experimental course in solutions containing Fe (II) alone. Addition of Fe (II) to the nanocrystalline iron oxide suspensions increased the rate and efficiency of CT dechlorination. A nearly complete dechlorination of CT was observed within 48 h in the suspension containing 10 mM hematite and 3 mM Fe(II). Good removal efficiency (92 %) of CT by Fe(II) were also observed in suspensions of ferrihydrite after 48 h of incubation.

Chloroform (CF) was found to be the major product in both the surface-bound Fe (II) systems. This result agrees with the previous observations that CT was dechlorinated by different types of Fe (II)/Fe (III) systems such as surface-bound Fe(II) associated with goethite and biogenic magnetite [26, 27]. Because of the formation of chloroform, it is clear that reductive

dechlorination is the prominent pathway for CT transformation. The maximum concentrations of CF in both the iron oxide systems were in the range of 10.5 – 13 μ M. The carbon mass balance with respect to chloroform formation in surface-bound Fe (II) systems is 73.5 % for ferrihydrite and 54.3 % for hematite, clearly showing that there may exist other degradation mechanism for CT dechlorination.

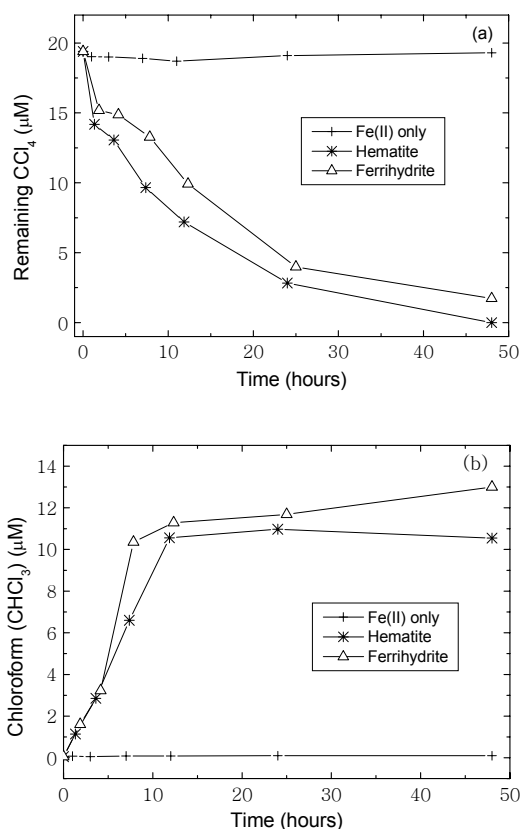


Figure 5. (a) Dechlorination of CT and (b) production of chloroform (CF) by Fe(II) in the presence of nanocrystalline iron oxide minerals at pH 7.2 under anoxic condition.

The dechlorination of CT by the surface-bound Fe (II) species followed pseudo first-order kinetics:

$$\ln \left[\frac{C_t}{C_0} \right] = k_{obs} t \quad (2)$$

Where C_0 and C_t are the concentrations of CT at the initial and at time t , respectively, and k_{obs} is the observed pseudo first-order rate constant. A good linearity was found in the plot of $\ln(C_t/C_0)$ vs time during the first 10 - 20 h and then the slope decreased slightly. Such a deviation in the linearity has been reported to be a common phenomenon in reduction of various compounds such as nitroaromatic compounds and polyhalogenated alkanes by surface-bound Fe (II) species [2, 10]. The k_{obs} for CT dechlorination in hematite system (0.0836 h^{-1}) was slightly higher than that in ferrihydrite system (0.0609 h^{-1}). When the normalized surface area rate constant (k_{sa}) was used by dividing the k_{obs} with available surface area of iron oxides in the serum bottoms, the k_{sa} for hematite ($0.0265 \text{ Lh}^{-1} \text{ m}^{-2}$) was 5 times higher than that for ferrihydrite ($0.0051 \text{ Lh}^{-1} \text{ m}^{-2}$). Since crystal property of the iron mineral is one of the important factors influencing the efficiency of CT dechlorination, the high dechlorination rate in hematite system may probably be attributed to that hematite is a well crystalline and the most stable iron oxide in natural environment, while ferrihydrite is an amorphous iron mineral.

3.5 Dechlorination of CCl_4 by surface-bound Fe (II) species in the presence of Cu(II)

The effect of catalytic Cu (II) ions on the reactivity of surface-bound Fe (II) systems is not well-known. Therefore, the effect of Cu (II) ions on the dechlorination of CT by Fe (II) with iron oxide was studied. As shown in Figure 6, addition of Cu (II) enhanced the rate and efficiency of CT dechlorination. The

Fe(II)-hematite suspensions showed high enhanced 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 about 40 times greater than that without Cu (II) in Fe (II)-hematite suspension. The CT degradation pattern in ferrihydrite-Fe(II) suspension was different from that in nanocrystalline hematite system. Only 50 % of the initial CT was dechlorinated within 2.8 h, and a nearly complete dechlorination was observed after the incubation of 16 h (data not shown). This proves again that Fe (II) bound to crystal surfaces may be more effective than amorphous Fe (III) oxide in the presence of Cu (II). In addition, the dechlorination of CT by Fe (II)-iron oxides in the presence of Cu (II) also followed first-order reaction kinetics. The k_{obs} for CT dechlorination in the presence of Cu (II) were 2.476 h^{-1} for hematite and 0.196 h^{-1} for ferrihydrite, which corresponds to 3 – 30 times higher than those in the absence of Cu (II).

Chloroform (CF) was found as the major chlorinated byproduct. The production of CF increased with the decrease in CT concentrations in Cu(II)-amended systems. The maximum concentrations of CF were in range of 10.7 - 11.7 μM , which accounted for 55 – 60 % of the CT concentration. It is noted that the maximum concentration of CF in the ferrihydrite-Fe (II)-Cu(II) system corresponded to around 95 % of the dechlorinated CT, clearly showing that reductive dechlorination is still the major pathway for CT dechlorination in the presence of Cu (II).

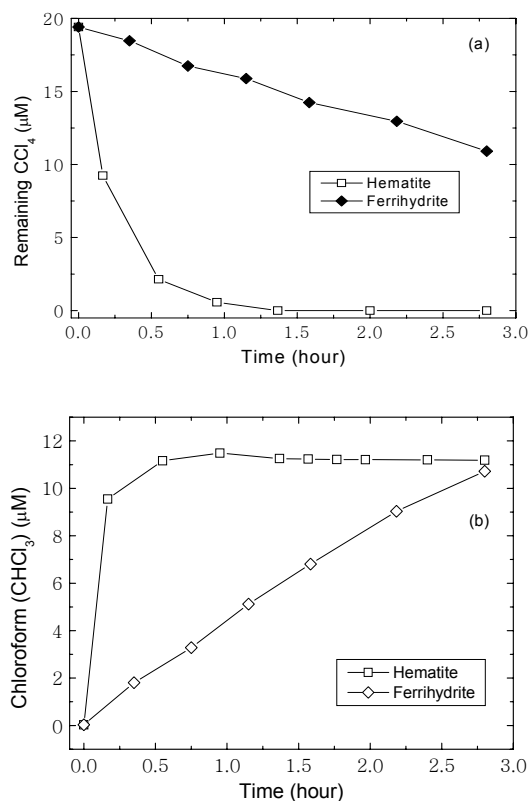


Figure 6. Reductive dechlorination of 20 μM CCl₄ by 3 mM Fe(II) and 0.5 mM Cu(II) with different iron oxides at pH 7.2 for (a) dechlorination of CCl₄ and (b) formation of CHCl₃.

4. CONCLUSIONS

In this study, Fe (II) associated with nanocrystalline iron oxides has demonstrated to be the effective natural reductants to sorb heavy metals and to dechlorinate chlorinated methanes. Nanocrystalline iron oxides has good capability to sorb Fe (II) and Cu (II) under anoxic conditions. The adsorption constant (K_{ads}) for Cu (II) is several hundreds times higher than that for Fe (II) on iron oxides minerals under the experimental conditions. The reactivity of

surface-bound Fe (II) species on the dechlorination is iron oxide-dependent. Comparison of the CT dechlorination by Fe (II) associated with iron oxides using normalized surface area rate constant (k_{sa}) shows that crystalline iron oxide (hematite) is more reactive than amorphous ferrihydrite. The chlorinated product generated during reductive transformation of CT shows that the formation ratio of CF varies from 35 to 65 %, which is dependent on the iron oxide minerals and copper ions. Results obtained in this study clearly show the possibility of the coupled removal of heavy metals and chlorinated hydrocarbons by surface-bound iron species under anaerobic conditions.

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奈米鐵氧化物與亞鐵離子共分解四氯化碳 與銅離子之研究

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摘要：奈米級鐵氧化物與亞鐵離子形成的鐵面結合鐵系統具有廣大比表面積及強還原力，適合作為吸附重金屬及分解氯化有機物之用途。本研究主要針對奈米級赤鐵礦與氫氧化鐵所形成之表面結合鐵系統進行銅離子與四氯化碳之共分解研究。X-光粉末繞射及掃描式電子顯微鏡分析結果發現，所合成之奈米鐵氧化物顆粒大小約為 30 - 100 nm，比表面積為 39.8 - 222 m²/g，亞鐵離子在赤鐵礦表面的吸附符合 Langmuir 等溫吸附模式，而在氫氧化鐵表面的吸附則可用 Freundlich 方程式描述。奈米鐵氧化物對銅離子的吸附能力高於亞鐵離子，其吸附行為符合 Langmuir 等溫吸附方程式。奈米級表面結合鐵系統對四氯化碳也有不錯的還原脫氯能力，其擬一階反應動力常數(k_{obs}) 在赤鐵礦及氫氧化鐵系統中分別為 0.0836 及 0.0609 h⁻¹，氯仿產生量則為 7.3 - 13 M 間。銅離子的存在則大幅增加表面結合鐵分解氯化有機物的能力，當添加 0.5 mM Cu(II) 時，其 k_{obs} 值可增加 3 - 30 倍，顯示奈米表面結合鐵系統在厭氧環境中能同時去除銅離子與氯化有機物。

關鍵詞：四氯化碳，奈米鐵氧化物，表面結合鐵系統，脫氯反應，銅離子

