Effects of key reaction parameters on the reductive dechlorination of chloroform with Pd/Fe\(^0\) bimetal in aqueous solution

XIAO-LI XUAN\(^1\), XIANG-ZHONG LI\(^1\)*, CHUAN WANG\(^2\), and HONG LIU\(^2\)

\(^1\)Department of Civil and Structural Engineering, The Hong Kong Polytechnic University
Hong Kong, China

\(^2\)School of Chemistry and Chemical Engineering, Sun Yat-sen University
Guangzhou, 510275, China

ABSTRACT

In this study, bimetallic Pd/Fe\(^0\) particles were synthesized and employed to reduce chloroform in aqueous solution. The investigation emphasized on the effects of key reaction parameters of Pd/Fe\(^0\) dosage, pH, oxidation-reduction potential (ORP) and presence of anions on the reductive dechlorination reaction. The experimental results showed that high Pd/Fe\(^0\) dosage, low initial pH and low ORP benefited the reductive dechlorination of chloroform. The ORP values in the aqueous chloroform solution bubbled with different gases of N\(_2\), O\(_2\) and air varied significantly and the degradation efficiency of chloroform under different atmospheres followed an order from high to

* Address correspondence to X. Z. Li, Department of Civil and Structural Engineering The Hong Kong Polytechnic University, E-mail: cexzli@polyu.edu.hk

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low as N\textsubscript{2} > air > O\textsubscript{2}. The experiments also demonstrated that the SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-} ions inhibited the dechlorination reaction significantly, while the H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} had no significant influence on the dechlorination.

**Keywords:** Chloroform; dechlorination; palladium; reduction; zero-valent iron.

**INTRODUCTION**

Chlorination, as the most common disinfection method of drinking water, plays a central role in the supply of safe drinking water. However, formation of chlorinated byproducts such as trihalomethanes (THMs) that are recognized to cause adverse health effects is of great concern.\textsuperscript{[1,2]} Besides the employment of advanced oxidation processes such as ozonation, photocatalytic oxidation, and Fenton reaction for oxidative degradation, the chlorinated byproducts could be alternatively reduced to their nonchlorinated analogues\textsuperscript{[3]} with less toxicity and better biodegradability.

Zero-valent iron (Fe\textsuperscript{0}) as a reducing agent has been used for the decomposition of contaminants including the chlorinated organics in groundwater with relatively high redox potentials.\textsuperscript{[4,5-8]} However, shortcomings such as accumulation of chlorinated byproducts to decrease the Fe\textsuperscript{0} activity have been reported.\textsuperscript{[9-11]} Among the approaches to overcoming these shortcomings, deposition of a second metal onto the Fe\textsuperscript{0} surface is attractive due to the rapid dechlorination, and Pd, Pt, Ag, Ni and Cu are the candidates for such a purpose,\textsuperscript{[9,12-14]} while the palladium (Pd) appears to be the most effective one.
In this study, a Pd/Fe\textsuperscript{0} bimetal system was employed for the accelerated dechlorination of THMs in aqueous solution. Effects of some key factors including the Pd/Fe\textsuperscript{0} dosage, initial pH, initial oxidation-reduction potentials (ORP) and presence of anions on the dechlorination reaction were investigated. The kinetics was discussed to fully understand the Pd/Fe\textsuperscript{0} bimetal system with application potential in the advanced purification of drinking water.

**EXPERIMENTAL**

**Materials and Chemicals**

Iron powder and PdCl\textsubscript{2} solid (purity 99.5\%) were obtained from the International Laboratory, USA. Gases of oxygen, air, nitrogen and hydrogen (purity > 99.9\%) in cylinders were supplied by Hong Kong Oxygen & Acetylene Co. Ltd. Chloroform (CHCl\textsubscript{3}) chemical with HPLC grade (> 99.0\%) was obtained from the Fisons USA and its aqueous stock solution was prepared at 200 mg L\textsuperscript{-1}. All other chemicals with analytical grade were used without further purification. Deionized distilled water was used in the reaction and was boiled for 2 h prior to use under a N\textsubscript{2}-purge condition to remove the dissolved oxygen.

**Preparation of Pd/Fe\textsuperscript{0}**

The Pd/Fe\textsuperscript{0} bimetallic particles were prepared by mixing acidic PdCl\textsubscript{2} solution with iron powder to allow Pd\textsuperscript{2+} to be coated onto the iron surface through the following reaction:
$$Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+}$$  \hspace{1cm} (1)

Prior to the preparation, the iron powder was washed with 0.1 mM HNO₃ solution. The PdCl₂ solution was prepared with an initial concentration of 0.2 mM by dissolving PdCl₂ into 1% HCl solution and then mixed with 20 g of iron powder. The mixture was placed on a rotary shaker at 300 rpm for 30 min with continuous bubbling of N₂ gas. When the color of the solution changed from orange-red to colorless, the mixture was filtered to obtain a prime product of bimetal particles. The product was then washed with distilled water until no chloride residue was detected in the washing solution. Thereafter, the obtained particles were then dried at 80 °C in a vacuum oven for 24 h prior to characterization.

**Experimental Procedure**

The experiments to determine the effects of Pd/Fe⁰ dosage, pH and anionic ions on the reductive dechlorination of chloroform were performed in 14 mL serum bottles that were well capped with septum without any headspace. These vials were placed on an end-to-end rotary shaker at a speed of 30 rpm. The experiments to determine the effect of ORP were performed in a 250 mL glass cell sealed with a PTFE septum, in which different gases were initially bubbled for 15 min. Then the cells were well sealed and placed on a shaker at 250 rpm. During the reaction, an ORP probe was immersed in the solution to determine the ORP values. The initial pH of all reaction solutions was adjusted to 5.13 with 0.1 M H₂SO₄ and 0.1 M NaOH solutions, and the initial concentration of aqueous CHCl₃ solutions was prepared at 20 mg L⁻¹.
Characterization and Analyses

Scanning electron microscope (SEM) and X-ray diffraction (XRD) were employed to investigate the surface morphology and chemical composition of the prepared Fe⁰ and Pd/Fe⁰ samples, respectively. The SEM was performed on a Philips Quanta 400 FE environment scanning electron microscope (FEI, Holland) coupled with an INCA energy dispersive X-ray spectrometer (EDS, Oxford, England) to obtain the atom composition. The XRD measurements were performed at 45 kV and 30 mA on a D/MAX 2200 VPC (RIGAKU, Japan) equipped with a graphite monochromator (Cu Kα radiation, λ = 1.54056 Å).

Chloroform concentration was analyzed by gas chromatography-mass spectrometry (GC/MS Virian CP-3380/MS1200L) with a headspace autosampler (Teledyne Tekmar 7000). The injection temperature and detector temperature of the GC were set at 200 and 300 °C, respectively, and a gradient program was applied in the oven with an initial temperature of 35 °C held for 2 min and then gradually increased to 200 °C at a rate of 5 °C min⁻¹, and remained at 200 °C for 2 min. Chloride ion concentration was determined by spectrophotometry at a wavelength of 460 nm after reaction with mercury thiocyanate to form an orange-red compound (15). The efficiency of chloroform degradation was calculated by the percentage of chloroform concentration reduction at 8 h-reaction, and the chloride formation was evaluated according to the molar ratio of chloride formed at a preset time (Cᵢ) to the original chlorine in CHCl₃ (Cₘₐₓ).
RESULTS AND DISCUSSION

Characterization of Pd/Fe₀ Sample

The as-prepared Pd/Fe₀ sample was characterized by the means of SEM and XRD and the results are shown in Figure 1. The SEM image showed that the as-prepared sample was spherical with a diameter of 1-6 μm, and some fine particles could be observed to be residing on the surface of the spherical particles. Furthermore, the XRD results revealed that a phase of Pd was present in the sample. Thus, it could be concluded that the Pd was well coated onto the Fe₀ surface.

[Fig. 1]

Effect of Pd/Fe₀ Dosage

To determine the effect of Pd/Fe₀ dosage, a set of experiments with a fixed initial CHCl₃ concentration of 20 mg L⁻¹ but different Pd/Fe₀ dosages in the range of 5-50 g L⁻¹ was conducted for 8 h. The experimental results of chloroform reduction (Cᵥ/C₀) and chloride formation (Cᵥ/Cₘₐₓ) are presented in Figure 2. It is clear that both the chloroform reduction and chloride formation with the Fe₀/Pd powder were more effective than those with the Fe₀ powder as shown in Figure 2A. These results showed that the reductive reaction of chloroform was significantly accelerated by coating iron with Pd. In the meantime, a much lower efficiency of chloroform degradation at 38.2% for the pure Fe₀ was obtained. Furthermore, the results of chloride formation in a blank experiment ([Pd/Fe₀] = 0) was 4.6% (not shown in Fig. 2B). When the dosage of Pd/Fe₀ increased from 5 to 20
g L⁻¹, the percentage of dechlorination increased from 21% to 31%. When the dosage further increased to 50 g L⁻¹, the dechlorination increased only slightly to 33%. These results indicated that the dosage of Pd/Fe⁰ beyond 20 g L⁻¹ may not be cost effective from an engineering point of view.

[Fig. 2]

In the Pd/Fe⁰ system, Fe⁰ is still the electron donor. It has been established that in the presence of Fe⁰ particles, such a reductive dechlorination reaction may include three possible pathways of: (i) direct electron transfer from iron metal at the metal surface; (ii) reduction by ferrous ions, which act as an immediate product of corrosion and are capable of causing dehalogenation of some alkyl halides, although these reactions are sometimes quite slow; and (iii) catalyzed hydrogenolysis by H₂ that is formed by reduction of H₂O during deoxygenated corrosion.⁴,¹⁶-¹⁹

The coating of Fe⁰ particles with Pd can accelerate the reductive dechlorination reaction through two possible pathways of: (i) favoring the adsorption and the subsequent surface reaction of the corresponding precursors. It was found that, chlorinated organics adsorption on the Pd metal occurs by scission of a C–Cl bond rather than a C–H in any cases, because the former is thermodynamically more favored. Actually, the bonding energy for C–Cl in CHCl₃ is 307.2 kJ mol⁻¹ while for C–H is 422.2 kJ mol⁻¹.⁵ The adsorption of C–Cl bond favored the dechlorination reaction; and (ii) favoring the formation of hydrides on the Pd surface from protons or water, and then the hydrogen reduction reaction occurred to realize the hydrodechlorination. It is known that the Pd is an excellent catalyst of hydrogen. Thus, the hydrogen density is much higher than that on the iron surface and the hydride reaction is rapid. The newly generated hydrogen phase [H] can

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reduce the chloroform more rapidly. To further confirm the role of \([H]\), hydrogen gas was applied to blow the reaction solution and the results showed that the much higher efficiency of chloroform degradation at nearly 100% was obtained at 8-h reaction. At the same time, the presence of hydrogen could result in a significant decrease in the ORP value of the system. It was detected that the initial ORP value of the system was only 97 mV, much lower than at the N\(_2\)-bubbled or air-bubbled system (Fig. 3). Therefore, after the coating of Pd onto the Fe\(^0\) surface, the acceleration mechanism could be mainly attributed to the [H]-induced one.

**Effect of ORP**

The main reaction of dechlorination is expressed by Equation 2, while side reactions involving metal corrosion could occur through Equations 3 and 4 to generate O\(_2\) and H\(_2\), respectively.

\[
Fe^0 + R\cdots Cl + H^+ \rightarrow Fe^{2+} + R\cdots H + Cl^- \tag{2}
\]

\[
Fe^0 + O_2 + 4H^+ \rightarrow Fe^{2+} + H_2O \quad \text{(under an oxygenated condition)} \tag{3}
\]

\[
Fe^0 + H^+ \rightarrow Fe^{2+} + H_2 \quad \text{(under a deoxygenated condition)} \tag{4}
\]

Certainly, O\(_2\) could alter the ORP in the solution that played an important role in the redox reactions. To disclose the effects of ORP on the reductive dechlorination, N\(_2\), air and O\(_2\) in gas was respectively bubbled into the reaction solutions for 15 min to adjust their initial ORP values, and the initial concentrations of dissolved oxygen (DO) in the four solutions were found to be DO < 0.01 mg L\(^{-1}\) (N\(_2\)), DO = 7.8 mg L\(^{-1}\) (air), and DO = 32 mg L\(^{-1}\) (O\(_2\)), respectively. Figure 3 showed that the different gases led to different initial ORP values in the solution. Consequently, different
experimental results about dechlorination were obtained and are shown in Figure 4. It can be seen that the N₂-bubbled solution led to the fastest reaction, while the O₂-bubbled solution led to the slowest reaction. It is interesting that the ORP values in the three reaction systems approached to a similar value of approximately 400 mV after 10 h reaction without any further gas blowing. These results indicated that a low ORP value was beneficial to the chloroform reduction in such as a reaction system and three reaction systems with different initial ORP values could be automatically balanced to approach a same final ORP value.

Effect of pH

The effect of initial pH on the reduction reaction of chloroform by the Pd/Fe⁰ is shown in Figure 5. Evidently, the faster rates of chloroform reduction were achieved at the lower pH. When the initial pH was 3.0, the degradation efficiency of chloroform at 8 h reaction was 77.5%, and the dechlorination efficiency at 8 h reached by 49%. When the initial pH was 8.5, degradation efficiency of chloroform at 8 h reaction was 47.3 min⁻¹, and the dechlorination efficiency was achieved by 9%, much smaller than that at pH 3.0. At the same time, the initial pH values did not vary significantly after 8-h reaction, and typically, Figure 5C presented the variation of initial pH 5.1 during the reactions at different atmospheres.
The higher rate of chloroform reduction at the lower pH could be relevant to the corrosion behavior of Fe\(^0\) bulk. Under the extremely acidic condition, the Fe\(^0\) corroded rapidly to generate Fe\(^{2+}\) and H\(_2\) gas. During the formation of H\(_2\) gas, atomic hydrogen was present as an intermediate. The presence of the Fe\(^{2+}\), particularly of the atomic hydrogen could lead to effective hydrodechlorination.\(^{[17]}\) Moreover, the reaction of hydrodechlorination demanded hydrogen atom to add into the product. Obviously, the acidic medium was favorable. By contrast, in the alkaline medium, the surface passivation of Fe\(^0\) particles occurred and iron corrosion ceased at above pH 8.8.\(^{[21]}\) Also, in this case, the hydrogen atom demanded by the reaction of hydrodechlorination was extracted from the H\(_2\)O molecule, and such extraction needed a higher energy penalty than from the acid.

[Fig. 5]

**Effect of Anions**

Inorganic ions coexist with the chloroform in the solution and may influence the degradation of chloroform by the Fe\(^0\) reduction.\(^{[22,23]}\) In this study, the effects of anions of SO\(_4^{2-}\), NO\(_3^-\), and H\(_2\)PO\(_4^-\) on the chloroform degradation were investigated. Three salts of NaNO\(_3\), NaH\(_2\)PO\(_4\), and Na\(_2\)SO\(_4\) in 10 mM aqueous solutions were added into the reaction system of Pd/Fe\(^0\), and the results of chloroform reduction are shown in Figure 6. The experiments demonstrated that the degradation efficiency of chloroform decreased from 76.4% (no anion) to 20.0% (NO\(_3^-\)) and 12.0% (SO\(_4^{2-}\)), respectively, while the degradation efficiency with H\(_2\)PO\(_4^-\) remained almost unchanged as high as 74.3%. It is obvious that the presence of sulfate ion caused the most remarkable decrease in the
efficiency of chloroform reduction, while the presence of nitrate ions caused a significant decrease of the chloroform reduction. As an inhibitor anion, the sulfate ions could impact the adsorption characters of iron particles. Fourier Transform Infrared Spectroscopy (FTIR) study showed that the sulfate forms both outer-sphere and inner-sphere surface complexes on goethite as sulfate green rust as follows:[23]

\[ 4Fe^{2+} + 2Fe^{3+} + SO_{4}^{2-} + 12H_{2}O \leftrightarrow Fe_{6}(OH)_{12}SO_{4} + 12H^{+} \]  

Equation 5 shows that the sulfate ions compete adsorption sites with chloroform. The active reaction sites on the iron could be quickly covered with the sulfate ions.

The nitrate ion was a strong competitor with chloroform to accept the electrons by means of Equation 6, in which nitrate could be reduced by the Fe\(^0\) to form NH\(_4^+\).

\[ NO_{3}^{-} + 4Fe^{0} + 10H^{+} \leftrightarrow NH_{4}^{+} + 4Fe^{2+} + 3H_{2}O \]  

At its low concentration, nitrate ion could stimulate pitting corrosion of iron oxides within a certain potential region where the passive oxide film was characterized by low stability. Hence, the impact of nitrate ion on the Pd/Fe\(^0\) solid phase depended on its concentration. Since there was a broad range of nitrate concentrations in natural water, care should be taken on the critical concentration of nitrate ion in the application of such a Pd/Fe\(^0\) system.
Compared with other anions, the presence of phosphate caused almost no significant variation in the chloroform removal efficiency. Research \cite{22,23} revealed that the phosphate could form inner-sphere complexes with the functional groups at the surfaces of iron and iron oxides. The stability constant of phosphate with Fe$^{2+}$/Fe$^{3+}$ was larger than that of the sulfate. Thus, when the phosphate existed in the solution, a steady complex of phosphate with Fe$^{2+}$ or Fe$^{3+}$ generated. This complex possibly served to enhance the corrosion of Fe$^0$ to Fe$^{2+}$ or Fe$^{3+}$. However, this complex might also act as a colloid \cite{24} to inhibit the reaction between the Fe(II) and the chloroform. As a result, it might be indicated that the phosphate caused no significant influence on the reaction of chloroform reduction.

**CONCLUSIONS**

Results obtained under the laboratory conditions demonstrated that the bimetallic Pd/Fe$^0$ particles could dechlorinate chloroform with much more rapid rates than the Fe$^0$ particles. With the Pd coating on the Fe$^0$ surface, the chloroform degradation efficiency and dechlorination efficiency increased over twice and nearly 8 times after 8 h reactions, respectively, compared with those without Pd coating. With different factors, the kinetic trends of chloroform removal remained the same pattern that the higher Pd/Fe$^0$ dosage, lower initial pH and lower initial ORP values could achieve the higher reaction rate. The aqueous chloroform solutions bubbled with different gases had different ORP values from low to high as N$_2$ < air < O$_2$, and the degradation efficiency of chloroform in different atmospheres followed an order from high to low as N$_2$ > air > O$_2$. The SO$_4^{2-}$...
and NO$_3^-$ ions inhibited the dechlorination reaction significantly, while the H$_2$PO$_4^-$ had no influence on the dechlorination.

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