Catalytic reduction of chlorinated and recalcitrant compounds in contaminated water

Xinhua Xu [*], Mi Zhou, Ping He, Zhiwei Hao

Department of Environmental Engineering, Zhejiang University, Hangzhou 310027, PR China

Abstract

Catalysis dechlorination of chlorinated organic matter by palladium/iron bimetallic particles represents one of the latest innovative technologies for contaminated soil and groundwater remediation. The reaction of dechlorination is believed to take place on the surface site of the catalyst in a pseudo-first-order mode. The dechlorination rate increases with an increase of the bulk loading of palladium due to the increase of both the surface loading of palladium and the total surface area exposed. The results show that no other intermediates were generated besides Cl^-, benzene and chlorobenzene during dechlorination of *o*-dichlorobenzene.
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1. Introduction

The use of zero-valent iron (Fe^0) for the treatment of contaminants in waste and groundwater has been the focus of much recent research. Researchers have studied different classes of compounds such as halogenated organics [1–4], azoaromatics [5,6], nitroaromatics [7] and inorganics [8]. The majority of these studies are concerned with chlorinated organics, because they are widespread and mobile, and represent important environmental contaminants. For their acute toxicity and strong bioaccumulation potential, chlorobenzenes are of great health and environmental concern and the US EPA lists most of them as priority pollutants. So there is an urgent need to development effective control methods.

Recently, it has been found that the addition of palladium as a catalyst can shorten the dechlorination time. Zero-valent iron was found to serve as the electrons in the reaction and palladium as a catalyst at the same time. The dechlorination reaction between Pd/Fe and low-molecule hydrocarbons was found to be so fast that it is suitable for in situ treatment of wastewater. This method has been revealed to be effective for treatment of a variety of toxic substances such as polychorinated biphenyls, chlorinated methanes, chlorinated ethenes, chlorophenols, pentachlorophenol and PCBs [9,10]. In this paper, we investigate the dechlorination of *o*-dichlorobenzenes.

## 2. Experiments and methods

2.1. Chemicals

Potassium hexachloropalladate (99%, Aldrich, USA), *o*-dichlorobenzene (>98.5%), methanol (reagent for HPLC, >99.9%), iron powder (>200 mesh, >98.0%), chlorobenzene, benzene, acetone, sulfuric acid (H_2SO_4) and other reagents are of analytic grade.

2.2. Pd/Fe preparation and characterization

Palladium/iron (Pd/Fe) powder was used as the catalytic reductant. It was prepared by wet impregnation of

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[*] Corresponding author. Tel.: +86 571 87951239; fax: +86 571 87952771.
E-mail address: xhxu@hzcnc.com (X. Xu).

the iron powder with an aqueous solution of potassium hexachloropalladate through the following redox reaction:

$$2Fe^0 + Pd^{4+} = 2Fe^{2+} + Pd^0 \tag{1}$$
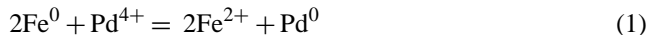
The iron powder was pretreated by washing with $0.1 \, mol \, l^{-1}$ H_2SO_4, subsequently with acetone and rinsed with distilled water to remove surface oxide layers and undesired organic compounds prior palladization. An aqueous solution of potassium hexachloropalladate was prepared and added to a bottle containing iron powder. The solution was continuously stirred until the dark orange solution turned to pale yellow. The palladized iron was where after rinsed twice with deionized water and used for reaction without drying.

The surface area (BET area) of iron and palladized iron was measured using the nitrogen adsorption method with a ST-03 adsorption apparatus (Beijing Beifenruili Analytic Instrument (Group) Co. Ltd.). Prior to the measurements, Pd/Fe was obtained with the same way as described above and dried at $100\,°C$ under a flow of N_2. The morphology of the iron powder was observed with a XL30 (Philips, Holand) environmental scanning electron microscope (ESEM) at 20 kV under the magnification of $20,000×$.

2.3. Experimental procedure

Batch experiments for *o*-dichlorobenzene dechlorination were conducted in 30 ml bottles. In most cases, the bottles containing 2 g Pd/Fe were filled with an *o*-dichlorobenzene solution, leaving no headspace and were sealed immediately with butyl rubber septa. Each bottle was placed in an incubator shaker (200 rpm, $25 ± 1\,°C$). In a fixed time period, samples were withdrawn from the liquid using a syringe and filtered with a piece of 0.45 μm filter, then used for subsequent analysis.

2.4. Analytic method

Organic compounds such as benzene, chlorobenzene, *o*-DCB, etc., were measured by HPLC, TRACE 2000GC/MS also was used to characterize the intermediates. Chloride analysis was performed by ion chromatography (792 Basic IC, Metrohm). Before injection, sample solutions were always filtered through a 0.45 μm membrane filter.

The concentration of ferrous ions in solution were determined by the 1,10-phenanthroline colorimetry method at 510 nm. In order to determine the total amount of Fe in solution, hydroxylamine hydrochloride ($NH_2OH·HCl$) was used to reduce ferric into ferrous at pH < 2. Analysis of Fe(II) was carried out with ferrozine. Fe(II)aq was measured by filtering a 0.05 ml sample through a 0.2 μm nylon syringe filter before directly into ferrozine and then reading the 510 Å immediately.

3. Results and discussion

### 3.1. Characterization results of the catalyst

The surface morphology of both the Fe and Pd/Fe powders is shown in Fig. 1. The surface of Pd/Fe is rough due to palladium deposition on the iron surface, and with the increase of Pd loading, the more white dots appear due to the Pd deposition. The specific surface area of the Fe and Pd/Fe measured by BET-N_2 was 0.49 and 0.62 m^2/g, respectively. The increased surface indicated that Pd is dispersed on the surface rather than clustered. It is consistent with the information revealed in the SEM image of the catalyst.

3.2. Dechlorination of chlorobenzene

Fig. 2 shows the GC/MS chromatogram of the sample. Fig. 3 displays the HPLC chromatogram of the solution during the dechlorination reaction, where only imme-
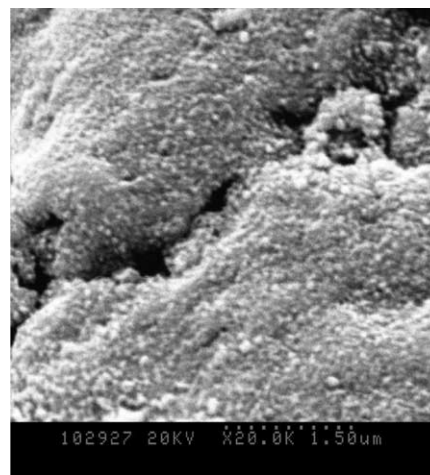
(a) before dechlorination
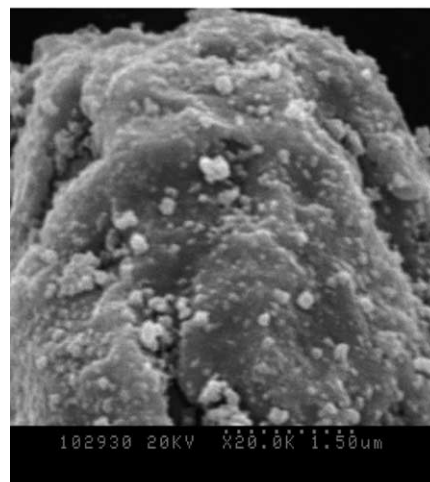
(b) after dechlorination

Fig. 1. SEM image of Pd/Fe ($20,000×$): (a) before dechlorination reaction and (b) after dechlorination reaction.
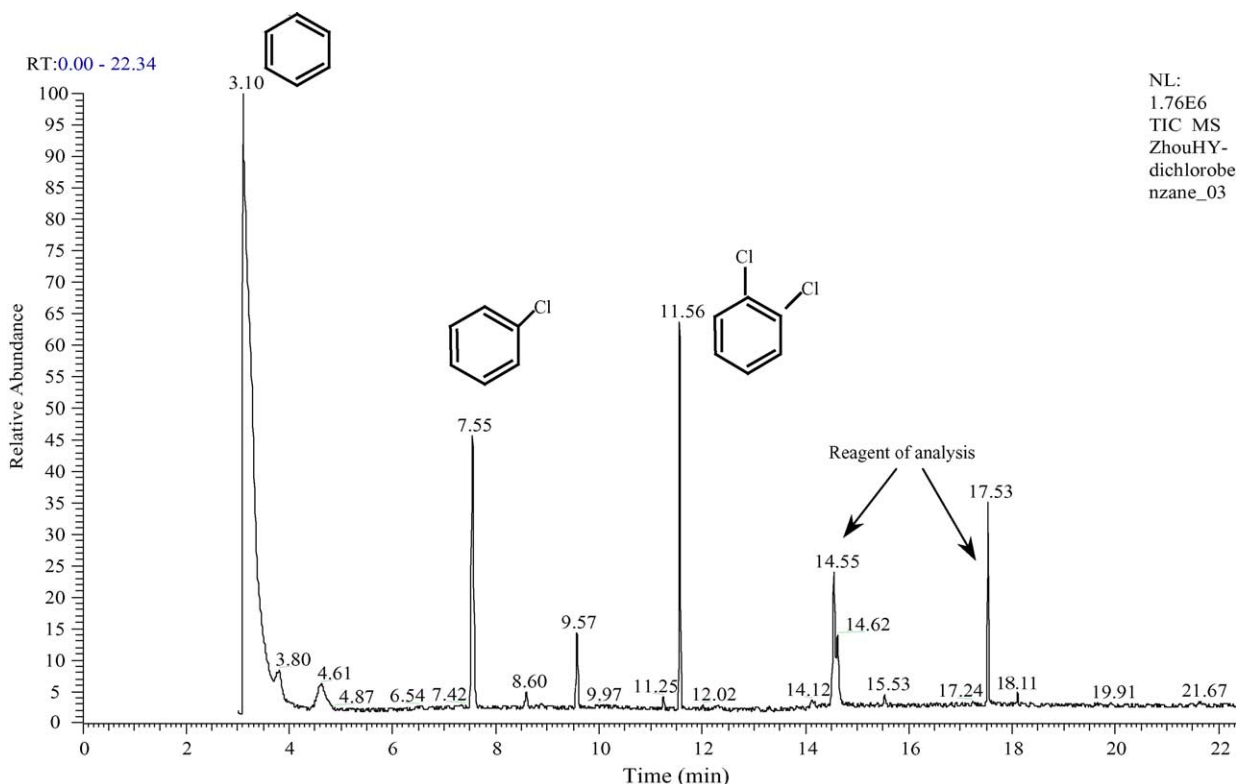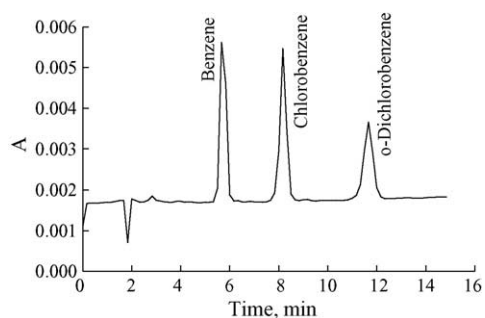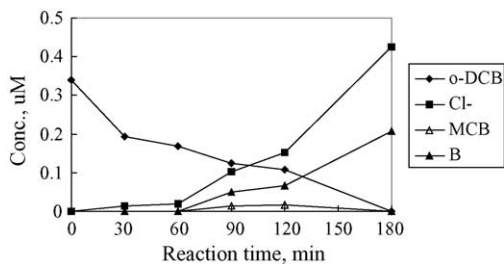
Fig. 2. The GC/MS chromatogram of a sample.

Fig. 3. HPLC chromatograms of o-DCB dechlorination over Pd/Fe.

diate appearance of chlorobenzene and benzene was observed during the dechlorination of o-DCB according to Figs. 2 and 3. Catalytic properties of the Pd/Fe bimetallic catalyst are presented in Fig. 4. Concentrations in the figure are expressed as the molar ratio to initial organic concentrations. As shown in Fig. 4, the concentration of o-DCB declined rapidly. The immediate appearance of chlorobenzene and benzene was observed corresponding to the disappearance of o-DCB. The overall experiment mass balance was close at around 80% in the entire experiment, because of the adsorption of benzene or chlorobenzenes on the surface of Pd/Fe or inside the passivation layers (e.g. $Fe(OH)_2$, $Fe(OH)_3$), about 18–20% adsorption of benzene by Pd/Fe power were found.

It should be pointed out that total Fe concentration in the aqueous solution increases and decreases significantly during dechlorination as shown in Fig. 5. It can be seen that total Fe concentration in the system increases at the start of the dechlorination, but the Fe concentration begins to drop after 120 min in many experiments,
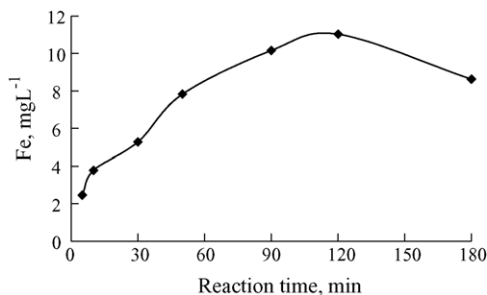

Fig. 4. Results of Pd/Fe catalyst for o-DCB dechlorination: $C_0 = 50$ mg l^{-1}, Pd loading 0.005%, Pd/Fe powder 4 g vs. 75 ml, $T = 25\,^\circ$C, pH 6.5.

Fig. 5. Total Fe concentration in the aqueous solution during dechlorination.
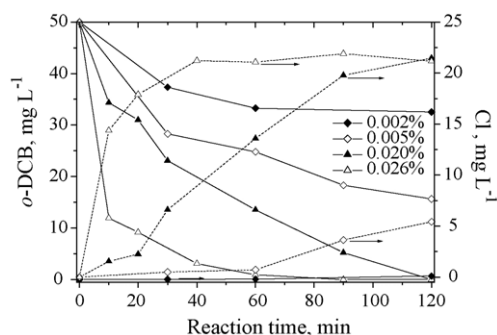
Fig. 6. Effect of Pd mass-fraction on the removal efficiency of o-DCB and generated chloride ion: $C_0 = 50\,\text{mg\,l}^{-1}$, Pd/Fe powder 4 g vs. 75 ml, $T = 25\,^\circ\text{C}$, pH 6.5.

probably as a result of the formation of surface passivation layers or due to the precipitation of metal hydroxides (Fe(OH)_2, Fe(OH)_3) and metal carbonates (FeCO_3) on the surface of iron and Pd/Fe as the pH increases (see Fig. 1(b)).

The variation of the dechlorination efficiency during the reaction over the Pd/Fe catalyst with various Pd mass-fractions is presented in Fig. 6. As expected, the dichlorobenzene removal was observed to increase with the increase of Pd fractions. For example, with a 0.02–0.026% Pd ratio, a removal of about 90% dichlorobenzene was achieved after 120 min of dechlorination. However, with a 0.002% Pd ratio, the dichlorobenzene removal was only 35% after the same reaction time. That is, the more Pd loading, the higher remove efficiency.

Rearranging the removal efficiency of o-DCB under different Pd weight ratio with a linear increase of $-\ln(C/C_0)$ over time was obtained (as shown in Fig. 7). This linear relationship reveals a pseudo-first-order reduction reaction regarding the o-DCB removal efficiency. The reaction rate constants (k) were determined from the slopes of the lines as 0.0032, 0.0092, 0.0237 and 0.0610 min^{-1}, for particles with Pd/Fe weight ratio of 0.002, 0.005, 0.020 and 0.026%, respectively.

3.3. Mechanism of catalytic dechlorination

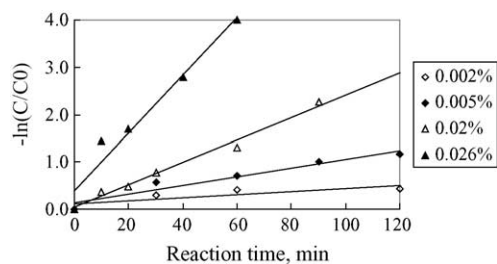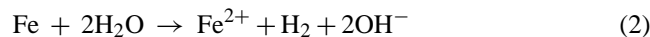It is assumed that the dechlorination of o-DCB occurs when adsorbed on the surface of Pd/Fe. The Pd on the Fe surface acts as a collector of hydrogen gas produced by the reaction of Fe with water, i.e., the corrosion reaction of iron:

$$\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \tag{2}$$

On the palladium surface, the produced hydrogen is dissociated into H atoms. The o-DCB adsorbed on the Pd/Fe surface is reductively dechlorinated through the following reaction:
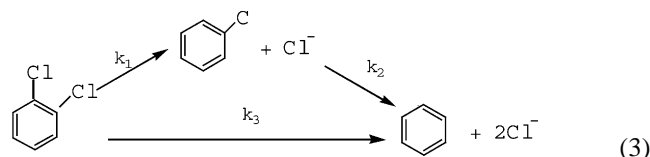
The reaction products, benzene and chloride, are released into the solution. The chlorine in o-DCB is substituted by hydrogen with the formation of benzene. The hydrogen atom is solely supplied by H_2O as proved by an experiment conducted in a D_2O solution. In the presence of dissolved oxygen under weak acidic or neutral conditions, the following reaction also occurs:

$$4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)}_3 \downarrow + 8\text{H}^+ \tag{4}$$

Pd can adsorb hydrogen dissociatively in addition to o-DCB. On the catalyst surface, the hydrogen produced in reaction (2) is adsorbed and dissociated into atomic H. Atomic H attacks chlorobenzene to replace the chlorine and to form benzene and chloride. The Pd^0 dispersion therefore enhances the conversion.

The implementation of the zero-valent iron and the Pd/Fe technology is still suffering from some limitation, especially the decrease of the iron and Pd/Fe reactivity over time, which probably because of the formation of surface passivation lay-

Fig. 7. Linear decrease of normalized o-DCB removal efficiency (ln) with reaction time: $C_0 = 50\,\text{mg\,l}^{-1}$, Pd/Fe powder 4 g vs. 75 ml, $T = 25\,^\circ\text{C}$, pH 6.5.
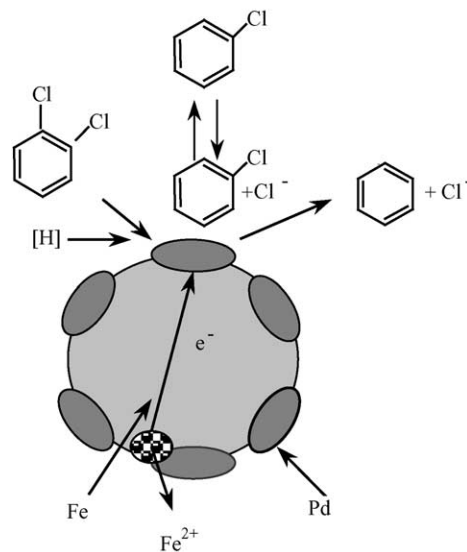

Fig. 8. Representation of a bimetallic particle and the dechlorination mechanism.

ers or due to the precipitation of metal hydroxides ($Fe(OH)_2$, $Fe(OH)_3$) and metal carbonates ($FeCO_3$) on the surface of iron and Pd/Fe (see Figs. 1(b) and 8). But freshly synthesized nanoscale Pd/Fe bimetallic particles with high ratio of surface area to volume were more reactive than the commercial grade Fe or Pd/Fe powers, and can reduce the formation of metal hydroxides and metal carbonates [4]. Nanoscale metal particles can furthermore be anchored on solid supports such as activated carbon, zeolite and silica, offers great opportunities for ex situ treatment of contaminated water and industrial effluent.

4. Conclusions

Catalytic dechlorination of chlorinated organic compounds by palladium/iron bimetallic particles represents one of the latest innovative technologies for contaminated soil and groundwater remediation through catalytic reduction. The dechlorination is believed to take place on the surface site of the catalyst via a pseudo-first-order mode. The dechlorination rate increases with the increase of the bulk loading of palladium due to the increase of both the surface loading of palladium and the total surface area. Furthermore, the results show that no other intermediates were generated besides Cl^-, benzene and chlorobenzene during dechlorination of *o*-dichlorobenzene. The decrease of the iron and Pd/Fe reactivity over time is probably due to the formation of surface passivation layers or due to the precipitation of metal hydroxides and metal carbonates on the surface of iron and Pd/Fe. The present results would be valuable for further study.

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