



## Dechlorination of disinfection by-product monochloroacetic acid in drinking water by nanoscale palladized iron bimetallic particle

CHEN Chao<sup>1,2</sup>, WANG Xiangyu<sup>1,2</sup>, CHANG Ying<sup>1,2</sup>, LIU Huiling<sup>1,2,\*</sup>

1. State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, Harbin 150090, China.

E-mail: [chenchao03456@yahoo.com.cn](mailto:chenchao03456@yahoo.com.cn)

2. Department of Environmental Science and Engineering, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

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### Abstract

Nanoscale palladized iron (Pd/Fe) bimetallic particles were prepared by reductive deposition method. The particles were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM), transmission electron microscope (TEM), and Brunauer-Emmett-Teller-nitrogen (BET-N<sub>2</sub>) method. Data obtained from those methods indicated that nanoscale Pd/Fe bimetallic particles contained  $\alpha$ -Fe<sup>0</sup>. Detected Pd to Fe ratio by weight (Pd/Fe ratio) was close to theoretical value. Spherical granules with diameter of  $47 \pm 11.5$  nm connected with one another to form chains and the chains composed nanoscale Pd/Fe bimetallic particles. Specific surface area of particles was 51 m<sup>2</sup>/g. The factors, such as species of reductants, Pd/Fe ratio, dose of nanoscale Pd/Fe bimetallic particles added into solutions, solution initial pH, and a variety of solvents were studied. Dechlorination effect of monochloroacetic acid by different reductants followed the trend: nanoscale Pd/Fe bimetallic particles of 0.182% Pd/Fe > nanoscale Fe > reductive Fe. When the Pd/Fe ratio was lower than 0.083%, increasing Pd/Fe ratio would increase dechlorination efficiency (DE) of MCAA. When the Pd/Fe ratio was higher than 0.083%, increasing Pd/Fe ratio caused a decrease in DE. Adding more nanoscale Pd/Fe bimetallic particles to solution would enhance DE. The DE of MCAA decreased as initial pH of solution increased.

**Key words:** nanoscale Pd/Fe bimetallic particles; dechlorination; monochloroacetic acid

### Introduction

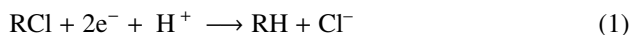
Haloacetic acids (HAAs) are important disinfection by-products (DBPs) in drinking water. During chlorination of drinking water, large amount of hypochlorous acid (HOCl) is formed in water, meanwhile, some free chlorine reacts with bromide in drinking water to form hypobromous acid (HOBr). Both HOCl and HOBr react with organic matter in drinking water to form DBPs: trihalomethanes (THMs), HAAs, haloacetanitriles (HANs), haloketones (HKs), haloaldehydes (CH), and chloropicrin (CP). It has been reported (Wei and Wang, 2004) that DBPs in drinking water disinfected by liquid chlorine contained 46 wt.% THMs and 42 wt.% HAAs, and DBPs in drinking water disinfected by chloramine contained 24 wt.% THMs and 52 wt.% HAAs. American Water Works Association Research Foundation has reported that unit cancer risk of HAAs (dichloroacetic acid (DCAA):  $2.6 \times 10^{-6}$ , trichloroacetic acid (TCAA):  $5.5 \times 10^{-6}$ ) is obviously higher than that of THMs (trichloromethane (TCM):  $0.056 \times 10^{-6}$ , tribromomethane (TBM):  $0.10 \times 10^{-6}$ , bromodichloromethane (BDCM):  $0.35 \times 10^{-6}$ ) (Bull and Kopfler, 1991). On the basis of concentration ( $\mu\text{g/L}$ ) and

unit cancer risk of DBPs in drinking water, the conclusion that cancer risk (cancer risk of the matter in solution = unit cancer risk concentration) of HAAs is much higher than that of other kinds of DBPs could be obtained. Zhang and Li (2000) have proposed that the concentration of HAAs should be regarded as main parameters to control total cancer risk of DBPs in drinking water. The United States Environmental Protection Agency made regulation about HAAs concentration in drinking water as part of the Disinfectants/Disinfection By-Products Rule (USEPA, 1998), which established the maximum contaminant level for the sum of five HAAs (monochloroacetic acid (MCAA), DCAA, TCAA, bromoacetic acid (MBAA), dibromoacetic acid (DBAA)) of 60  $\mu\text{g/L}$ . Effective methods on treating HAAs in drinking water have been the focus of the study.

Some researchers (De Wever *et al.*, 2000; Boethling and Alexander, 1979; Yu and Welandar, 1995; McRae *et al.*, 2004) conducted studies on biodegradation of HAAs. However, it is hard to use biodegradation method to dechlorinate HAAs in large scope because of long reaction time and strict reaction condition requirements. Therefore, the study on dechlorination of HAAs by zero-valent Fe (Hozalski *et al.*, 2001) is attractive to researchers. Standard electrode potential of Fe<sup>2+</sup>/Fe is  $-0.44$  V, and the electrode potential of Reaction (1) is from  $+0.5$  to  $+1.5$  V, which

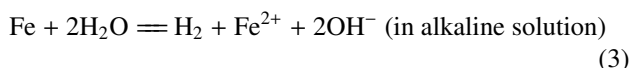
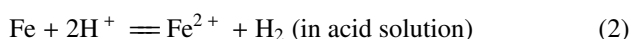
\* Corresponding author. E-mail: [hlliu2002@163.com](mailto:hlliu2002@163.com).

indicates that Fe could dechlorinate chlorohydrocarbon (Reaction (1)).



Since Gillham and O'Hannesin (1994) proposed that scrap Fe could be used for *in situ* remediation of groundwater, researchers have conducted large amount of studies on dechlorination of chlorinated organic contaminants with zero-valent Fe. Then, it is found that zero-valent Fe has shortcomings of low reactivity and incomplete dechlorination. To resolve the problems mentioned above, researchers try to use bimetallic particles to dechlorinate contaminants. Ni/Fe (Wei *et al.*, 2004), Cu/Fe (Fennelly and Roberts, 1998), Pt/Fe (Kim and Carraway, 2000; Liu *et al.*, 2000), and Ag/Fe (Xu and Zhang, 2000) are used to treat chlorinated organic contaminants. Muftikian *et al.* (1995) first use Pd/Fe bimetallic particles to dechlorinate chlorinated organics and the dechlorination efficiency (DE) was greatly enhanced. It is possible to further enhance DE with nanoscale particles because of its high surface area and high activity. Using nanoscale Pd/Fe bimetallic particles, Lien and Zhang (1999, 2001) have dechlorinated chlorinated methanes and chlorinated ethenes, and Xu *et al.* (2004) have dechlorinated 2,4-dichlorophenol (2,4-DCP).

By studying the mechanisms of dechlorination by Pd/Fe bimetallic particles, researchers (Quan *et al.*, 1998; Cheng *et al.*, 1997; Grittini *et al.*, 1995) propose that: in Pd/Fe bimetallic particles, metal Pd not only serves as catalyst absorbing  $\text{H}_2$  but also reduces activation energy of reaction by combining the p electron of chlorine of chlorinated organics or by combining the electron of chlorine with double bonds to form transition complex compound. During dechlorination of chlorinated organics with Pd/Fe bimetallic particles, Fe reacts with  $\text{H}_2\text{O}$  to generate  $\text{H}_2$  (Reactions (2) and (3)).



The chlorinated organics that form transition complex compounds with Pd and  $\text{H}_2$  are absorbed by Pd. On the

surface of metal Pd,  $\text{H}_2$  reduces transition complex compounds, removing chlorine from organics to form chlorine ion. Schematic diagram of the mechanism is given in Fig. 1.

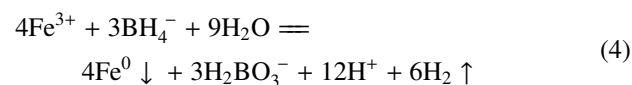
Hozalski *et al.* (2001) have studied dechlorination of HAAs by zero-valent Fe with some success. However, MCAA could not be dechlorinated by zero-valent Fe and it existed as product of dechlorination of TCAA. While  $\text{LD}_{50}$  for oral-rat of TCAA, DCAA, and MCAA are 400, 2,820, and 580 mg/kg, respectively (Lenga and Votoupal, 1993). This means that dechlorination of TCAA to MCAA could not decrease toxicity of water, and dechlorination of MCAA is necessary. In this study, nanoscale Pd/Fe bimetallic particles were prepared by reductive deposition method and were applied to dechlorinate MCAA in drinking water. Systematic study on dechlorination effect was carried out.

## 1 Materials and methods

### 1.1 Preparation of reductants

#### 1.1.1 Preparation of nanoscale Fe

Thirty grams of  $\text{KBH}_4$  were added into 179 ml KOH solution (5 g/L) to prepare  $\text{KBH}_4$  solution. In an anaerobic box, which was full of nitrogen, nanoscale Fe was produced by adding  $\text{KBH}_4$  solution dropwise to 179 ml  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution (1 mol/L) (Reaction (4)):



The nanoscale Fe particles were rinsed three times with de-ionized water.

#### 1.1.2 Preparation of nanoscale Pd/Fe bimetallic particles

Under the protection of nitrogen, nanoscale Fe particles were suspended in ethanol, and then the mixture were charged into a solution of  $(\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2)_3$  in 30 ml of ethanol to generate nanoscale Pd/Fe bimetallic particles according to Reaction (5).

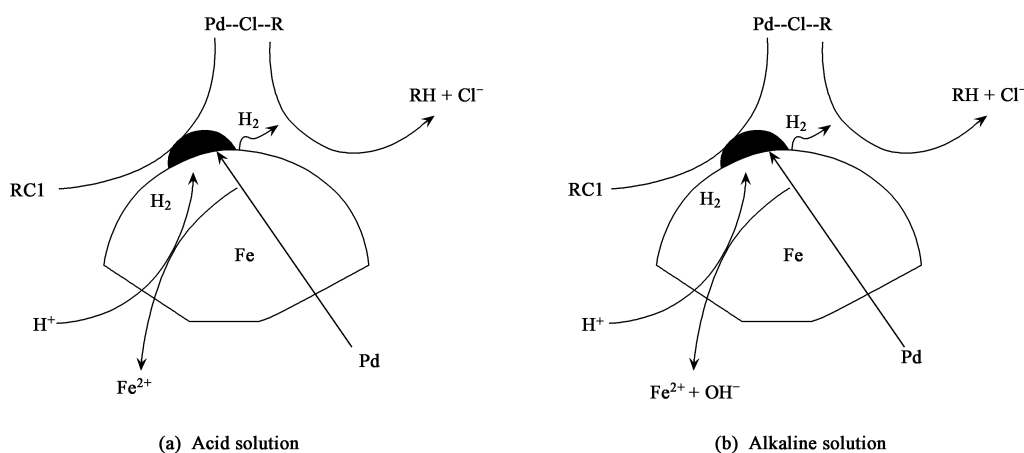


Fig. 1 Schematic of dechlorination of chlorinated organics on the surface of Pd/Fe bimetallic particles.

After being rinsed with dehydrated alcohol and acetone, nanoscale Pd/Fe bimetallic particles were put into vacuum drying oven and heated for 8 h at 100°C. The particles remained in the oven to cool down naturally and then, the particles were ground with one pestle in a mortar. Finally, the particles were preserved in sealed vessels.

### 1.1.3 Preliminary treatment of reductive Fe

Reductive Fe (98%, 200 mesh) was washed with H<sub>2</sub>SO<sub>4</sub> solution (0.1 mol/L) and de-ionized water before reaction. After treatment, the reductive Fe was charged into serum bottle for reaction immediately. And the amount of reductive Fe dissolving into solution by H<sub>2</sub>SO<sub>4</sub> washing was analyzed using a 721 spectrophotometer (Shanghai Precision and Scientific Instrument Corporation Limited, China).

## 1.2 Experiment of dechlorination of MCAA

One hundred milliliters MCAA solution (100 mg/L) and some dose of reductants were added into a 100-ml serum bottle with a rubber stopper packed with Teflon film. The control bottle with MCAA solution only was prepared similarly at the same time. The bottles were oscillated on a platform shaker (170 r/min) at ambient temperature. Samples were taken at stated intervals. And one serum bottle supplied only one sample to avoid the effect of headspace. Also the sample in the control bottle was taken by the same operation. The pH value of solution was adjusted by sulfuric acid and sodium hydroxide. The solution used in this study was prepared by de-ionized water if there was not any special instruction.

## 1.3 Analytical method

### 1.3.1 Analytical method for nanoscale Pd/Fe bimetallic particles

The ratio of Pd to Fe by weight of Pd/Fe bimetallic particles was examined by an AXIOSPW4400 X-ray fluorescence (XRF) (PANalytical Company, The Netherlands). Crystal structure was studied by a D/MAX-RB X-ray diffraction (XRD) (Rigaku Company, Japan). Granule size, shape, and surface morphology were observed by a MX2600FE scanning electron microscope (SEM) (Camscan Company, U.K.) and a JEM-1200EX transmission electron microscope (TEM) (JEOL Company, Japan). Specific surface area was detected by an Autosorb-1 Automatic surface area and pore size analyzer (Quantachrome Company, USA). Element content was analyzed by an energy dispersive spectroscope (EDS) (Oxford instruments, U.K.). The amount of Fe in particles was analyzed by a 721 spectrophotometer.

### 1.3.2 Analytical method for dechlorination of MCAA

Dechlorination effect of MCAA by nanoscale Pd/Fe bimetallic particles was expressed by two parameters, dechlorination efficiency (DE) and generation efficiency (GE). DE was defined as the percentage of metrical chlorine ion in solution to total chlorine element in solution by weight. GE was defined as the percentage of metrical acetic acid (HAc) in solution to HAc generated

from complete dechlorination of MCAA in solution by weight. Concentration of chlorine ion was observed by an ICS 3000 ion chromatograph (IC) (DIONEX Corporation, USA). The quantity of HAc was measured by a HP6890N Gas Chromatograph (GC) (Agilent Company, USA) with flame ionization detection (FID) and a HP-INNDWAX column (30 m × 0.53 μm × 1.0 μm). The quantity of MCAA was analyzed via HP4890 GC (Agilent Company, USA) with electron capture detection (ECD) and a HP-5 column (30 m × 0.53 μm × 1.0 μm).

## 2 Results and discussion

### 2.1 Characterization of nanoscale Pd/Fe bimetallic particles

#### 2.1.1 Pd/Fe ratio and Fe content of nanoscale Pd/Fe bimetallic particles

The Pd/Fe ratio of nanoscale Pd/Fe bimetallic particles were analyzed by XRF, and the results are shown in Table 1. It can be seen that metrical Pd/Fe ratio was in close agreement with theoretical value.

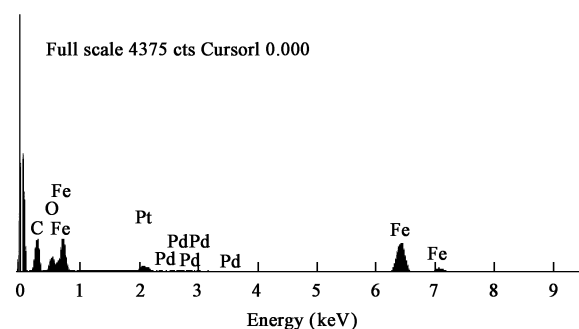
The elements of C, O, Fe, and Pd were detected on the particle surface by EDS (Fig.2). The carbon element might be from ethanol and acetone, which were used to rinse nanoscale Pd/Fe bimetallic particles when particles were prepared. The oxygen element might be from Fe-oxides, ethanol, and acetone. Platinum oxygen was introduced as conductive material coated on specimens when the nanoscale Pd/Fe bimetallic particles were detected by SEM. Spectrophotometer data showed that nanoscale bimetallic particles contained about 90 wt.% Fe.

#### 2.1.2 Crystal structure of nanoscale Pd/Fe bimetallic particles

Crystal structure of nanoscale Pd/Fe bimetallic particles was analyzed by XRD (Fig.3). The *d* spacings (0.202 nm (110), 0.144 nm (200), and 0.117 nm (211)) from XRD

**Table 1** Comparison of theoretical and metrical Pd/Fe ratio

Theoretical Pd/Fe ratio (wt.%)	Metrical Pd/Fe ratio (wt.%)	Standard deviation
0.05	0.051	0.003
0.07	0.067	0.003
0.10	0.083	0.005
0.20	0.182	0.004



**Fig. 2** EDS image of nanoscale Pd/Fe bimetallic particles.

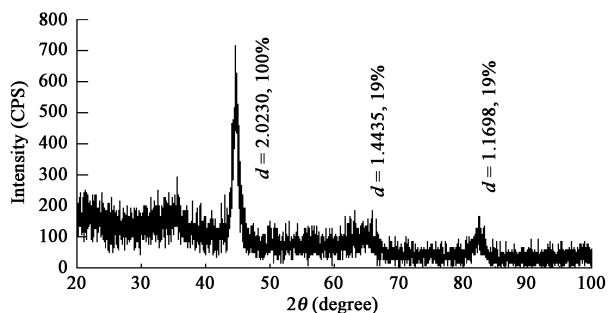


Fig. 3 XRD pattern of nanoscale Pd/Fe bimetallic particles.

pattern were consistent with that for the three strongest reflections of bcc  $\text{Fe}^0$  (0.203 nm (110), 0.143 nm (200), and 0.117 nm (211)), suggesting the presence of  $\alpha\text{-Fe}^0$  in nanoscale Pd/Fe particles. The  $\text{Fe}_3\text{O}_4$  diffraction peak (0.253 nm (311)) and  $\text{Fe}_2\text{O}_3$  diffraction peak (0.252 nm (311)) were also detected, but the intensity was negligible compared to that of  $\text{Fe}^0$ . This indicated that the Fe in nanoscale Pd/Fe bimetallic particles was not oxidized obviously. Pd diffraction peak was not detected because of low Pd/Fe ratio (about 0.05%), and that, it could be detected only when Pd/Fe ratio is higher than 1%.

### 2.1.3 Surface morphology and granule shape of nanoscale Pd/Fe bimetallic particles

The particles were characterized by SEM and TEM. The results showed that some spherical granules were composed of chains (Fig.4), and some chains connected with each other to form particles with reticular structure (Fig.5). It was difficult to observe the size of particles from SEM and TEM images statistically because of complicate interaction between granules. Figs.4 and 5 show that spherical granules were the basic part of nanoscale Pd/Fe bimetallic particles. This study assumed that the width of

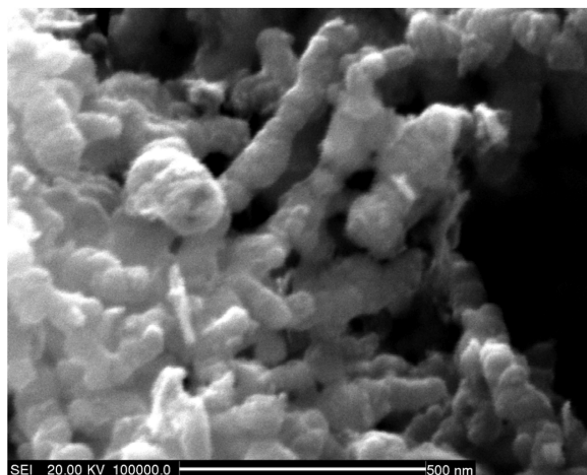


Fig. 4 SEM image of nanoscale Pd/Fe bimetallic particles with magnification of 100,000.

chains in TEM image was consistent with the diameter of spherical granules. And an average granule size of 47 nm with size distribution standard deviation of 11.5 nm was obtained by analyzing 68 spherical granules statistically.

### 2.1.4 Specific surface area of nanoscale Pd/Fe bimetallic particles

Specific surface area of nanoscale Pd/Fe bimetallic particles was  $51 \text{ m}^2/\text{g}$ . This specific surface area was much higher than that of Fe and Pd/Fe (0.49 and  $0.62 \text{ m}^2/\text{g}$ , respectively) reported in published works (Zhou *et al.*, 2003).

## 2.2 Dechlorination of MCAA

### 2.2.1 Dechlorination of MCAA using different reductants

Nanoscale Pd/Fe bimetallic particles, nanoscale Fe, and

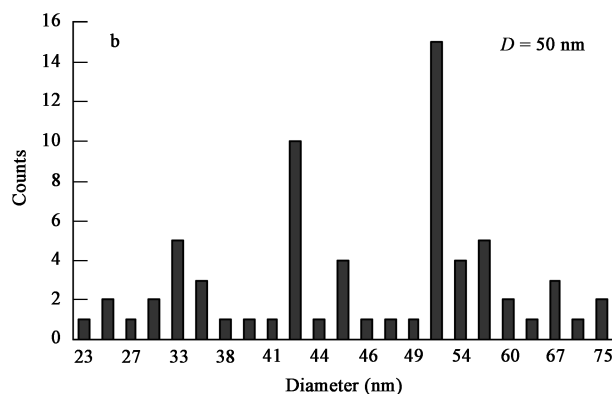
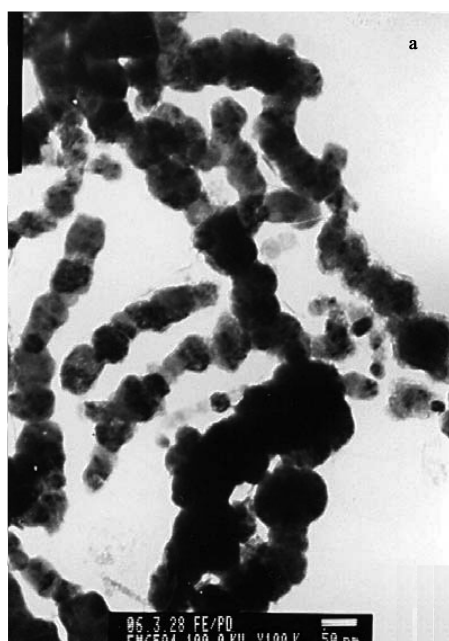


Fig. 5 TEM images of nanoscale Pd/Fe bimetallic particles. (a) magnification of 100,000 $\times$ ; (b) histogram from the TEM image of 68 nanoscale Pd/Fe bimetallic granules.

reductive Fe were used to dechlorinate MCAA, and the results are shown in Fig.6. Dechlorination efficiency of different reductants followed the trend: nanoscale Pd/Fe bimetallic particles of 0.182% Pd/Fe ratio > nanoscale Fe > reductive Fe. High specific surface area and high surface activity enabled nanoscale Fe dechlorinate MCAA with a higher DE than reductive Fe with the same reaction time. Further, nanoscale Pd/Fe bimetallic particles possessed a higher DE than nanoscale Fe because nanoscale Pd/Fe bimetallic particles not only had the characteristic of nanoscale Fe of high surface area and high surface activity but also had the characteristic of Pd of facilitating reaction between  $H_2$  and chlorinated organics by absorbing these species.

### 2.2.2 Effect of Pd/Fe ratio of nanoscale Pd/Fe bimetallic particles

Figure 7 shows that when Pd/Fe ratio was less than 0.083%, increasing the Pd/Fe ratio would increase the DE, but when Pd/Fe ratio was more than 0.083%, increasing the Pd/Fe ratio would decrease the DE. Xu and Bhattacharyya (2007) have found that by normalizing surface-area-normalized rate constant ( $k_{SA}$ ) in terms of Pd content, the nanoscale Pd/Fe bimetallic particles with different Pd/Fe ratio studied in their published work possessed the same reaction rate. The result indicated that Pd contents in bimetallic particles played a major role in

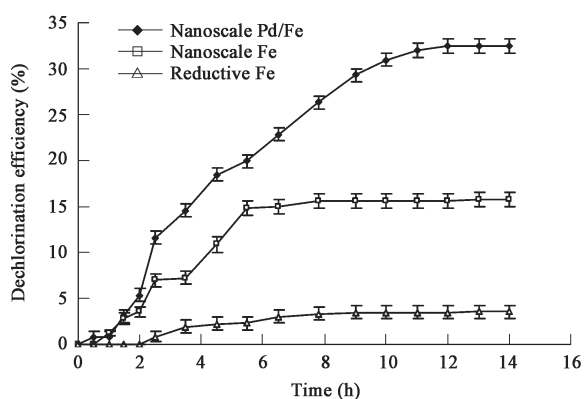


Fig. 6 Dechlorination of MCAA using different reductants.

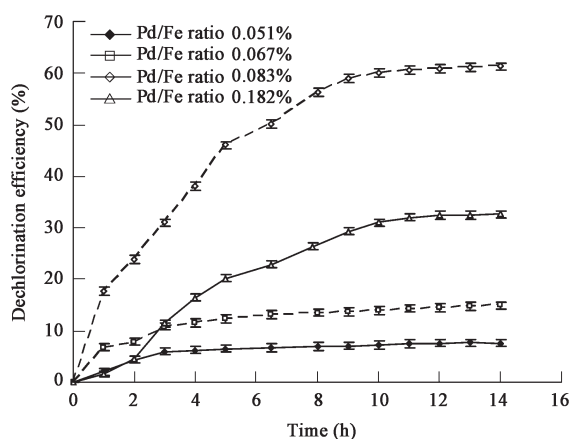


Fig. 7 Effect of Pd/Fe ratio of nanoscale Pd/Fe bimetallic particles on dechlorination of MCAA.

dechlorination of chlorinated organics. The Pd atoms are commonly regarded as surface reactive sites according to Fig.1, and Pd atoms would accelerate  $H_2$  generation rate. In this study, when the Pd/Fe ratio was lower than 0.083%, increasing the Pd/Fe ratio would increase the generation rate of  $H_2$ , resulting in increase of instantaneous output of  $H_2$  and DE of MCAA. When Pd/Fe ratio was higher than 0.083%, large amount of  $H_2$  was generated instantly, which was far more than that required for dechlorination of MCAA and  $H_2$  accumulated on nanoscale Pd/Fe bimetallic particle surface. The accumulated  $H_2$  would block mass transfer of MCAA from solution to Fe surface and decrease DE of MCAA.

### 2.2.3 Effect of dose of nanoscale Pd/Fe bimetallic particles

The results of dechlorination of MCAA with different nanoscale Pd/Fe bimetallic particle dose are shown in Fig.8. After 5 h of reaction, DE of MCAA with different nanoscale Pd/Fe bimetallic particle dose followed the trend (metal to solution ratio) 12 g/L > 10 g/L > 7 g/L > 3 g/L. The reason could be that increasing the amount of nanoscale Pd/Fe bimetallic particles in solution would increase more surface area for reaction between MCAA and Fe, and enhance DE. However, during the first 4 h of reaction, DE with 12 g/L nanoscale Pd/Fe bimetallic particles was lower than that with 10 g/L nanoscale Pd/Fe bimetallic particles. It was possibly because that large amount of  $H_2$  generated from large amount of Fe reduced the mass transfer of MCAA from solution to Fe surface and decreased DE.

### 2.2.4 Effect of initial pH of solution

The dechlorination efficiency of MCAA with different initial pH is shown in Fig.9. When pH values were 2.98, 7.00, and 9.00, the DE of MCAA were 61.32%, 53.90%, and 43.54%, respectively. As can be seen from Fig.1, dechlorination of MCAA consumed  $H^+$ , and decrease of  $H^+$  concentration would cause DE of MCAA to decrease. Also in alkaline solution, Reaction (6) occurred easily, and the consumption of electron by  $O_2$  would decrease DE of MCAA. However, DE of MCAA with pH 9 was 71% of

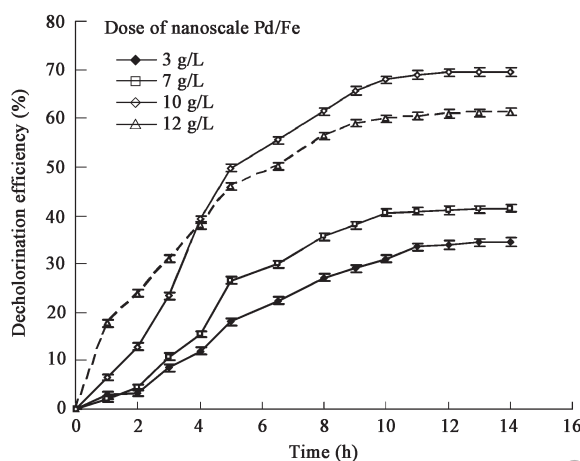
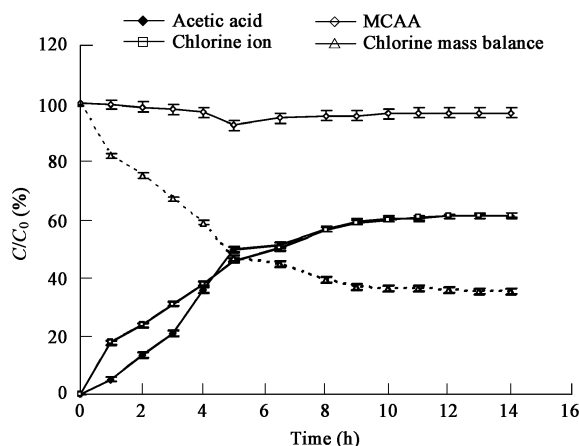
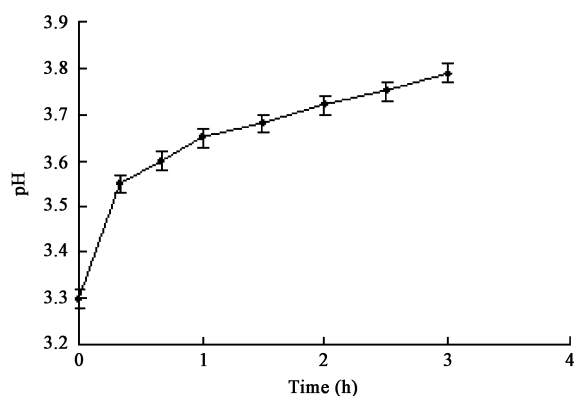


Fig. 8 Effect of dose of nanoscale Pd/Fe bimetallic particles on dechlorination of MCAA.

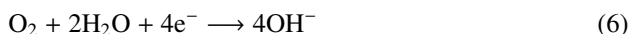


**Fig. 9** Effect of solution initial pH on dechlorination of MCAA. Condition: metal to solution ratio, 1 g/100 ml; Pd/Fe ratio, 0.083%.



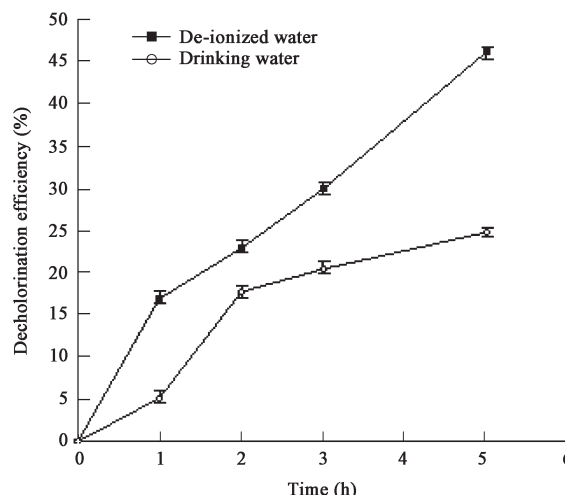
**Fig. 10** Concentration change of reactant during dechlorination of MCAA.

that with pH 2.98, indicating the possibility of application of this technology in a larger pH scope. This result could be proved by results reported by other researchers. Wu *et al.* (2004) found that Fe/Cu bimetallic systems dechlorinated  $\text{CCl}_4$  well when pH value of solution ranged from 2 to 9, and the lowest DE of  $\text{CCl}_4$  was about 75% of the highest DE of  $\text{CCl}_4$ . Liu and Lowry (2006) studied the effect of pH value on dechlorination of trichloroethene (TCE) with nanoscale Fe particle and found that decreasing pH from 8.9 to 6.5 increased the  $\text{H}_2$  evolution rate constant 27 folds and increased the TCE dechlorination rate constant only 2 folds. These results showed that pH did not have great impact on dechlorination of chlorinated organics, and the technology could be applied in a larger pH scope.



### 2.2.5 Concentration of reactant in solution during dechlorination of MCAA

Concentration change of reactant during dechlorination of MCAA was studied. The results from Fig.10 suggested the discrepancy between GE and DE during the first 4 h of dechlorination. The reason could be that nanoscale Pd/Fe bimetallic particles adsorbed some HAc and prolonged the release of HAc to solution. The chlorine mass balance in this study was 96.8%.



**Fig. 11** Dechlorination of MCAA in drinking water and de-ionized water.

### 2.2.6 Dechlorination of MCAA in drinking water and de-ionized water by Pd/Fe bimetallic particles

Figure 11 shows that DE of MCAA in drinking water was lower than that of MCAA in de-ionized water. It is likely that impurity in drinking water affected the DE of nanoscale Pd/Fe bimetallic particles. Lo *et al.* (2006) have found that hardness ions and carbonate in groundwater decreased Cr(VI) removal capacity of zero-valent iron by the formation of passivated precipitates on the  $\text{Fe}^0$  surface. It is possible that hardness ions and carbonate were present in drinking water and decreased the DE of MCAA by the same passivated precipitates formed on nanoscale Pd/Fe bimetallic particle surface. Meanwhile, anions such as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  present in water have been found to inhibit dechlorination of TCE with nanoscale zero-valent Fe particles (Liu *et al.*, 2007). Some further research is needed to study the effect of impurity in drinking water on nanoscale Pd/Fe bimetallic particle reactivity with chlorinated organics in detail.

## 3 Conclusions

The nanoscale Pd/Fe bimetallic particles prepared in this study were characterized. The particles had high specific surface area of  $51 \text{ m}^2/\text{g}$ ; the diameter of granules was  $47 \pm 11.5 \text{ nm}$ ; the particles contained 90 wt.% Fe. Meanwhile, the study on dechlorination of MCAA with nanoscale Pd/Fe bimetallic particles was conducted. The results showed that dechlorination efficiency of MCAA with nanoscale Pd/Fe bimetallic particles was higher than those with nanoscale Fe and reductive Fe. The optimal condition for dechlorination of MCAA was when Pd/Fe ratio of nanoscale Pd/Fe bimetallic particles was 0.083% and particle dose was 12 g/L. During reaction DE of MCAA decreased as solution initial pH increased and DE of MCAA in drinking water was lower than that in de-ionized water.

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