Bull Environ Contam Toxicol (2009) 82:137–144
DOI 10.1007/s00128-008-9574-7

The Dechlorination of Pentachlorophenol by Zerovalent Iron in Presence of Carboxylic Acids

**Meifang Hou · Hongfu Wan · Qixing Zhou ·
Xinming Liu · Wei Luo · Yanning Fan**

Received: 20 December 2007 / Accepted: 2 October 2008

Abstract The dechlorination of pentachlorophenol (PCP) by zerovalent iron (Fe^0) in presence of low molecular weight carboxylic acids was investigated. The experimental results showed that oxalic acid was advantaged among the selected acids for the dechlorination of PCP. The lower pH value and the higher dosage of Fe^0 were favorable for the enhancement of dechlorination efficiency. With their strong complexing and pH buffering properties, carboxylic acids favored the fresh surface of iron, which benefits to the dechlorination of PCP by Fe^0. Moreover, the oxalate-iron complexes have more reductive activities and then lead to the highest dechlorination efficiency of PCP by Fe^0.

Keywords Dechlorination · Pentachlorophenol · Zerovalent iron · Carboxylic acid

Pentachlorophenol (PCP, C_6Cl_5OH), as a kind of ionizable hydrophobic organic contaminants, has been used extensively in the agricultural, industrial and domestic application as a component of fungicides, bactericides, herbicides, insecticides, molluscides, biocides, and wood preservatives. Based on the evidences from animal toxicity studies and human clinical data, the United States Environmental Protection Agency (USEPA) has classified PCP as a probable human carcinogenic chemical (B_2). PCP and its impurities not only give rise to accumulation and biological amplification, but also cause immunological and endocrine disorders and infertility problems in human. The degradation and transformation of PCP have been paid great attention because its adverse effects on environment and human being might continue for a long time (Hyun and Lee 2004).

Recently, reductive dechlorination by zerovalent iron based on the permeable reactive barrier (PRB) technology as an economic alternative is of environmental importance and has been paid great attention (Kim and Carraway 2000; He et al. 2004; Leen et al. 2005), because the less-chlorinated products are generally less toxic and decomposed more easily through a natural biodegradation than the more highly chlorinated parent compounds.

It is generally believed that a two-electron transfer directly or indirectly at the iron surface might be involved in the process of dechlorination, while zerovalent iron (Fe^0) is oxidized into ferrous irons, iron oxides or hydroxides on the surface of zerovalent iron, which might influence the effectiveness and longevity of PRB for in situ environmental remediation of pollutants.

Carboxylic acids, such as oxalic acid and citric acid, are the common low molecular weight organic acids in the soils and surface water environments (Cotter-Howells et al. 2000). These low molecular weight organic acids are usually involved in the enhancement of mineral dissolution processes, which plays an important role in the soil formation process, the mobility and bioavailability of toxic metal and organic contaminants and in the industrial processes such as the removal of rusts during metal treatment and textile cleaning processes (Stumm and Sulzberger 1992; Anderson et al. 1994; Cotter-Howells et al. 2000; Johnson et al. 2004; Jordi and Jiechar 2006). However, there are few reports about the dechlorination process of

---

M. Hou · H. Wan (✉) · Q. Zhou · X. Liu · W. Luo · Y. Fan
Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, People's Republic of China
e-mail: hfwan@soil.gd.cn

Q. Zhou
e-mail: zhouqx523@yahoo.com

PCP by Fe^0 in the presence of the low molecular weight organic acids.

The objective of this study is to investigate the effect of carboxylic acids on the dechlorination of PCP by Fe^0. Oxalic acid, acetic acid, tartaric acid and citric acid as carboxylic acids were used in the experiments. For comparison, nitric acid as an inorganic acid, was also studied since nitrate was common contaminant found in the soils and surface water environments. In the presence of carboxylic acids, the pH value and Fe^0 dosage for the reductive dechlorination of PCP were also examined.

Materials and Methods

The zerovalent iron (Fe^0) powder of 100 mesh was purchased from Tianjin Kermel Chemical Reagent Development Center, China. The specific surface area of the iron powder measured by the Brunauer-Emmett-Teller (BET) analysis and N_2 adsorption was 7.5 $m^2\ g^{-1}$. PCP with a purity of >99% (w/w) was purchased from Aldrich. Oxalic acid, citric acid, tartaric acid, acetic acid and other chemicals with analytical reagent grade were purchased from Shanghai Chemical Co., China. The reaction solutions were prepared with the deionized water which was free of O_2 and CO_2.

Aqueous PCP solution was prepared with an initial concentration of 10 mg L^{-1} and iron power was added into the reaction solution with a dosage of 3 g L^{-1}. The batch dechlorination experiments of PCP in aqueous solution were carried out in a 250 mL flask under N_2 gas flow at temperature of 298 ± 1 K in the dark. The effect of various factors including different acids, pH and the dosage of Fe^0 on the dechlorination of PCP was investigated. In all experiments, 200 mL of PCP solution at the desired pH was first purged with N_2 gas for 30 min prior to reaction, and then the Fe^0 powder was added into the reaction solution under the vigorous stirring. During the reaction, N_2 gas was continuously bubbled to keep an oxygen-free status in the solution. The suspension samples were taken at different time intervals and then centrifuged at 4,500 rpm for 30 min to remove particulates prior to analysis.

The concentration of chloride ion released during the reaction was determined by ionic chromatography (IC, Dionex 120 equipped with a conductivity detector) with a 4-mm anionic exchange column (IonPack AS4A-SC-Dionex). The pH value during the reaction was determined by a pH meter (pHS-3C, Shanghai, China). The concentration of PCP was determined by HPLC (Waters 1,525/2,487), in which a mobile phase consisted of 1% (w/w) acetic acid (20%) and methanol (80%) was used and PCP was detected by a UV detector at 295 nm.

The surface morphologies and surface elemental composition of the Fe^0 powder before and after reaction were examined by the Scanning Electron Micrograph and Energy Dispersive X-Ray Spectrometer (JSM-5910 Microscope and Noran EDS, Japan). The X-Ray Powder Diffraction (XRD) was used for characterization with a Rigaku D/max 2500 diffractometer using Cu Kα radiation; an accelerating voltage was 40 kV and an emission current was 40 mA. The Fourier transform infrared (FTIR) spectra of the Fe^0 powder before and after reaction were recorded as KBr pellets in the spectral range 4,000–400 cm^{-1} by a Perkin–Elmer 1725X FTIR spectrometer at room temperature.

Results and Discussion

Since the toxicity of chlorinated phenols can be reduced by removing chlorine from their molecules, the dechlorinatinon of PCP by Fe^0 can be evaluated by a degree of organic chlorine mineralization (*OCM*). On the basis of the literature (Ma et al. 2005), *OCM* was defined by the following equation (Eq. 1) in this paper. The higher *OCM* value means the lower toxicity and the higher biodegrability.

$$OCM(\%) = 100 \times (\mathrm{Cl_t}/\mathrm{Cl_0}) \qquad (1)$$

where Cl_0 represents the supposed total amount of chlorine released completely from PCP in the experiments (mg); Cl_t is the amount of chloride ion released in the reaction solution at time t (mg).

One set of experiments was carried out to study the effect of different carboxylic acids on the reduction and dechlorination of PCP in aqueous solution by Fe^0 powder. The experimental results about the reduction and dechlorination of PCP are shown in Fig. 1. The results demonstrated that in the absence of acid, the reduction of PCP by Fe^0 alone was very weak. However, in the present of acids, PCP was reduced much faster. It is noted that PCP can be almost completely reduced by Fe^0 in the presence of oxalic acid within 30 min. It is also evidenced that the dechlorination of PCP in terms of *OCM* was more slowly than the PCP reduction significantly. After 120 min reaction under N_2 gas flow, *OCM* was achieved by 53.3% (A), 41.1% (B), 7.57% (C), 6.90% (D), and 6.61% (E) for oxalic acid, citric acid, tartaric acid, acetic acid and nitric acid, respectively. It is clear that the effects of oxalic acid and citric acid were remarkably significant than any other acids. Furthermore, it was found that the dechlorination of PCP by Fe^0 in the presence of oxalic acid under an air flow condition (F) was much more slowly than that under the N_2 gas flow (A).

By fitting with the pseudo-first-order kinetic model, the kinetic constants for the reduction reaction of PCP by Fe^0 in the presence of 0.1 mol L^{-1} different carboxylic acids were

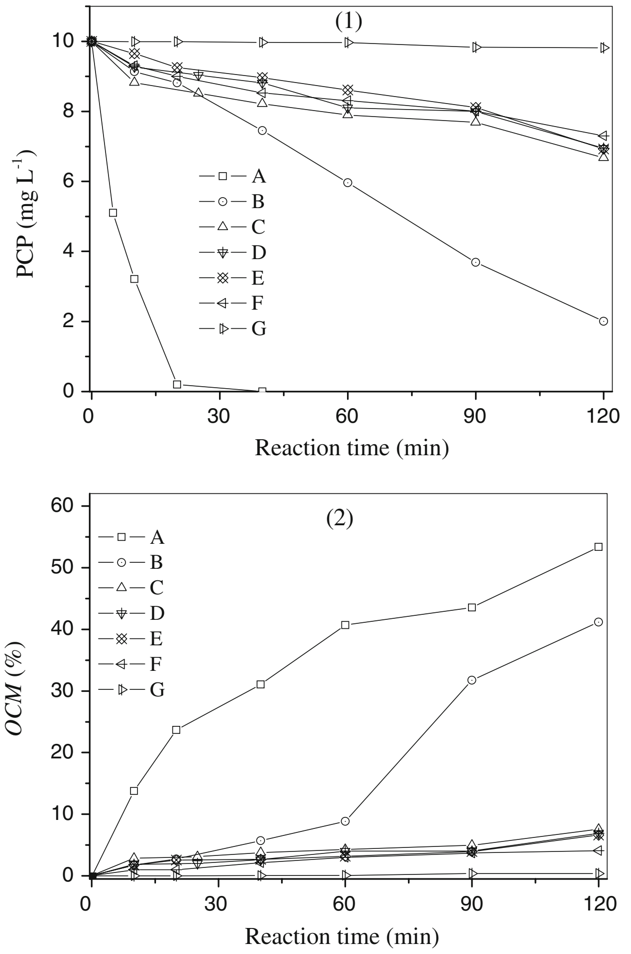


Fig. 1 The degradation of 10 mg L^{-1} PCP (1) and dechlorination efficiencies (2) by Fe^0 in the presence of 0.1 mol L^{-1} oxalic acid + N_2 (**a**), 0.1 mol L^{-1} citric acid + N_2 (**b**), 0.1 mol L^{-1} tartaric acid + N_2 (**c**), 0.1 mol L^{-1} acetic acid + N_2 (**d**), 0.1 mol L^{-1} nitric acid + N_2 (**e**), 0.1 mol L^{-1} oxalic acid + air (**f**) and without acids + N_2 (**g**) (Fe^0 dosage = 3.0 g L^{-1}, initial pH = 3.00)

determined to be 277.68 × 10^{-3} min^{-1} (R = 0.985) for oxalic acid + N_2, 13.04 × 10^{-3} min^{-1} (R = 0.979) for citric acid + N_2, 2.73 × 10^{-3} min^{-1} (0.950) for tartaric acid + N_2, 2.67 × 10^{-3} min^{-1} (0.975) for acetic acid + N_2, 2.75 × 10^{-3} min^{-1} (0.980) for nitric acid + N_2, 2.28 × 10^{-3} min^{-1} (0.972) for oxalic acid + air and 0.16 × 10^{-3} min^{-1} (0.932) for N_2 without acid.

With the increasing of reaction time, the pH values of reaction solutions increased gradually. The pH value increased after 1 h reaction (Table 1). It should be noted that the increased value of pH in the presence of nitric acid was much higher than those in the presence of carboxylic acids, although the same initial pH values of the reaction solution were derived from 0.1 mol L^{-1} nitric acid, acetic acid, tartaric acid, citric acid and oxalic acid by the neutralization of 1.0 mol L^{-1} NaOH.

From Table 1, it can be seen that oxalic, acetic, tartaric, citric acid and acetic acid are weak organic acids (Su and Puls 2004) and most of them dissociate in aqueous solution by several steps with multiple pK_a values (Oxalic acid, $pK_{a1} = 1.21$ and $pK_{a2} = 4.13$; tartaric acid, $pK_{a1} = 2.99$ and $pK_{a2} = 4.23$; citric acid, $pK_{a1} = 3.08$, $pK_{a2} = 4.63$ and $pK_{a3} = 6.18$), except acetic acid ($pK_a = 4.71$) (Smith and Martell 1979). These dissociation characters of carboxylic acids allow a slow proton release to slow down the pH increase during the reaction. Compared to a strong inorganic acid, the weak organic acids might have much more pH buffering capacity. For example, nitric acid (HNO_3) as a strong inorganic acid has high dissociation ability in aqueous solution, which provides sufficient protons for reacting with Fe^0 and results in a rapid pH increase. From this point of view, the carboxylic acids might be more favorable than nitric acid for buffering the reaction solution, which might be beneficial to the dechlorination of PCP by Fe^0 in aqueous solution.

The experimental results showed that oxalic acid was the most favorable for the dechlorination of PCP than the other selected organic acids and nitric acid in the experiments. Moreover, derived from root exudates of plants and other natural sources, oxalic acid is abundant in the natural environment (Jordi and Jiechar 2006; Wang and Stone 2006). Thus, oxalic acid was used in the following experiments for investigating the effects of pH value and Fe^0 dosage on the dechlorination of PCP by Fe^0. Moreover, *OCM* was chosen for characterizing the dechlorination efficiency of PCP by Fe^0 in the following experiments.

The effect of pH on the dechlorination of PCP was investigated at initial pH 2.00, 3.00, 4.00, and 5.00 adjusted by 1 mol L^{-1} NaOH when 0.1 mol L^{-1} oxalic acid was used, respectively. The results showed that the *OCM* after 2 h decreased with the increased initial pH (Fig. 2), and indicated that dechlorination of PCP was achieved by 65.3%, 53.3%, 16.0%, and 12.2% at pH 2.00, 3.00, 4.00, and 5.00, respectively, which means that the lower pH would achieve the higher *OCM*.

In general, PCP or its intermediates (designated as $PhCl_x$) in aqueous solution can be reduced by zerovalent iron under an oxygen-free condition by the following reactions (Eqs. 2–5).

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad E^0\left(Fe^{2+}/Fe\right) = -0.44\ V \qquad (2)$$

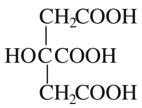
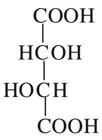
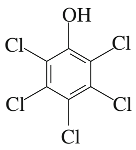
$$H_2 \rightarrow 2H^+ + 2e^- \quad E^0(H^+/H_2) = 0.00\ V \qquad (3)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^0\left(Fe^{3+}/Fe^{2+}\right) = 0.77\ V \qquad (4)$$

$$PhCl_x + e^- \rightarrow PhCl_{x-1} + Cl^- \; E^0(PhCl_x/\,PhCl_{x-1}) = 0.85 - 0.99\ V \text{ (Li and Hoffman 1999)} \qquad (5)$$

From the above equations, it is indicated that more hydrogen can be generated at lower pH to maintain a fresh surface of iron powder and also to stabilize the ferrous ion,

Table 1 The properties of organic acids and nitric acid and their effects on the dechlorination of PCP by Fe^0

Acids	Chemical structure	pK value	$pH_{0.1\ M}$[a]	ΔpH[b]	$LgK_{Fe(II)L}$	$LgK_{Fe(III)L}$	E^0, V[c]	El, wt.%[d]
Oxalic acid	HOOC—COOH	$pK_{a1} = 1.21$, $pK_{a2} = 4.13$	1.28	<0.15	3.50	8.59	0.21, 0.47	Fe, 98.76 C, 1.21 Cl, 0.03
Citric acid	 $\mathrm{CH_2COOH}$ $\mathrm{HOCCOOH}$ $\mathrm{CH_2COOH}$	$pK_{a1} = 3.08$, $pK_{a2} = 4.63$, $pK_{a3} = 6.18$	2.06	<0.15	5.53	12.30	0.37, 0.53	Fe, 99.32 C, 0.68
Tartaric acid	 COOH HCOH HOCH COOH	$pK_{a1} = 2.99$, $pK_{a2} = 4.23$	2.06	<0.15	2.73	7.22	0.51	Fe, 98.98 C, 0.94 Cl, 0.08
Acetic acid	CH_3COOH	$pK_a = 4.71$	2.89	0.86	1.22	3.75	–	Fe, 99.39 C, 0.61
Nitric acid	HNO_3	–	1.00	2.52	–	–	–	Fe, 91.65 O, 6.01 C, 2.38 Cl, 0.06
Pentachloro-phenol, PCP		$pK_a = 4.74$	–	–	–	–	–	Fe, 92.66 O, 3.84 C, 3.31 Cl, 0.19

[a] pH values when the concentration of 0.1 mol L^{-1} acids present in the solution

[b] The changes of pH values before and after reaction of 1 h (ΔpH)

[c] Standard reduction potentials for the complexes of iron-ligands (E^0/V)

[d] Elements compositions on the surface location of iron powder derived from the results of EDS, wt.%

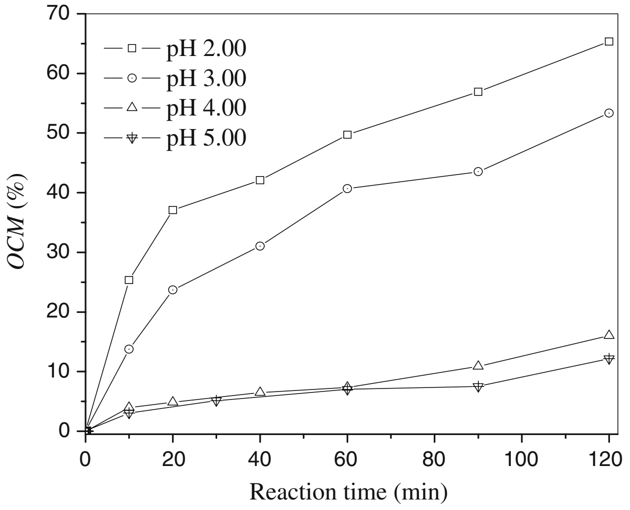


Fig. 2 The effect of initial pH on the dechlorination of 10 mg L^{-1} PCP with the Fe^0 dosage of 3.0 g L^{-1} in the presence of 0.1 mol L^{-1} oxalic acid under nitrogen gas condition

which might be favorable for the dechlorination of PCP in the experiments.

To study the effect of Fe^0 dosage on PCP dechlorination, one set of experiments was conducted in aqueous PCP solution with an initial concentration 10 mg L^{-1} at initial pH 3.0 in the presence of oxalic acid. The experimental results are presented in Fig. 3. It can be seen that *OCM* increased significantly with the increased Fe^0 dosage. The degree of *OCM* was achieved by 4.1%, 44.9%, 53.3%, and 71.3% after 2 h reaction by the Fe^0 dosages of 1.0, 2.0, 3.0, and 5.0 g L^{-1}, respectively. It is believed that the effective area of fresh iron surface would be a critical factor to affect the reactions of PCP reduction and dechlorination. Hence, the higher Fe^0 dosage leads to the larger fresh surface of iron and results in a higher degree of PCP dechlorination.

Carboxylic acids such as oxalic acid, citric acid, tartaric acid and acetic acid can provide sufficient protons to form complex with metal ions and may influence the redox potential of the iron surface in the soil and surface environments. In the above experiments, the used iron powder samples were collected after 1 h reaction and characterized by SEM, EDS, FTIR and XRD after dried in N_2 gas. The analytical results were compared with that of the raw iron powder.

The SEM patterns of the iron powder samples were shown in Fig. 4. Compared with the morphology of the raw iron powder, it can be seen that there were the obvious surface pulverization and particle aggregation of iron powder in the nitric acid system and the bulk system without any acids, but there were fresh surface with just a few of pit corroded sites on the surface of iron powder in the carboxylic acids' systems. It is suggested that carboxylic acids favor for removing the coating of iron oxides or hydroxides on the raw iron powder in the initial period of reaction and for inhibiting the formation of the coating of iron oxides or hydroxides during the reaction.

The EDS and FTIR results were presented in Table 1 and Fig. 5. The EDS results confirmed the existence of Fe and C elements on the surface of the raw iron powder and the used iron powders with citric acid and acetic acid; Fe, C and Cl elements on the surface of the used iron powders with oxalic acid and tartaric acid; and Fe, O, C or Cl elements on the surface of the used iron powders with nitric acid and without any acids (Table 1). Fe element on the surface of the raw iron powder and the used iron powder was ascribed to the bulk Fe^0 and a little amount of iron oxides or hydroxides. C element might result from the EDS sampling preparation or the adsorption of PCP or its intermediates. Cl might be due to the adsorption of PCP or its intermediates. Thus, it can be deduced that some iron oxides or hydroxides were formed on the surface of the iron powder used in the systems with nitric acid and without any acids. Figure 5 showed the FTIR spectra of the raw iron powder and the used iron powder. The band at 3,428 cm^{-1} was ascribed to OH stretching vibration and the one at 1,641 cm^{-1} to the OH bending vibration of surface adsorbed water (Klose et al. 2005). The bands at 587 and 579 cm^{-1} were assigned to the Fe–O vibrations of iron oxide-hydroxides (Mikhlin et al. 2002; Cornell and Schwertmann 2003; Xu and Axe 2005; Fu and Quan 2006). The results showed that there were the obvious Fe–O vibrations and OH stretching vibrations of the raw iron powder and the used iron powder in the system either with nitric acid or without any acids, which suggested that some iron oxides or hydroxides was formed on the surface of the iron powder during the reaction, while there was only a little coating of iron oxides or hydroxides on the surface of the raw iron powder under the natural environment before reaction. Thus, the results of SEM, EDS and FTIR were coincident one another.

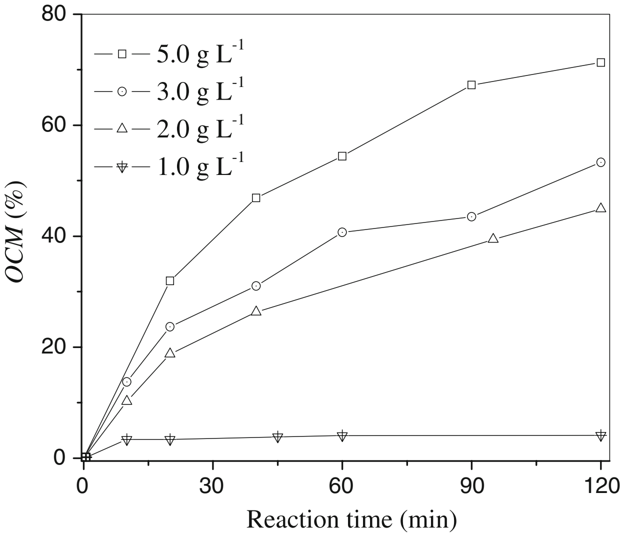


Fig. 3 Dechlorination of 10 mg L^{-1} PCP with different Fe^0 dosage at pH 3.00 in the presence of 0.1 mol L^{-1} oxalic acid under nitrogen gas condition

The XRD patterns (Fig. 6) showed that no crystalline iron oxides or hydroxides were found on the surface of either raw or used iron powder but the crystallinity of Fe^0 increased in the existence of carboxylic acids, which indicates that the existence of carboxylic acids could inhibit any coating of iron oxide or hydroxides on the surface of iron powder during the reaction and would be beneficial to dechlorination reaction of PCP with fresh surface of iron powder.

As shown by the experimental results, carboxylic acids were more favorable for improving the dechlorination of PCP by Fe^0 in anaerobic environments. On one hand, the positive effect of carboxylic acids on the dechlorination of PCP by Fe^0 might be attributed to their strong complexing and pH buffering properties. The critical stability constants of Fe(II)-ligands ($LogK_{Fe(II)\text{-}L}$) were 3.50, 5.53, 2.73, 1.22 for oxalate, citrate, tartarate and acetate (Smith and Martell, 1979), respectively. The critical stability constants of Fe(III)-ligands ($LogK_{Fe(III)\text{-}L}$) were 8.59, 12.30, 7.22, 3.75 for oxalate, citrate, tartarate and acetate (Smith and Martell, 1979), respectively. The strong complexing and pH buffering properties of carboxylic acids can help them dissolve iron and the surface iron oxides or hydroxides, inhibit the formation of novel iron oxides or hydroxides and buffer the reaction solution, which can effectively advance the dechlorination of PCP by Fe^0.

On the other hand, the complexes of carboxylic-iron might play much more important role in the improvement of the dechlorination of PCP since the complexes of carboxylic-iron have much stronger reductive activities for the homogeneous reductive dechlorination of PCP. The standard reduction potentials of Fe^{II}-Oxalate, Fe^{II}-Oxalate$_2$, Fe^{II}-Citrate, Fe^{II}-HCitrate and Fe^{II}-Tartarate are 0.47, 0.21, 0.37, 0.53 and 0.51 V (Stumm and Morgan 1996), respectively. Among the carboxylic acids, besides of its

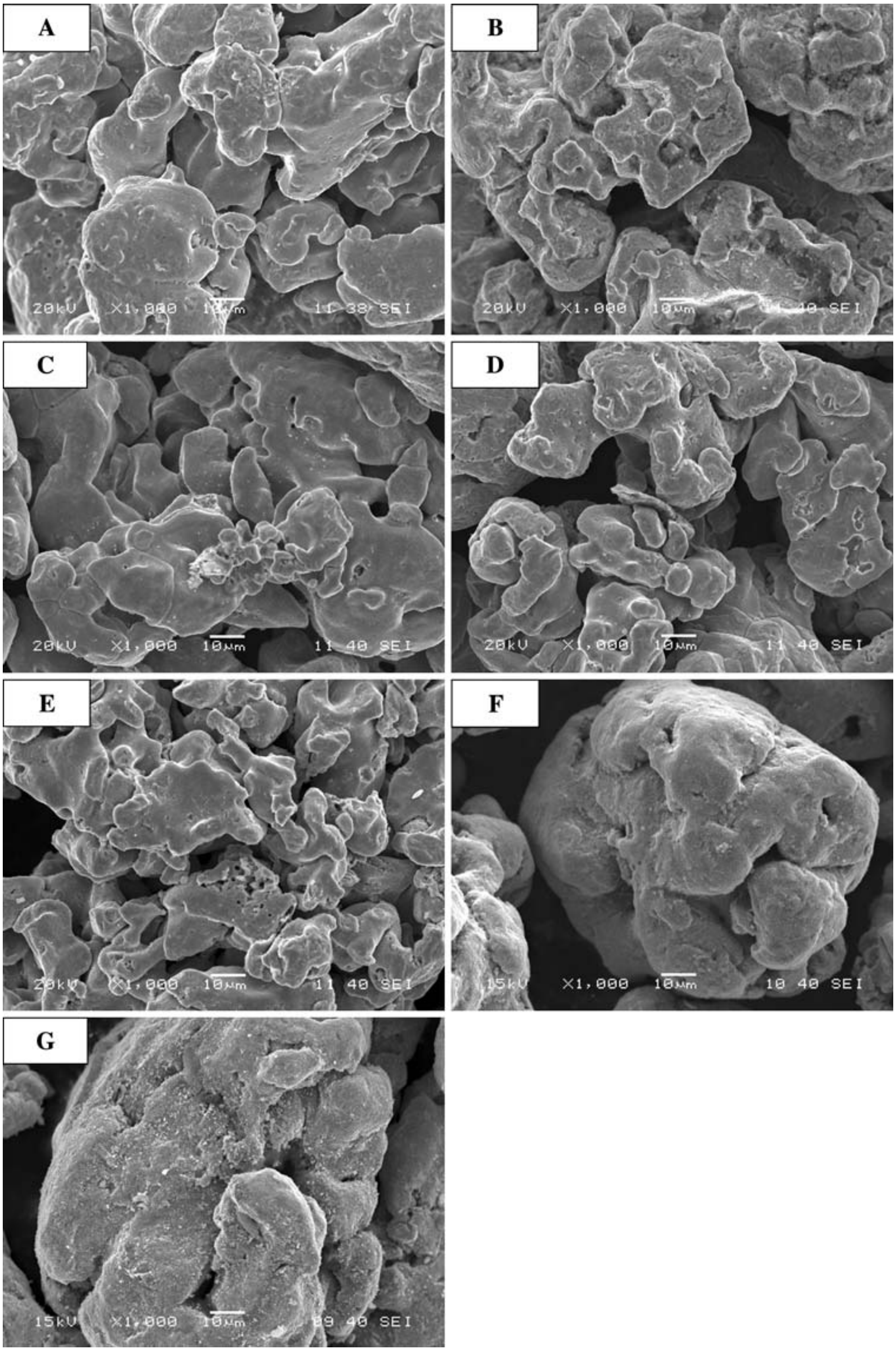


Fig. 4 The SEM patterns of the raw iron powder (**a**) and the collected iron powder after 1 h reduction of 10 mg L^{-1} PCP by Fe^0 in the presence of 0.1 mol L^{-1} oxalic acid + N_2 (**b**), citric acid + N_2 (**c**), tartaric acid + N_2 (**d**), acetic acid + N_2 (**e**) and nitric acid + N_2 (**f**) and in the bulk system without acids + N_2 (**g**). (Fe^0 dosage = 3.0 g L^{-1}, initial pH = 3.00)

strong complexing and pH buffering properties, oxalic acid has the strongest reductive activities favorable for the dechlorination of PCP by Fe^0.

It can be seen from the experimental results above that the organic chloride mineralization (*OCM*) for PCP was influenced by carboxylic acid, initial pH value and Fe^0 dosage. Due to their complexing abilities, pH buffering properties and reductive activities, the carboxylic acids are more favorable than nitric acid for improving the dechlorination of PCP by Fe^0. A higher *OCM* for PCP would obtain in the presence of oxalic acid, or at a lower pH value, or with a higher Fe^0 dosage. The *OCM* increased significantly with the increase of Fe^0 dosage or the decrease of pH value. It can be concluded that the addition

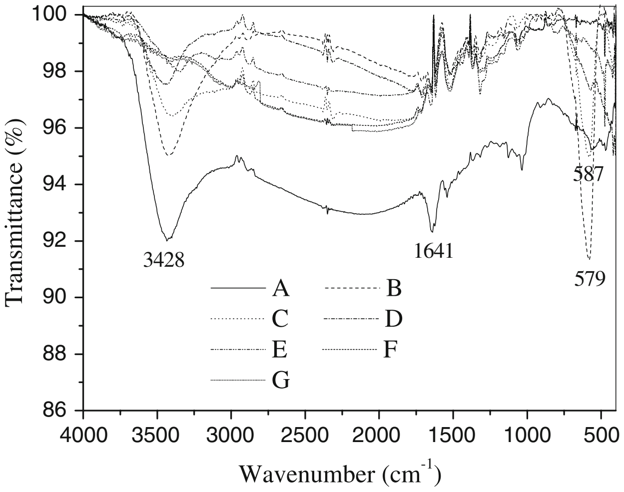


Fig. 5 The FTIR spectra of the raw iron powder (**a**) and the collected iron powder after 1 h reduction of 10 mg L^{-1} PCP by Fe^0 in the presence of 0.1 mol L^{-1} nitric acid + N_2 (**b**), in the bulk system without acids + N_2 (**c**) and in the presence of 0.1 mol L^{-1} acetic acid + N_2 (**d**), oxalic acid + N_2 (**e**), citric acid + N_2 (**f**) and tartaric acid + N_2 (**g**). (Fe^0 dosage = 3.0 g L^{-1}, initial pH = 3.00)

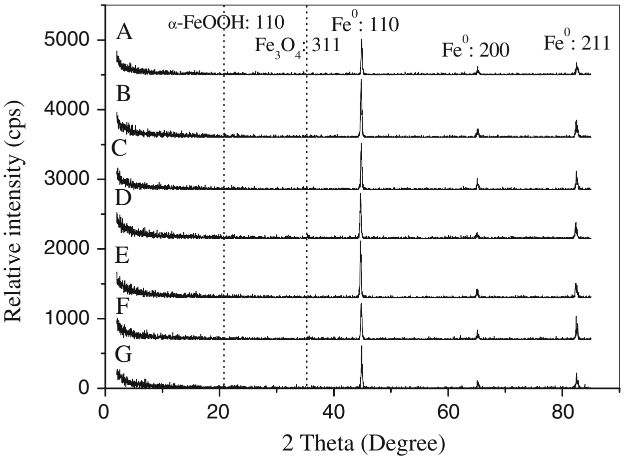


Fig. 6 The XRD patterns of the raw iron powder (**a**) and the collected iron powder after 1 h reduction of 10 mg L^{-1} PCP by Fe^0 in the presence of 0.1 mol L^{-1} oxalic acid + N_2 (**b**), citric acid + N_2 (**c**), tartaric acid + N_2 (**d**), acetic acid + N_2 (**e**) and nitric acid + N_2 (**f**) and in the bulk system without acids + N_2 (**g**). (Fe^0 dosage = 3.0 g L^{-1}, initial pH = 3.00)

of oxalic acid should be an effective way to enhance the dechlorination efficiency of pentachlorophenol significantly. The mechanism of PCP by Fe^0 in presence of oxalic acid would be concentrated in detail in the future.

Acknowledgements The authors would like to thank the suggestions of Prof. X. Z. Li from The Hong Kong Polytechnic University, and thank the Foundation of Natural Science of Guangdong Province (No. 04002223; No. 7006764) and Guangdong Technological Foundation (No. 2006B14801002; No. 2005B10301001) for financial supports to this work.

References

Anderson LD, Kent DB, Davis JA (1994) Batch experiments characterizing the reduction of chromium(VI) using suboxic material from a mildly reducing sand and gravel aquifer. Environ Sci Technol 28:178–185. doi:10.1021/es00050a025

Buerge IJ, Hug SJ (1998) Chromium(VI) reduction by iron(II). Environ Sci Technol 32:2092–2099. doi:10.1021/es970932b

Cornell RM, Schwertmann U (2003) The iron oxides structure, properties, reactions occurrences and uses. WILEY-VCH Verlag GmbH & Co, KgaA, Weinheim

Cotter-Howells JD, Campbell LS, Valsami-Jones E, Batchelder M (2000) Environmental mineralogy: microbial interactions, anthropogenic influences. contaminated land and waste management. The Mineralogical Society of Great Britain & Ireland, London, UK

Fu HB, Quan X (2006) Complexes of fulvic acid on the surface of hematite, goethite, and akaganeite: FTIR observation. Chemosphere 63:403–410. doi:10.1016/j.chemosphere.2005.08.054

He JH, Ela WP, Betterton EA, Arnold RG, Eduardo Saez A (2004) Reductive dehalogenation of aqueous-phase chlorinated hydrocarbons in an electrochemical reactor. Ind Eng Chem Res 43:963–7974

Hyun S, Lee LS (2004) Hydrophilic and hydrophobic sorption of organic acids by variable-charge soils: effect of chemical acidity and acidic functional group. Environ Sci Technol 38:413–5419. doi:10.1021/es0494914

Johnson SB, Yoon TH, Slowey AJ, Brown GE Jr (2004) Adsorption of organic matter at mineral/water interfaces: 3 implications of surface dissolution for adsorption of oxalate. Langmuir 20:11480–11492. doi:10.1021/la048559q

Jordi C, Jiechar G (2006) The effects of organic acids on the dissolution of silicate minerals: a case study of oxalate catalysis of kaolinite dissolution. Geochim Cosmochim Acta 70:191–2209

Kim Y-H, Carraway ER (2000) Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons. Environ Sci Technol 34:2014–2017. doi:10.1021/es991129f

Klose BS, Jentoft FC, Schlögl R, Subbotina IR, Kazansky VB (2005) Effect of Mn and Fe on the reactivity of sulfated zirconia toward H_2 and *n*-butane: a diffuse reflectance IR spectroscopic investigation. Langmuir 21:10564–10572. doi:10.1021/la051574q

Leen JD, Dirk B, Agathos SN, Diels L (2005) Combined removal of chlorinated ethenes and heavy metals by zerovalent iron in batch and continuous flow column systems. Environ Sci Technol 39:8460–8465. doi:10.1021/es050251d

Li C, Hoffman MZ (1999) One-electron redox potentials of phenols in aqueous solution. J Phys Chem B 103:6653–6656. doi:10.1021/jp983819w

Ma XD, Zheng MH, Liu WB, Qian Y, Zhang B, Liu WX (2005) Dechlorination of hexachlorobenzene using ultrafine Ca–Fe composite oxides. J Hazard Mater B 127:156–162. doi:10.1016/j.jhazmat.2005.06.034

Mikhlin YL, Kuklinskiy AV, Pavlenko NI, Varnek VA, Asanov IP, Okotrub AV, Selyutin GE, Solovyev LA (2002) Spectroscopic and XRD studies of the air degradation of acid-reacted pyrrhotites. Geochimica et Cosmochica Acta 66:4057–4067. doi:10.1016/S0016-7037(02)00989-4

Smith RM, Martell AE (1979) Critical stability constants. Plenum Press, New York, USA

Stumm W, Morgan JJ (1996) Aquatic chemistry, chemical equilibria and rates in natural waters. John Wiley & Sons, Inc, New York, USA

Stumm W, Sulzberger B (1992) The cycling of iron in natural environments: considerations based on laboratory studies of heterogeneous redox processes. Geochim Cosmochim Acta 56:3233–3257. doi:10.1016/0016-7037(92)90301-X

Su CM, Puls RW (2004) Nitrate reduction by zerovalent iron: effects of formate, oxalate, citrate, chloride, sulfate, borate, and phosphate. Environ Sci Technol 38:2715–2720. doi:10.1021/es034650p

Wang Y, Stone Alan T (2006) Reaction of $Mn^{III, IV}$(hydr)oxides with oxalic acid, glyoxylic acid, phosphonoformic acid, and structurally-related organic compounds. Geochim Cosmochim Acta 70:4477–4490. doi:10.1016/j.gca.2006.06.1548

Xu Y, Axe L (2005) Synthesis and characterization of iron oxide-coated silica and its effect on metal adsorption. J Colloid & Interface Sci 282:11–19. doi:10.1016/j.jcis.2004.08.057