



Dechlorination of carbon tetrachloride by the catalyzed Fe-Cu process

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Abstract

The electrochemical reduction characteristics of carbon tetrachloride (CT) were investigated using cyclic voltammetry in this study. In addition, the difference in reduction mechanisms of CT between Master Builders' iron and the catalyzed Fe-Cu process was discussed. The results showed that CT was reduced directly on the surface of copper rather than by atomic hydrogen produced at the cathode in the catalyzed Fe-Cu process. The reduction was realized largely by atomic hydrogen in Master Builders' iron. The entire CT in 350 ml aqueous solution with 320 mg/L was reduced to trichloromethane and dichloromethane in 2.25 h when 100 g of scrap iron with Fe/Cu ratio of 10:1 (w/w) were used. Moreover, the reduction rate slowed with time. CT could be reduced at acidic, neutral and alkaline pH from solution by Fe-Cu bimetallic media, but the mechanisms were different. The degradation rate was not significantly influenced by pH in the catalyzed Fe-Cu process; in Master Builders' iron it clearly increased with decreasing pH. The kinetics of the reductions followed pseudo-first order in both cases. Furthermore, the reductions under acidic conditions proceeded faster than that under the neutral and alkaline conditions. The catalyzed Fe-Cu process was superior to Master Builders' iron in treating CT-containing water and this advantage was particularly noticeable under alkaline conditions. The reduction was investigated in the cathode (Cu) and anode (Fe) compartments respectively, the results showed that the direct reduction pathway played an important role in the reduction by the catalyzed Fe-Cu process. The catalyzed Fe-Cu process is of practical value.

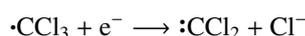
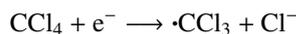
Key words: carbon tetrachloride; electrochemical reduction characteristics; catalyzed Fe-Cu process; reduction mechanisms

Introduction

Carbon tetrachloride (CT) is widely used in industry; mostly as a complex raw material and solvent. Carbon tetrachloride is capable of dissolving fat, oil paint, resin, rubber and similar substances easily; in addition, it is used frequently as a solvent for dry cleaning. Carbon tetrachloride is an onerous contaminant due to its carcinogenicity, environmental persistence, and relatively high solubility in water (805 mg/L at 20°C) (Sweeney and Fischer, 1972); it is commonly found in public water systems and in groundwater and surface water supplies at concentrations exceeding the maximum contaminant level of 5 µg/L (Reynolds *et al.*, 1990). Microbial degradation of CT can be relatively slow, and may be inhibited by the toxicity of CT or its dechlorinated product, chloroform (Helland *et al.*, 1995). There are strong environmental and economic incentives for improving existing methods of remediation and/or developing new treatment technologies for CT. Seeking to treat water containing this refractory compound, scientists performed extensive research and found that reductive dechlorination can occur abiotically under strongly reducing conditions, especially in the presence of galvanized steel, stainless steel and iron. Zero-

valent iron process and the iron-based bimetallic systems (Hooker and Klaubunde, 1994; Matheson and Tratnyek, 1994; Muftikian *et al.*, 1995; Li and Farrell, 2000) have provided an effective approach to treat wastewater. The reduction mechanisms related to iron-based bimetallic system are not fully understood. The mechanisms of contaminant degradation in these systems are of particular interest because they have direct bearing on the design of full-scale treatment operations.

Li and Farrell (2000) showed that CT was reduced to methane in a reactor with Fe and Pd/Fe electrodes. They came to a conclusion that the one-electron reduction of CT with the formation of trichloromethane free radical was the first step of the reductive reaction of CT:



Hooker and Klaubunde (1994) proposed that dissociation and chemical adsorption occurred and C-Cl bonds fractured when CT contacted the iron surface. Dechlorination rates and byproducts for most environmentally relevant halocarbons have been determined under a wide range of experimental conditions (Johnson *et al.*, 1996; Su and Puls, 1999; Wust *et al.*, 1999; Farrell *et al.*, 2000; Arnold and Roberts, 2000). Arnold and Roberts (2000)

reported that dechlorination rates for a series of chlorinated ethenes decreased with increasing degree of chlorination. Farrell *et al.* (2000) reported faster reaction rates for trichloroethylene (TCE) than for perchloroethylene. Finally, Wust *et al.* (1999) found that the relative rates of TCE and dichloroethylene reduction varied along the length of column reactors and also varied between batch and column systems. All these observations suggest that there may be multiple mechanisms for chlorinated ethane reduction on iron surface. The multiple mechanisms may include direct and indirect electron-transfer reactions. Halocarbons may also be reduced indirectly via reaction with atomic hydrogen produced from water reduction. These reactions may involve formation of hydrocarbon-hydride complexes on the iron surface (Li and Farrell, 2001).

CT was abiotically dechlorinated to chloroform and methylene chloride by zero valent iron (Helland *et al.*, 1995). Dechlorination of CT was rapid, and approximately followed first-order kinetics in the range of concentration tested (CT: 1.5–5.5 $\mu\text{mol/L}$; Fe^0 powder: 1–10 g per 265 ml distilled water). The initial dechlorination rate coefficient increased with iron surface area. Rate coefficients also increased with time, probably because of an increase in reactive surface area due to cathodic depolarization and pitting of the iron surface. Dechlorination also occurred under oxidic conditions, although the rates were significantly slower. A rapid pH increase was synchronous to dissolved oxygen consumption, and the pH remained constant after the oxygen was depleted. This was attributed to the proton and oxygen consuming aerobic corrosion of the Fe^0 surface. Elemental iron reduced part-per-thousand levels of aqueous-phase carbon tetrachloride to chloroform in a few hours (Warren *et al.*, 1995). Free metal ions, chloride and hydrogen gas were produced in the reaction; protons were consumed. Process kinetics was dependent on solution pH, surface area of the elemental, CT concentration, buffer selection and solvent composition (volume fraction 2-propanol). Reaction rate was first order with respect to CT at concentrations less than 7.5 mmol/L. This class of reaction offers promise as a means for initiating the destruction of heavily halogenated organic compounds.

According to a previous report (Ma, 2002), if a material having relatively high hydrogen overpotential, like copper, is used as a cathode, halo-hydrocarbon can be dehalogenated partly at the cathode. For example, CT can be dechlorinated to dichloromethane at a copper electrode. The ability of halo-hydrocarbons to reduce directly at an electrode decreases in the following order: RI > RBr > RCl > RF, because electro withdrawing power increases with increasing electron density descending down a group. In general, the C-I bond fractures at first, and C-F bond fractures at last, when various C-X (X: halide) bonds coexist in a molecule.

Our early work (Xu *et al.*, 2005a) showed that nitrobenzene was reduced directly on the surface of copper rather than by the hydrogen evolved at cathode in the catalyzed Fe-Cu process. Both acidity and alkalinity favored the direct reduction at the copper electrode. The catalyzed Fe-Cu process was superior to Master Builders' iron in

treating nitrobenzene-containing water. This advantage was particularly noticeable under alkaline conditions. The direct pathway had an important role in the reduction by the catalyzed Fe-Cu process. Reducing nitrobenzene directly at the copper electrode was found easier than reducing it by the hydrogen evolved at the cathode, so copper could be regarded as the electrocatalyst.

The electrochemical reduction characteristics of the chlorinated hydrocarbons were investigated using the cyclic voltammetry technique (Xu *et al.*, 2005b). The experiments indicated chlorinated alkanes and a part of chlorinated aromatic hydrocarbons were capable of being reduced directly at the copper electrode, but chlorinated aromatic hydrocarbons were not as easily reduced at the copper electrode as alkanes. Both acidity and alkalinity favor dechlorination of chlorinated hydrocarbons at the copper electrode.

The goal of this research was to investigate the mechanisms involved in reduction of CT from solution by Fe-Cu bimetallic media. The reduction mechanism at the copper electrode was discussed using cyclic voltammetry in this article. Meanwhile, the difference in reduction mechanisms between the Fe-Cu bimetallic system and Master Builders' iron was put forward. The dechlorination of CT by the catalyzed Fe-Cu process was analyzed, and the role of copper in this process was investigated. Additionally, batch experiments were performed at different pH to study the effect of solution pH on the reductions of CT by Fe-Cu bimetallic media and Master Builders' iron. The practicality of the catalyzed Fe-Cu process was also discussed.

1 Experimental

1.1 Reagents and instruments

Waste scrap iron (scrap cast iron) with a surface area of 0.3–0.4 m^2/g was received from the Mechanical Factory of Tongji University, washed with soap to remove oil and rinsed with doubly distilled water, thereafter the concentration of chlorine ion (Cl^-) was determined by titration with a 0.025 mol/L 1/2 $\text{Hg}(\text{NO}_3)_2$ solution (State Bureau of Environmental Protection, 1997) until the Cl^- concentration reached zero in its washing liquid. The catalyst was pure copper tinsel with a 0.12 mm thickness offered for sale in the market, and was cut into thin 5 cm \times 1 cm pieces before the experiments. Distilled water was used for conducting batch experiments and investigating the role of Cu in the reduction, the electrolyte for cyclic voltammetry was prepared using doubly distilled water. All reagents applied in the process of the experiments were analytical grade (AR).

A HYG-A shaker (Taicang Experimental Equipment, China) was applied to conducting the batch experiments. All the measurements of cyclic voltammetry were done with a conventional three-electrode configuration. A graphite electrode and a homemade copper electrode, whose surfaces are 1.33 cm^2 and 1.44 cm^2 respectively, were used as working electrodes. A Pt electrode served as

an auxiliary electrode and a model 232 saturated calomel electrode (SCE) (Shanghai Analytical Instrument, China) was used as a reference electrode. Cyclic voltammetry scanning was conducted using a CHI600A electrochemical station (Shanghai Chenhua Instrument), as was the stochastic software used to collect data and plot the cyclic voltammograms. Electrolysis was conducted using a DJS-292 Rex potentiostat (Shanghai Rex Instrument Co. Ltd., China) and a LW3J3 (30 V, 3 A) stabilized current supply (Shanghai Liyou Electric, China). A DDS-11C digital conductivity detector (Shanghai Tianda Instrument Co. Ltd., China) was used to measure conductance. A portable sensION2 pH/ISE meter (Hach, USA) was used to measure solution pH.

1.2 Experimental methods

1.2.1 Batch experiments

Dried the above-mentioned iron scrap of a 100-g weight by heating at 120°C, thereafter 100 g of the dry iron scrap was thoroughly mixed with Cu pieces in a desired proportion (10:1, w/w) and held them down so that the observed density reached approximately 0.5 kg/L. The mixture was then placed in a 500-ml wide neck ground-glass stoppered flask, and 350 ml of 320 mg/L CT-containing solution was added to the flask which was then covered. Afterwards, the flask and water was placed in the HYG-A shaker and shaken at 140 r/min for desired time (30, 60, 90, 120 min). A 50-ml aliquot was sampled from the flask with a close 10-ml injector and its composition was analyzed with Finnigan Voyager GC/MS.

1.2.2 Electrolysis

Electrolysis for determining the reactions corresponding to the reduction waves at the copper cathode was conducted in a non-diaphragm electrolytic cell; electrolysis for investigating the role of copper in reduction by the catalyzed Fe-Cu process was conducted in an electrolytic cell separated into 2 compartments by a permeable cellulose acetate membrane (Fig.1), each compartment is of size 5 cm × 5 cm × 10 cm. In the latter case, electrode processes were investigated in the anode compartment and cathode

compartment respectively. As shown in Fig.1, an iron piece sized 9 cm × 3.5 cm was used as anode, and a copper piece sized 9 cm × 3.5 cm was used as cathode.

Five hundred milliliters of CT-containing solution with 640 mg/L was electrolyzed for investigating the role of copper in the reduction by the catalyzed Fe-Cu process having the current under control at 0.5 A for a certain time (1, 2, 3, 3.5, 4, 4.5, 5 h). A 20-ml aliquot of water was sampled from the cathode and anode compartments respectively. The pH and conductance of the solution were measured, the solution was analyzed with GC/MS and part of the solution was titrated with Hg(NO₃)₂.

1.2.3 Cyclic voltammetry scanning

A 20-ml aliquot of aqueous organic solution was flushed with nitrogen gas continuously for about 1 min to drive away the O₂ dissolved in the water, then stabilized for 10–15 s. Cyclic voltammetry scanning rate was set at 4 V/s. In order to avoid oxidation of Cu, the highest scanning potential at the copper electrode was set at –0.2 V. The homemade copper electrode lay soaked in 10% (w/w) hydrochloric acid for approximately 2 h and acetone for 2 h separately to clean its surface.

1.2.4 Analytical methods

A Finnigan Voyager spectrometer (GC-MS) was used to analyze compositions of organic compounds in the water after the treatment. Ten liter of water was extracted with 1 ml of methane before injecting onto the column, and 1 µl of extracted sample was injected for analysis. The flow rate of helium, a carrier gas, was set at 1 ml/min. The MS was operated in electron impact mode (70 eV). Injection port temperature was 250°C and the column temperature started at 50°C for 2 min, was ramped to 250°C at a rate of 20°C/min and was finally held for 10 min. A non-polar capillary column of model DB/5 (30 m in length, 0.25 mm in diameter, the thickness of the stationary liquid 5% phenylpolydimethylsiloxane is 0.25 µm) was used in the analytical process. Cyclohexanone was used as an internal standard (IST) while determining the concentration of the CT-containing aqueous solutions after the treatment by the catalyzed Fe-Cu process.

2 Results and discussion

2.1 Cyclic voltammograms of CT at the graphite and the copper electrodes

Fig.2 represents the cyclic voltammetric response of 160 mg/L CT in 0.1 mol/L Na₂SO₄ aqueous solution for (a) the graphite and (b) the copper electrodes at a scan rate of 4 V/s. No response was found at the graphite electrode, indicating that CT is incapable of reducing directly at the graphite electrode. Only the hydrogen evolution wave was shown at the graphite electrode, so CT is mainly reduced by the hydrogen produced at the cathode.

Cast iron is an alloy of pure iron, carbon and some other impurities. Carbon and impurities are dispersed evenly as small granules in cast iron. Numerous corrosion cells are formed when the cast iron is immersed in an electrolyte so-

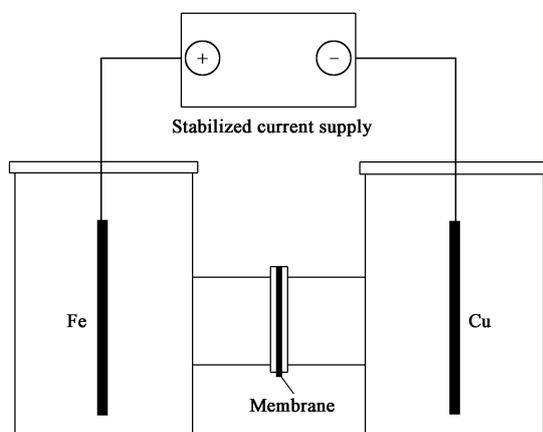


Fig. 1 Electrolytic cell for investigating the role of copper in the catalyzed Fe-Cu process.

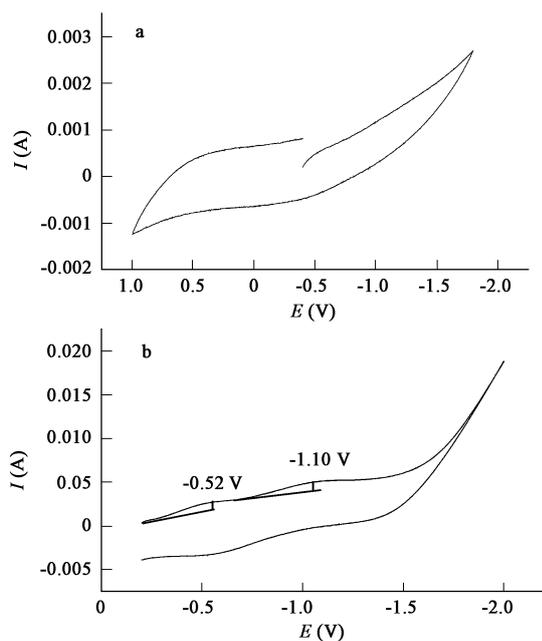


Fig. 2 Cyclic voltammograms of 160 mg/L CT in 0.1 mol/L Na₂SO₄ aqueous solution, supporting electrolyte: 0.1 mol/L Na₂SO₄. (a) graphite electrode; (b) Cu electrode.

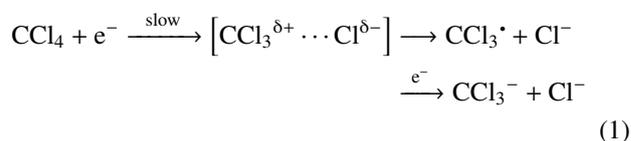
lution. In this case pure iron acts as the anode, and carbon acts as the cathode. CT is reduced indirectly at the cathode in Master Builders' iron; more specifically it is primarily reduced by the hydrogen produced at cathode and thus acidity of the solution strongly favors the reduction (Zhou and Fu, 2002; Li *et al.*, 2003). The results in Fig.2a are identical with previous findings.

CT gives two peaks corresponding to the irreversible electrochemical reduction at the copper electrode (Fig.2b), one is at -0.52 V, the other is at -1.10 V. The result indicates CT is irreversibly reduced at the copper electrode at the potentials of -0.52 V and -1.10 V or thereabout. In order to determine the reactions corresponding to the reduction waves at the copper cathode, electrolysis was conducted for $t = 16$ h having the cathodic potential under control at -0.52 V and -1.10 V (vs. S.C.E) respectively and using the copper electrode as cathode. GC/MS analysis showed that trichloromethane and dichloromethane were by far the dominating reduction products corresponding to the waves at -0.52 V and -1.10 V respectively. It suggests that the wave at -0.52 V corresponds to a reduction for formation of trichloromethane, and the wave at -1.10 V corresponds to a reduction for formation of dichloromethane. Trichloromethane corresponds to the more negative reduction peak, i.e., it is harder to be reduced directly at the copper electrode compared to CT.

A molecule of CT is liable to gain an electron due to the inductive electron-withdrawing effect (-I effect) of chlorine atoms. The C-Cl bond in the molecule extends and weakens as an electron nears a chlorine atom Cl, which causes this Cl atom with originally bonding electron pairs to leave the C atom gradually. Throughout all this the system's energy increases gently. The Cl atom draws nearer to the electron as the reaction proceeds further; then

it gradually leaves the C atom with an electron pair so that its negative charges increase continuously. Mean while, the remaining three Cl atoms associated with the C atom deflect from the first chlorine atom due to repulsion of particles with the same charge. As a result, a transition complex is formed in the system, which raises the system to a maximum energy level. Afterwards, the system's energy decreases with the further departure of the Cl atom from the C atom. The Cl atom leaves finally and converts to a Cl⁻, meanwhile the C atom turns electropositive and makes ready to be attacked by a new electron. In this way a carbanion is formed and stabilized due to dispersion of electrical charges in the system (Xu, 1993). The stability of carbanions greatly depends on the ability of substituent groups to disperse charges (Yu, 1981; Liang and Cheng, 1993).

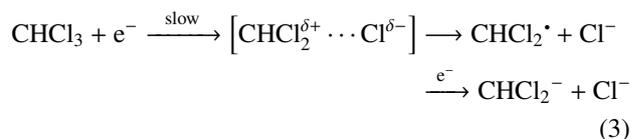
The formation of carbanions CCl₃⁻ at the copper electrode can be expressed figuratively as (Yu, 1981; Li and Farrell, 2001):



Annotation: the black point represents the gained electron, and the same thereafter.



The carbanion CCl₃⁻ transforms into electrochemically active trichloromethane after association with a H⁺ (Reaction (2)) present in the system (Yu, 1981; Li and Farrell, 2001). In the later cathodic scanning process trichloromethane turns into CHCl₂⁻ after gaining 2 electrons and thus forms the second cathodic wave (Yu, 1981; Li and Farrell, 2001):



Then the carbanion CHCl₂⁻ transforms into dichloromethane after association with a H⁺ (Reaction (4)):



Hence, the direct reduction of CT at the copper electrode comes down to the formation of carbanions and its association with hydrogen ions.

2.2 Effect of pH on the reduction by the catalyzed Fe-Cu process

Fig.3 shows the voltammograms of 160 mg/L CT in 0.1 mol/L Na₂SO₄ aqueous solution at the copper electrode under acidic (pH 3.0) and alkaline (pH 9.0) conditions.

The figures show that the reduction of CT takes place in both cases. At acidic pH the first wave has a lower current compared to that in Fig.2b, this is because carbanion—the

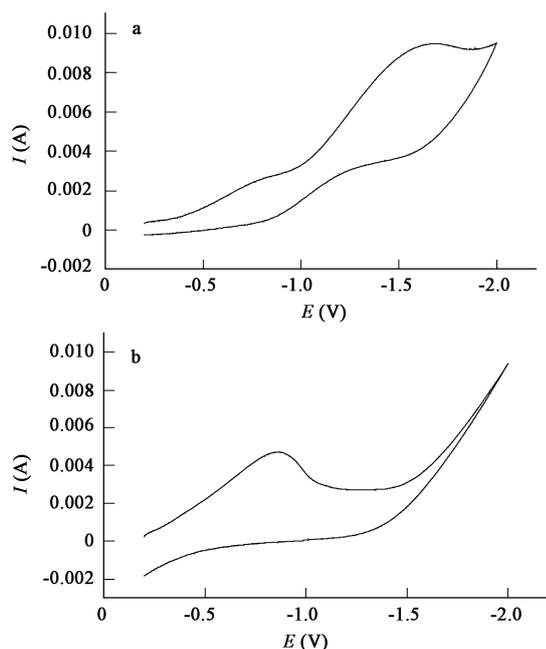


Fig. 3 Cyclic voltammograms of 160 mg/L CT in 0.1 mol/L Na₂SO₄ aqueous solution at the copper electrode at acidic and alkaline pH, supporting electrolyte: 0.1 mol/L Na₂SO₄. (a) pH 3.0; (b) pH 9.0

important intermediate of the direct reduction, is harder to form under acidic conditions. However, the current through the solution still remains high. This suggests that for the most part CT is not reduced directly at the copper electrode, but indirectly by the hydrogen produced at cathode because hydrogen is easy to produce in an acidic medium. GC/MS analysis showed that after 30 min degradation by the catalyzed Fe-Cu process the majority of CT was reduced to trichloromethane in the various mediums. However, CT was reduced faster in the acidic medium (Fig.4a). This supports that H⁺ played an important role in the dechlorination.

At alkaline pH the peak current is observed higher (Fig.3b) compared to the first peak in Fig.2b. This phenomenon is caused by formation of carbanion. C-Cl bonds in CT are liable to break under alkaline conditions, allowing easy formation of carbanion. This kind of reaction could be understood as a simple acid-base reaction (Liang and Cheng, 1993). Two reduction peaks coincided because of the fast direct reduction at the cathode.

GC/MS analysis showed that the entire CT in 350 ml aqueous solution with 320 mg/L was reduced to

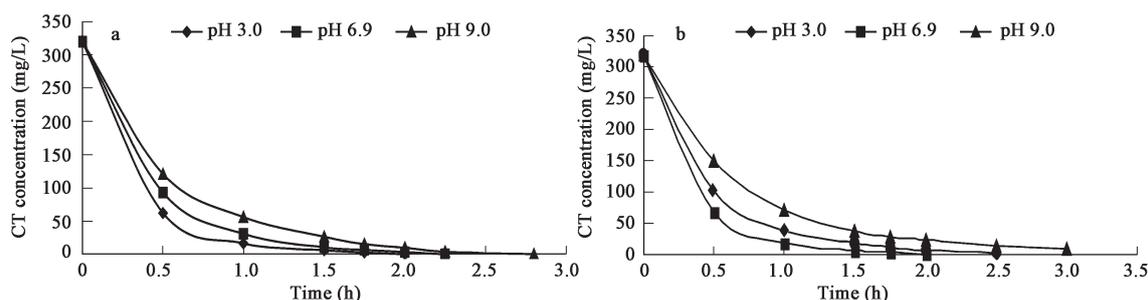
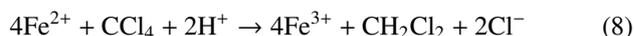
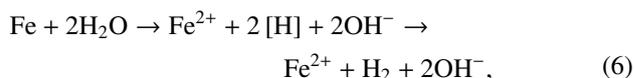
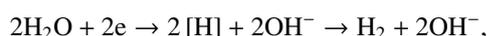
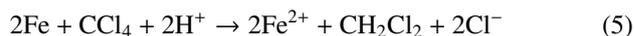


Fig. 4 CT concentration vs. time plot showing reduction of CT by the catalyzed Fe-Cu process (a) and Master Builders' iron (b). The initial concentration of the CT-containing aqueous solution approximately 320 mg/L, supporting electrolyte: 0.1 mol/L Na₂SO₄.

trichloromethane and dichloromethane in 2.0 h in the acidic medium, in 2.25 h in the neutral medium, and in 2.8 h in the alkaline medium (Fig.4a). The experimental results indicated that reduction by the catalyzed Fe-Cu process was not strongly influenced by solution pH as with Master Builders' iron (Fig.4b), it is noteworthy that the direct pathway can to a certain extent relieve the hydrogen ion shortage, characteristic of Master Builders' iron.

On the whole, the reduction of CT by the catalyzed Fe-Cu process is due to the net effect of the following pathways:



At acidic pH the heterogeneous process involving the oxidation and dissolution of iron in conjunction with the dechlorination of CT (Pathway (5)) performs an important function in the reduction of CT (Gillham and O'hannesin, 1994; Matheson and Tratnyek, 1994), but the Pathway (6) cannot be neglected because hydrogen is liable to evolve at lower pH. It is also possible that the acidic medium affects the iron surface, forming more corrosion crevices, which could increase the reduction rate. At neutral pH mainly the Pathways (6) and (7) (Pathways (7) is the sum of the Reactions (1)–(4)) contribute to the reduction. However, primarily CT is not reduced by hydrogen because it is a less facile reducing agent in the system. pH increase enhances the direct Pathway (7). Furthermore, hydrogen is not readily produced at alkaline pH, so the Pathway (7) becomes the dominating approach to the reduction of CT by the catalyzed Fe-Cu process. The Pathway (8) is negligible throughout the whole reduction because it is generally quite slow (Matheson and Tratnyek, 1994; Helland *et al.*, 1995).

An experiment was conducted to evaluate the contribution of the reduction by hydrogen gas. The results showed that the content of CT in the solution did not change in time, and it remained the same even one day later. This means H₂ is incapable of reducing CT without reference to

the existence of copper catalyst, only atomic hydrogen [H] takes part in the Pathway (6) because it loses the capacity to reduce CT after its conversion into H₂.

Wu *et al.* (2004) used the Fe-Cu bimetallic system to remediate CT-containing water and found that the faintly acidic conditions (pH approximately 5) favored the dechlorination most. Additionally, they found that the system covered a wide range of pH. The CT-containing water responded well to the dechlorination by the catalyzed Fe-Cu when pH changed from 2 to 10, pH did not significantly influence the degradation. The dechlorination rate fell drastically when pH > 10.5. The reasons for this phenomenon were not made clear in that research paper. Perhaps it was because the reduction mechanisms changed with pH. Under alkaline condition a certain number of H⁺ is also required for dechlorinating CT, although the direct Pathway (7) dominates in the system. When pH > 10.5, the system is lacking in hydrogen ions necessary for dechlorination of CT by the catalyzed Fe-Cu process. Chen *et al.* (2001) suggested that lowering solution pH might not expedite the degradation rate of trichloroethylene (TCE) by zero valent iron (ZVI) as it also caused faster disappearance of ZVI. This might also account for the phenomenon to a degree.

Our experimental results showed that the catalyzed Fe-Cu process was superior to Master Builders' iron in treating CT-containing water (Fig.4). This advantage was particularly noticeable under alkaline conditions; at acidic pH these 2 systems produced the similar results. This phenomenon was basically caused by the difference in reduction mechanisms between these 2 technologies. The kinetic study showed that the reduction of CT by the catalyzed Fe-Cu process conformed to pseudo-first order (Table 1). The reaction rate constant *K* equaled 2.6346, 2.2429 and 1.8409 h⁻¹ under the acidic, neutral and alkaline conditions respectively, this would mean the reduction under the acidic condition (pH approximately 3.0) proceeded faster than under the neutral (pH approximately 6.9) and faintly alkaline conditions (pH approximately 9.0). The dechlorination by Master Builders' iron approximately followed pseudo first-order kinetics as well (Table 1). But the reduction under the acidic condition (pH approximately 3.0) proceeded much faster than under faintly alkaline condition (pH approximately 9.0), i.e. acidity clearly increased the reduction rate. The reduction by the catalyzed Fe-Cu process was about 55% faster than by Master Builders' iron at pH approximately 9.0.

pH of alkaline wastewater does not need to be adjusted

Table 1 Reduction kinetics by the catalyzed Fe-Cu process and Master Builders' iron

Reduction condition (pH)	Equation of reduction kinetics	R ²	<i>K</i> (h ⁻¹)
3.0	ln (C ₀ /C) = 2.6346 <i>t</i>	0.9924	<i>K</i> _{cat} = 2.6346
	ln (C ₀ /C) = 2.4663 <i>t</i>	0.9912	<i>K</i> _{Mas} = 2.4663
6.9	ln (C ₀ /C) = 2.2429 <i>t</i>	0.9980	<i>K</i> _{cat} = 2.2429
	ln (C ₀ /C) = 1.8826 <i>t</i>	0.9945	<i>K</i> _{Mas} = 1.8826
9.0	ln (C ₀ /C) = 1.8409 <i>t</i>	0.9849	<i>K</i> _{cat} = 1.8409
	ln (C ₀ /C) = 1.1850 <i>t</i>	0.9746	<i>K</i> _{Mas} = 1.1850

to 2–3 before the water is treated by the catalyzed Fe-Cu process. This process can be applied to treating faintly alkaline wastewater. Moreover, it will not give rise to a hydrogen ion shortage as seen in Master Builders' iron, which further slows the reduction. The need for aeration is eliminated in this process; accordingly, iron and energy consumption will be reduced drastically. Copper is not plated on the iron by exposing the iron to a solution of Cu²⁺; the process therefore is simplified. With all these advantages the catalyzed Fe-Cu process can be considered a significant improvement over conventional treatment.

2.3 The role of Cu in the reduction by the catalyzed Fe-Cu process

Electrolysis of a CT-containing aqueous solution with 640 mg/L was conducted in the diaphragm electrolytic cell to determine the role of copper in the reduction by the catalyzed Fe-Cu process. The results are shown in Table 2 and Fig.5.

Table 2 Change of conductance and pH of the catholyte and anolyte with time

	Time of electrolysis (h)	Conductance (ms)	pH
Catholyte	1	28	12.9
	1.5	32.8	12.8
	2	34.6	13.0
	2.5	31.6	13.1
	3	30.5	13.1
	3.5	28.8	13.2
	4	27.8	13.2
	Anolyte	1	37.8
1.5		38.6	1.9
2		40	2.2
2.5		39.8	1.9
3		39	2.1
3.5		35	2.2
4		32	2.4

Condition: electrolytic current *I* = 0.5 A; cathode area *S* = 31.5 cm².

As shown in Table 2, conductance and pH changed with time because of dissolution of Fe in the anode compartment and reduction of CT and water in the cathode compartment. The conductance first increased due to oxidation and dissolution of iron and reduction of water and then decreased as a result of the formation of black magnetic ferrous oxide Fe₃O₄ in the anode compartment.

On the evidence of the experimental data shown in Fig.5, CT was reduced much faster in the cathode compartment indicating the direct pathway was of great importance to the reduction by the catalyzed Fe-Cu process. In the cathode compartment nearly all CT in the solution was reduced to the final product dichloromethane after 3.0 h electrolysis (Fig.5a), in 4.5 h CT was entirely reduced to dichloromethane; in an equally long time, the majority of the CT in the solution was merely dechlorinated to trichloromethane in the anode compartment (Fig.5b), just a percentage of dichloromethane (12.3%) was found among the reduction products by that time. The reduction rate slowed with time in the cathode compartment: in the first

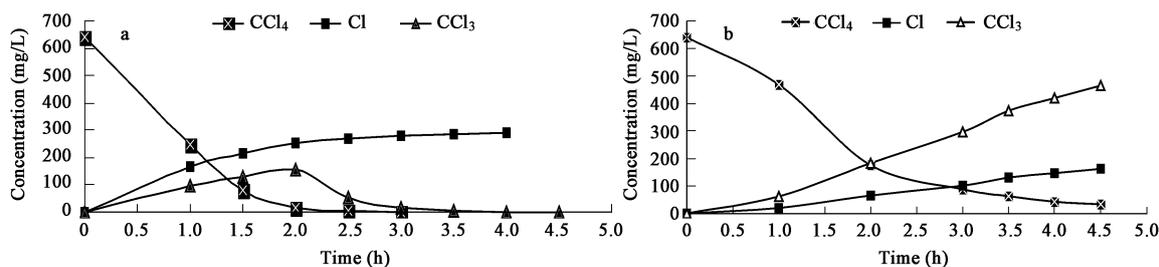


Fig. 5 Reduction of CT and production of Cl^- in Cu (a) and Fe (b) compartment with time. The initial concentration of the CT-containing aqueous solution approximately 640 mg/L, supporting electrolyte: 0.5 mol/L Na_2SO_4 .

hour of electrolysis more than 60% CT in the solution was reduced to trichloromethane and dichloromethane, in the second hour 36.02% CT was reduced, in the third hour merely 2.7% CT was dechlorinated (Fig.5a). This is because the intermediate reduction product trichloromethane was harder to reduce compared to CT.

The Pathway (5) seemed to play an important role in the anode compartment because the anolyte was highly acidic (pH approximately 1.9). Nevertheless the results differed at progressive stages: the concentration of CT decreased by 171.98 mg/L in the first hour of electrolysis; meanwhile merely a small number of Cl^- (20.32 mg/L) was produced in the anode compartment. The conversion rate of CT was not great (26.87%) in the first hour of electrolysis, it increased to 72.48% in the second hour. Cl^- grew in number simultaneously, but still remained much lower than that which should be produced in the anode compartment when the converted CT was just dechlorinated to trichloromethane, that is to say most of CT transformed was not reduced immediately but adsorbed to the surface of the iron electrode. After the surface of the iron electrode adsorbed sufficient CT molecules, its concentration markedly dropped to 102.13 mg/L, thereafter the dechlorination rate slowed. The production rate of chlorine ions in the cathode compartment was found much faster than in the anode compartment. The total chlorine decreased during the electrolysis in the anode compartment, according to mass balance 295.06 mg Cl^- should be produced in 1 L solution when 640 mg CT is completely reduced to dichloromethane. This suggested that a percentage of CT might not be desorbed from the iron surface.

From what is mentioned above we have reached a conclusion that the contribution of the Pathway (5) to the reduction was inconsiderable in the anode compartment in the first hour of electrolysis, in the latter 2 h it grew in strength, CT reduced faster as a result. Meanwhile, as a number of H^+ participated in the reduction, pH rose from 1.9 to 2.2. Afterwards, the reduction rate slowed. The reduction slowed in the cathode compartment. The Pathways (6) and (7) made a practical contribution to the reduction of CT. However, primarily CT was not reduced by hydrogen because it is a less facile reducing agent in the system. The cast iron used in the batch experiments has a large surface area (0.3–0.4 m^2/g), so absorption duration will probably be shorter in the catalyzed Fe-Cu process.

3 Conclusions

CT is reduced directly on the copper surface rather than by atomic hydrogen produced at cathode in the catalyzed Fe-Cu process. It is reduced largely by atomic hydrogen in Master Builders' iron. The reduction of CT by the catalyzed Fe-Cu process produced trichloromethane and dichloromethane. Moreover, the reduction slowed with time. The entire CT in 350 ml aqueous solution with 320 mg/L was reduced to trichloromethane and dichloromethane in 2.25 h when 100 g of scrap iron with Fe/Cu ratio of 10:1 (w/w) were used. CT is capable of reducing in acidic, neutral and alkaline mediums, but the mechanisms are different: atomic hydrogen produced at cathode and Fe^0 make a practical contribution in the acidic medium; in the neutral medium the direct pathway dominates in the system, but the reduction of water must be considered as well in the cathodic reduction; in the alkaline medium, due to ease of formation of carbanion—the important intermediate—the direct pathway becomes the dominating approach to the CT reduction. The dechlorination of CT by the catalyzed Fe-Cu process approximately followed pseudo-first order, the reduction under the acidic condition (pH approximately 3.0) proceeded faster than under the neutral (pH approximately 6.9) and the alkaline conditions (pH approximately 9.0). However, the treatment was not significantly influenced by solution pH in the catalyzed Fe-Cu process. Acidity clearly favored the reduction by the Master Builders' iron. The catalyzed Fe-Cu process was superior to Master Builders' iron in treating CT-containing water. This advantage was particular noticeable under alkaline conditions, the reduction by the catalyzed Fe-Cu process was about 55% faster than by the Master Builders' iron when pH = 9. This technology therefore is of practical value. The reduction rate of CT slowed in the cathode compartment because the intermediate reduction product-trichloromethane was harder to reduce. After the surface of the iron electrode adsorbed sufficient CT molecules in the anode compartment, the reduction rate increased. Thereafter the reduction rate slowed again.

References

- Arnold W A, Roberts A L, 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction

- with Fe(0) particles[J]. *Environ Sci Technol*, 34: 1794–1805.
- Chen J L, Al-Abed S R, Ryan J A *et al.*, 2001. Effects of pH on dechlorination of trichloroethylene by zero-valent iron[J]. *J Hazard Mater*, B83: 243–254.
- Farrell J, Melitas N, Kason M *et al.*, 2000. Electrochemical and column investigation of iron-mediated reductive dechlorination of trichloroethylene and perchloroethylene[J]. *Environ Sci Technol*, 34: 2549–2556.
- Gillham R W, O'hannesin S F, 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron[J]. *Ground Water*, 32: 958–967.
- Johnson T L, Scherer M M, Tratnyek P G, 1996. Kinetics of halogenated organic compound degradation by iron metal[J]. *Environ Sci Technol*, 30: 2634–2640.
- Helland B R, Alvarez P J J, Schnoor J L, 1995. Reductive dechlorination of carbon tetrachloride with elemental iron[J]. *J Hazard Mater*, 41: 205–216.
- Hooker P D, Klaubunde K J, 1994. Destructive absorption of carbon tetrachloride on iron(III) oxide[J]. *Environ Sci Technol*, 28: 1243–1247.
- Liang S Y, Cheng B C, 1993. High organic chemistry–structure–reaction–composition[M]. Beijing: Higher Education Press. 102–105; 113–119.
- Li T, Farrell J, 2000. Reductive dechlorination of trichloroethene and carbon tetrachloride using iron and palladized-iron cathodes[J]. *Environ Sci Technol*, 34: 173–179.
- Li T, Farrell J, 2001. Electrochemical investigation of the rate-limiting mechanisms for trichloroethylene and carbon tetrachloride reduction at iron surface[J]. *Environ Sci Technol*, 35: 3560–3565.
- Li T Y, Feng X X, Cheng L, 2003. Study on treatment of chlorinated organic wastewater by iron scrap fillings[J]. *Shanghai Environmental Sciences*, 22: 649–651.
- Ma C A, 2002. Introduction to organic electrosynthesis[M]. Beijing: Science Press. 211–213.
- Matheson L J, Tratnyek P G, 1994. Reductive dechlorination of chlorinated methanes by iron metal[J]. *Environ Sci Technol*, 28: 2045–2053.
- Muftikian R, Fernando Q, Korte Nic, 1995. Method for the rapid dechlorination of low molecular weight chlorinated hydrocarbons in water[J]. *Water Res*, 29: 2434–2439.
- Reynolds G W, Hoff J T, Gillham R W, 1990. Sampling bias caused by materials used to monitor halocarbons in groundwater[J]. *Environ Sci Technol*, 24: 135–139.
- State Bureau of Environmental Protection, 1997. The monitoring and analysis of water and wastewater[M]. Third ed. Beijing: China Environmental Science Press. 290–292.
- Su C, Puls R W, 1999. Kinetics of trichloroethene reduction by zerovalent iron and tin: pretreatment effect, apparent activation energy, and intermediate products[J]. *Environ Sci Technol*, 33: 163–168.
- Sweeney K H, Fischer J R, 1972. Reductive degradation of halogenated pesticides[P]. U.S. Patent, No. 3,640,821, 8.
- Warren K D, Arnold R G, Bishop T L *et al.*, 1995. Kinetics and mechanism of reductive dehalogenation of carbon tetrachloride using zero-valence metals[J]. *J Hazard Mater*, 41: 217–227.
- Wu D L, Ma L M, Wang Z *et al.*, 2004. Study on the contributing factors to variation of pH in dechlorination of chlorohydrocarbons by Fe-Cu bimetallic system[J]. *Industrial Water & Wastewater*, 35: 43–46.
- Wust W F, Kober R, Schlicker O *et al.*, 1999. Combined zero- and first-order kinetic model of the degradation of TCE and cis-DCE with commercial iron[J]. *Environ Sci Technol*, 33: 4304–4309.
- Xu S C, 1993. Organic chemistry[M]. Second ed. Beijing: Higher Education Press. 185–191.
- Xu W Y, Gao T Y, Fan J H, 2005a. Reduction of nitrobenzene by the catalyzed Fe-Cu process[J]. *J Hazard Mater*, B123: 232–241.
- Xu W Y, Gao T Y, Zhou R F *et al.*, 2005b. The electrochemical reduction characteristics of chlorinated hydrocarbon at the copper electrode and the impact of pH on them[J]. *Environmental Chemistry*, 24: 318–321.
- Yu L J, 1981. Basic theoretical organic chemistry[M]. Second ed. Beijing: People's Education Press. 181–192; 463–466; 477–479.
- Zhou H Y, Wang D H, Huang X W, 2002. Treatment of resistant–biodegradable dye wastewater with iron filling[J]. *Environ Pollution Control*, 24(4): 219–221.