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Hydrodechlorination of 2,4,6-trichlorophenol for a permeable reactive barrier using zero-valent iron and catalyzed iron

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Abstract−Dehalogenation of toxic organic compounds has been intensively studied during the last decade by using zero-valent iron (ZVI). However, the reactivity of iron is compound specific and very low reactivities were reported for aromatic compounds including chlorophenols. In this study, hydrodechlorination of 2,4,6-trichlorophenol (2,4,6-TCP) was conducted in a batch system by using ZVI and catalyzed iron. No degradation was observed with ZVI over the 40 days experiments. Catalyzed ZVIs removed 2,4,6-TCP and palladium-coated iron (Pd/Fe) and nickel-coated iron (Ni/Fe) showed relatively enhanced reactivity while copper-coated iron (Cu/Fe) and platinum-coated iron (Pt/Fe) showed lower reactivities. The surface area normalized kinetic constants (k_{SA}) of Pd/Fe, Ni/Fe, Cu/Fe, Pt/Fe are 2.54×10^{-4}, 1.01×10^{-4}, 2.24×10^{-5}, 2.56×10^{-5} L m^{-2} h^{-1}, respectively. The identification of less chlorinated phenols and phenol confirmed that the removal is dechlorination. Pd/Fe system exerts relatively low pH compared with the ZVI system, and the low pH is favorable for the dechlorination. The reactivity enhancement of catalyzed iron was discussed in terms of catalytic effects and the corrosion potential by the bimetal coupling. Variable Pd content on the Pd/Fe was tested, and the degradation rate of 2,4,6-TCP increased in proportion to the increase of Pd content.

Key words: 2,4,6-Trichlorophenol (2,4,6-TCP), Zero-valent Iron (ZVI), Catalyzed Iron, Hydrodechlorination

INTRODUCTION

In recent years, considerable attention has been given to the treatment of wastewater and groundwater contaminated by chlorinated organic compounds and inorganic compounds [1-9]. Industrial processes have widely used chlorinated aliphatic compounds (e.g., trichloroethylene and tetrachloroethylene) as organic solvents and also generated chlorinated solvent-contaminated wastewaters. The release of such chlorinated solvents into subsurface environments has led to extensive contamination of groundwater resources because they are widespread and mobile [10-12].

Chlorophenols are so widely used that they are nearly ubiquitous in all major environmental compartments [13]. Chlorophenols, from mono- to penta-chlorine substituted, are used as the intermediates for organic synthesis of dyestuffs and pesticides, as biocides themselves, and as wood preservatives [14,15]. Because of their numerous origins, chlorophenols can be found in groundwater, wastewater and soil [16] and even in the food chain [17,18]. They constitute a particular group of priority toxic pollutants listed by the US EPA [19,20], because most of them are toxic, hardly biodegradable, and difficult to remove from the environment. Particularly, 2,4,6-trichlorophenol (2,4,6-TCP) and 2,4-dichlorophenol (2,4-DCP) are listed in the Drinking Water Contaminant Candidate List (CCL) [21].

When chlorinated organic compounds in solution come in contact with zero-valent metals (ZVMs), they undergo a thermodynamically favorable reductive dechlorination that is equivalent to iron corrosion with the chlorinated organic compound serving as the oxidizing agent [22]. Numerous research groups have carried out investigations to treat halogenated hydrocarbons in wastewater and groundwater by using ZVMs, and halogenated aliphatics such as chlorinated methanes, ethanes, and ethenes were degraded successfully [4,6,23-26]. Since iron is relatively inexpensive (i.e., relatively low installation and operation costs) and nontoxic, it has been used as a reducing agent for chlorinated hydrocarbons in pilot-scale field studies as well as laboratory tests [2,4,27-29].

Chlorinated aromatics have not been as facilely dechlorinated as trichloroethylene (TCE) and tetrachloroethylene (PCE) by ZVMs. In the case of polychlorinated biphenyls (PCBs), they were hardly dechlorinated at room temperature [30]. Therefore, modified ZVMs such as nanoscale iron particles and bimetallic particles have been applied to enhance the dechlorination of chlorinated hydrocarbons [5,13,14,28,31-33]. PCBs could be degraded effectively by nanoscale iron particles and palladium-coated iron (Pd/Fe) with biphenyl detected as a byproduct [32,33]. Liu et al. [14] reported that three chlorophenol isomers, *o*-, *m*-, and *p*-chlorophenol, were completely dechlorinated by Pd/Fe powder in water within 5 hours and the reduction product for all the three isomers was phenol. It was also reported that the dechlorination rate increased with the increase of bulk loading of palladium (Pd). Morales et al. [34] examined uncatalyzed and palladium-catalyzed iron and magnesium on the dechlorination of 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-TCP, and pentachlorophenol (PCP) under room temperature. In their investigations, detectable products were cyclohexanol and cyclohexanone at 25% yield, and no other byproduct was observed by mass spectral analysis. Kim and Carraway [2] investigated the disappearance of PCP from aqueous solutions by zero-valent iron

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(ZVI) and four bimetallic irons (Pd/Fe, Pt/Fe, Ni/Fe, and Cu/Fe). In the study, tetrachlorophenol isomers appeared as the byproducts of PCP dechlorination, and a modified extraction method was try to confirm the total mass balance after the reaction. The study indicated that it is essential to separate the dechlorination reaction and adsorption processes in ZVM-chlorophenol systems.

The objective of this study is to investigate the feasibility of ZVI and catalyzed ZVI for the dechlorination of recalcitrant 2,4,6-TCP. Byproduct distribution and total mass balance in 2,4,6-TCP reduction are investigated and dechlorination rates by ZVI and amended irons are also determined in this study.

MATERIALS AND METHODS

1. Chemicals

2,4,6-TCP (98%), 2,6-DCP (99%), 2,4-DCP (99%), 4-CP (99+%), 2-chlorophenol (2-CP, 99+%), palladium(II) chloride (5 wt% solution in 10 wt% HCl), nickel(II) chloride hexahydrate, copper(II) chloride dihydrate (99.99+%), platinum(II) chloride (98%), hydrochloric acid (HCl 37%, ACS grade), and sulfuric acid (H_2SO_4 95-98%, ACS grade) were supplied by Aldrich Chemical Co., Inc. (Milwaukee, WI). Ethyl acetate (99.8%, HPLC grade), methyl alcohol (99.93%, ACS HPLC grade), p-xylene (Anhydrous, 99+%), phenol (loose crystals, 99+%, ACS reagent), cyclohexanol (99%), and cyclohexanone (99.8%) were obtained from Sigma-Aldrich, Inc. (St. Louis, MO). Iron metal powder (electrolytic, finer than 100 mesh) was obtained from Fisher Scientific (Fair Lawn, NJ). All chemicals were used as received without further purification. Deionized water (DI water) was generated by a Barnstead water purification system (resistivity ≥17.5 MΩ·cm and total organic carbon <1.0 mg/L) and used in all experiments.

2. Preparation of Catalyzed Iron

Catalyzed iron was prepared by mixing acidic solutions of catalytic metals with iron metal powder. The preparation method followed a previous report [2]. The content of the Pd, Ni, Cu, and Pt in the bimetals was calculated to be 636, 1,269, 1,272, and 887 ppm (mg of catalytic metal/kg of iron metal powder), respectively. Pd/Fe with various Pd mass fractions of 318, 636, 1,272, and 2,544 ppm (mg of Pd/kg of Fe) was also prepared to investigate the effect of Pd content. Subsequent preparations of bimetals and ICP analysis (ICP-OES, Optima™ 4300 DV, Perkin Elmer) of the catalytic metals in the diluted stock solutions before and after exposure to ZVMs showed that 90-98% of the catalytic metals were removed (data not shown).

3. Measurement of Specific Surface Area

The N_2-BET surface areas of the metals were measured with a Micromeritics ASAP-2010 (quadruplicate measurements). The specific surface areas (m^2/g) measured by N_2 adsorption were: Fe; 0.5278 (±0.0012), Pd/Fe (Pd content=636 ppm); 2.3195 (±0.0026), Ni/Fe (Ni content=1,269 ppm); 1.0709 (±0.0046), Cu/Fe (Cu content=1,272 ppm); 1.3862 (±0.0013), Pt/Fe (Pt content=887 ppm); 0.9371 (±0.0024), Pd/Fe (Pd content=318 ppm); 2.4787 (±0.0016), Pd/Fe (Pd content=1,272 ppm); 2.0481 (±0.0021), and Pd/Fe (Pd content=2,544 ppm); 1.9230 (±0.0020).

4. Reactor System

100,000 mg/L of 2,4,6-TCP in methyl alcohol was prepared as stock solution and diluted to 100 mg/L with purified water. EPA VOA amber vials (40 mL, Fisher Scientific) were used as batch reactors. 1.00 (±0.01) g of ZVI (or catalyzed ZVI) and 10.00 (±0.05) mL of diluted stock solution were added in the pre-washed vials. Immediately after addition of the chlorophenol solution, the vials were capped with Teflon-lined silicone septa and open-top screw caps. Control vials were prepared identically except for the exclusion of metallic reductants. All vials were placed on an orbital shaker at room temperature (25±0.5 °C) and shaken at 180 rpm. At each sampling time, three reaction vials and two control vials were removed for extraction and analysis of chlorinated phenols and phenol. Solution pH was also measured before and after extraction by using a Thermo Orion pH meter (model 720A$^+$). Two-point calibration (pH 4 and 7) was performed before the pH measurements.

5. Extraction and Analysis

For the GC analysis, a modified liquid-liquid extraction method was applied for the extraction of all experimental samples. Ethyl acetate (5.0 mL) was added to the sample (10 mL) and then was followed by the addition of 0.25 mL of concentrated sulfuric acid which increased the extraction rates [2]. *p*-Xylene (50 ppm) was added to the ethyl acetate before the extraction as an internal standard. Chlorinated phenols and byproducts in the extracted solution were analyzed with a gas chromatograph (Agilent Technology 6890N) with a mass selective detector (Agilent 5973 MS Detector) and a HP-5MS capillary column (Agilent Technology Inc., inner diameter 0.25 mm×0.25 mm film thin and length 30 m). Split mode injection of 1 mL of sample was used. The oven temperature program was 1 min at 60 °C, 10 °C/min to 160 °C (ramp 1), 25 °C/min to 240 °C (ramp 2), and 0.5 min at 240 °C. Highly pure grade helium (99.999%) was used as the carrier gas with a constant flow rate of 1.0 mL/min, and a mass range of 45-425 *m/z* was selected. The inlet temperature was fixed at 280 °C.

RESULTS AND DISCUSSION

1. Dechlorination of 2,4,6-TCP by Fe^0 and Pd/Fe

Uncatalyzed zero-valent iron (Fe^0) and palladium-coated iron (Pd/Fe) with Pd content of 636 ppm were applied to dechlorination of 2,4,6-TCP. In the ZVI system (1.0 g of Fe^0 per 10 mL of 2,4,6-TCP solution), as shown in Fig. 1(a), dechlorination of 2,4,6-TCP hardly occurred and no intermediate was found over a reaction period of 40 days. Most of the 2,4,6-TCP added was extracted through the acid-modified extraction method in both control and reaction vials. According to the previous study, 3.03 mM of 2,4,6-TCP was degraded to 2.12 mM by using the identical iron metal (1.31 g of Fe^0 per 10 mL of 2,4,6-TCP solution) after reaction for 30 minutes [34]. However, intermediates from the dechlorination reaction were not shown exactly in their report indicating that mass loss by adsorption onto the metal surface cannot be excluded when liquid-liquid extraction is applied. In the Pd/Fe system (Fig. 1(b)) 500 μM of 2,4,6-TCP was completely degraded within 5 days and the dominant byproduct was phenol. Besides the phenol, a small amount of less chlorinated intermediates (e.g., 2,6-DCP, 2,4-DCP, 4-CP, and 2-CP) was found during the reaction. Approximately 90% of mass recovery efficiency was achieved through the acid-modified extraction method. These results indicate that the removal of 2,4,6-TCP is mostly due to the dechlorination reaction. In our previous study, the protonation of phenol functional groups by adding acid in the

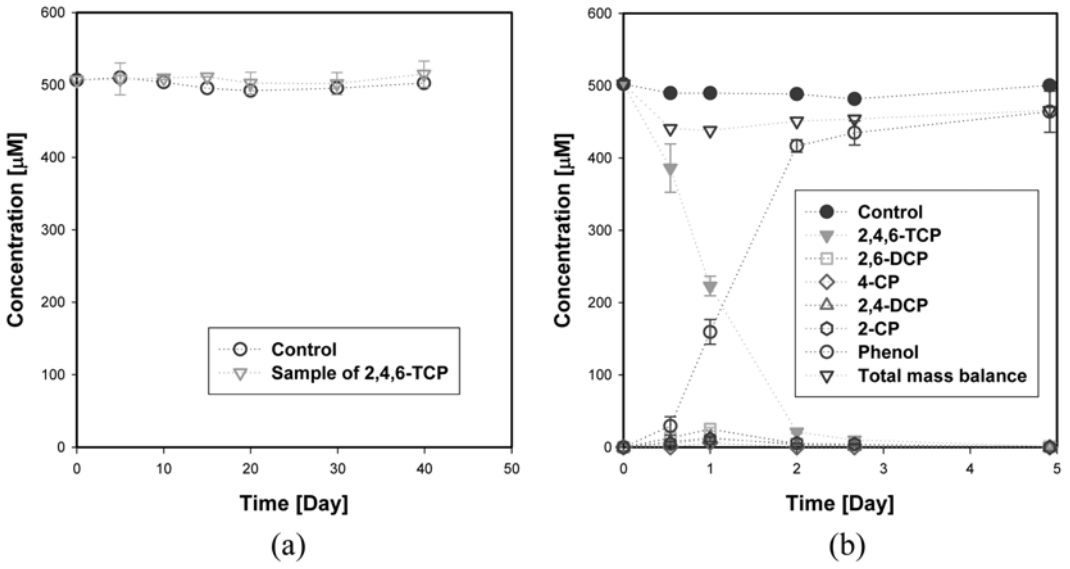

Fig. 1. (a) Degradation of 2,4,6-TCP by Fe^0 (1.0 g of Fe^0 per 10 mL of solution) and (b) dechlorination of 2,4,6-TCP and byproducts by Pd/Fe with Pd content of 636 ppm (1.0 g of Pd/Fe per 10 mL of solution). Error bars indicate 1 SD. Some error bars are smaller than data symbols.

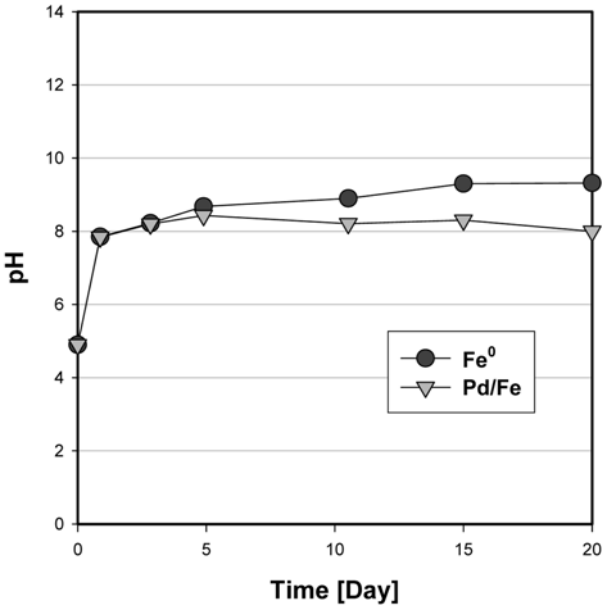

Fig. 2. Change of solution pH in Fe^0 and Pd/Fe system.

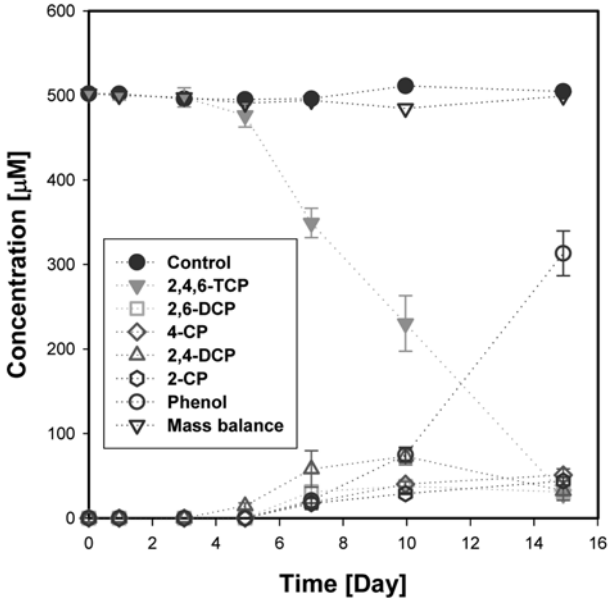

Fig. 3. Dechlorination of 2,4,6-TCP and byproducts by Ni/Fe with Ni content of 1,269 ppm (1.0 g of Ni/Fe per 10 mL of solution).

extraction process could increase the mass recovery rate [27].

The aqueous solution pH was monitored during the reactions. The solution pH increased from 4.9 to 9.3 in Fe^0 system and from 4.9 to 8.4 in Pd/Fe system without any pH buffer (Fig. 2). The solution pH increased steeply at the initial period of the reaction and increased gradually after that. In the Fe^0 system with no pH buffer, the solution pH increased to near 10 in other researches as well as this study [35,36]. The increase of pH is mainly due to the consumption of protons by the hydrodechlorination reaction (Eq. (1)) and the oxidation of metals (Eq. (2) and (3)). Lower pH is favorable for dechlorination reactions because the hydrodechlorination reaction consumes protons. A high pH accelerates the formation of metal (hydr)oxides and may lead to problems such as the clogging of flow reactors and decrease of surface reactivity [36].

$$Fe^0+RX+H^+ \rightarrow Fe^{2+}+RH+X^- \quad (1)$$

$$Fe^0+2H_2O \rightarrow Fe^{2+}+H_2(g)+2OH^- \quad (2)$$

$$2Fe^0+O_2+2H_2O \rightarrow 2Fe^{2+}+4OH^- \quad (3)$$

2. Dechlorination of 2,4,6-TCP Using Catalyzed Iron

Three other kinds of catalyzed iron (Ni/Fe, Cu/Fe, Pt/Fe) were also tested for 2,4,6-TCP degradation. The dechlorination result

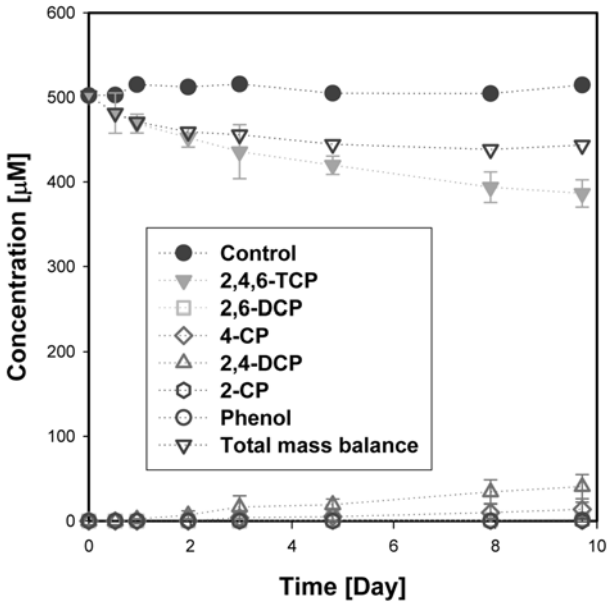

Fig. 4. Dechlorination of 2,4,6-TCP and byproducts by Cu/Fe with Cu content of 1,272 ppm (1.0 g of Cu/Fe per 10 mL of solution).

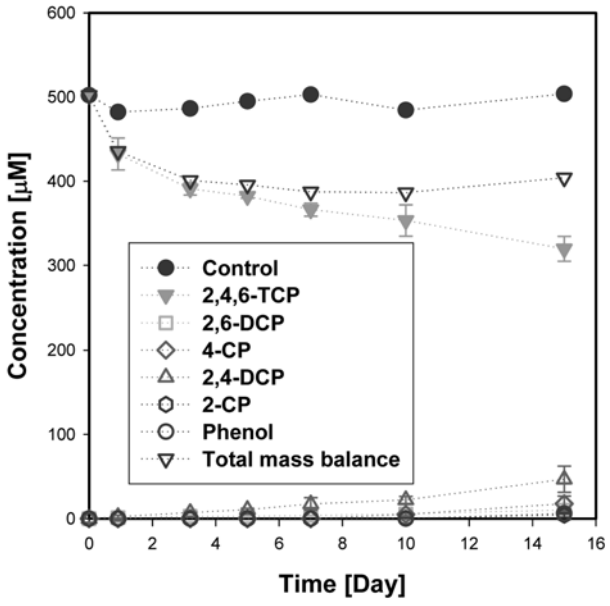

Fig. 5. Dechlorination of 2,4,6-TCP and byproducts by Pt/Fe with Pt content of 887 ppm (1.0 g of Pt/Fe per 10 mL of solution).

and byproducts generation in Ni/Fe, Cu/Fe, and Pt/Fe system are shown in Fig. 3-5, respectively. In the three catalyzed iron systems, relatively rapid dechlorination was observed in the Ni/Fe system (Fig. 3), and the dechlorination of 2,4,6-TCP was confirmed by the appearance of less chlorinated byproducts. 2,4-DCP was detected as the intermediate of the dechlorination reaction after 5 days and phenol appeared dominantly at the end of the reaction. Very close agreement between the control mass and the sample mass extracted was achieved in this system. Degradation of 2,4,6-TCP was not observed for the initial 3 days of reaction in the Ni/Fe system. It may be due to the limited availability of reactive surface sites [37,38] or sorption of 2,4,6-TCP to nonreactive surface sites [10,39-41]. In Cu/Fe and Pt/Fe system (Fig. 4 and 5) the appearance of less chlorinated byproducts accounts for the disappearance of 2,4,6-TCP. However, the 2,4,6-TCP degradation rate in Cu/Fe and Pt/Fe system was much slower than that in Ni/Fe system as compared over the same reaction period. The total amount of daughter compounds produced by dechlorination reaction was less than that of 2,4,6-TCP removed in Cu/Fe and Pt/Fe system, indicating that the extraction efficiency was relatively poor in the reaction vials compared with the controls. A small amount of byproducts was produced in Cu/Fe and Pt/Fe system over the reaction period, and 2,4-DCP and 4-CP were dominant intermediates via the dechlorination reaction.

3. Kinetic Analysis on 2,4,6-TCP Degradation

The degradation of 2,4,6-TCP by ZVI and several catalyzed irons was fit to a pseudo-first-order reaction model, and the resulting rate constants (k_{obs}, 95% confidence interval) are summarized in Table 1. Rate constants normalized by metal surface area per aqueous solution volume, based on linear dependence of the reaction rate constant on metal surface area, are commonly reported for ZVM reactions [4,26,42-45]. Previous studies have shown that the rate of contaminant reduction by iron metal is not only first order in contaminant concentration, but that it also appears to be first order with respect to the amount of metal available to serve as reductant. To describe this, the pseudo-first-order kinetic model used to determine k_{obs} can

Table 1. Surface area-normalized pseudo-first-order reaction rate constants in 2,4,6-TCP degradation by uncatalyzed and catalyzed iron

Type of ZVM	Catalytic metal content[a] [ppm]	k_{obs} [h^{-1}]	R^2	k_{SA}[b] [L m^{-2} h^{-1}]	$k_{SA,\,100}$ [L m^{-2} h^{-1}]	Difference in standard electrode potentials[c] [volt]
Fe^0	-	-	-	-	-	-
Pd/Fe	636	5.89 (±0.05)×10^{-2}	0.94	2.54 (±0.02)×10^{-4}	3.99 (±0.03)×10^{-5}	1.36
Ni/Fe	1,269	1.08 (±0.03)×10^{-2}	0.92	1.01 (±0.03)×10^{-4}	0.79 (±0.02)×10^{-5}	0.19
Cu/Fe	1,272	0.31 (±0.10)×10^{-2}	0.90	2.24 (±0.72)×10^{-5}	1.76 (±0.57)×10^{-6}	0.78
Pt/Fe	887	0.24 (±0.01)×10^{-2}	0.84	2.56 (±0.11)×10^{-5}	2.89 (±0.12)×10^{-6}	1.64

[a]Catalytic metal content based on mass.

[b]Uncertainties represent 95% confidence interval.

[c]Calculated from reference [55]. The positive value indicates that plain metal has a more negative standard electrode potential than the second metal (Pd=+0.92 V; Ni=−0.25 V; Cu=+0.34 V; Pt=+1.2 V; Fe=−0.44 V).

be expanded to

$$-\frac{d[C]}{dt} = k_{SA} a_s \rho_m [C] \quad (4)$$

or

$$-\frac{d[C]}{dt} = k_{SA} \rho_a [C] \quad (5)$$

where k_{SA} is the surface area-normalized reaction rate constant (L m^{-2} h^{-1}), a_s is the specific surface area of ZVM (m^2 g^{-1}), ρ_m is the mass concentration of ZVM (g L^{-1} of solution), ρ_a is the surface area concentration of ZVM (m^2 L^{-1} of solution), and C represents the reacting halocarbon [43]. Since $k_{obs}=k_{SA}\rho_a$ where $\rho_a=a_s\rho_m$, the model suggests that straight-line plots should be obtained from k_{obs} versus ρ_a, a_s, or ρ_m.

The surface area-normalized rate constants (k_{SA}) under our experimental conditions were in the order of Pd/Fe>Ni/Fe>Pt/Fe> Cu/Fe as shown in Table 1. The k_{SA} in Pd/Fe system was one order of magnitude higher than that in Pt/Fe and Cu/Fe system. The reaction rate constant in Ni/Fe system was shown to be relatively high with excluding the initial two data points in the kinetic analysis. In Cu/Fe and Pt/Fe system, the removal rate could not be considered as dechlorination rate directly because the mass recovery efficiency was relatively low. The determined reaction rate constants were normalized by the loading of the catalytic metal, assuming that the reactivity shows linear dependence on the amount of the catalytic metal. First-order reaction rate constants normalized by the metal surface area and normalized to 100 ppm of catalytic metal loading ($k_{SA,\,100}$) were also compared in Table 1. The order of reaction rate indicated by $k_{SA,\,100}$ is consistent with the order of k_{SA}.

In previous studies on the dehalogenation of chlorinated aliphatics and aromatics, the presence of the catalytic metal coating enhanced the reaction rates [3,5,34,46]. The enhanced dechlorination by Pd/Fe is also observed in this study. There are two expected roles of the catalytic metal coated on the base metal. One is the promotion of catalytic hydrodehalogenation and hydrogenation reaction on the catalytic metal surfaces [36]. Several metals such as Pt, Rh, Ni, and Pd are known as hydrodehalogenation and hydrogenation catalysts [47], and the catalytic hydrodechlorination of chlorophenols using palladium [48-50] and nickel [48] in the liquid phase has been reported. Cheng et al. [1] have proposed that hydrogen generation by hydrogenation at palladium catalyst surfaces plays an important role in the catalytic hydrodehalogenation reaction. Another expected role of the catalytic metal is to enhance the corrosion of the base metal [36]. In the combination of two metals with different electrode potential each other, the corrosion of the metal with more negative potential is enhanced. The extent of corrosion is related to the difference in standard electrode potential of the metal pair. Enhanced corrosion through this process can be considered as the provision of an electron sink in the form of the catalytic metal coating, which increases the rate of electron transfer [51]. The dechlorination reaction using ZVMs requires metallic corrosion to complete electron transfer. In this study, the two possible effects cannot be distinguished. The difference in standard electrode potential of the each catalyzed iron is calculated in Table 1. Although Pt/Fe (1.64 V) has the biggest differences in electrode potential among the bimetallic combinations used, Pd/Fe (1.36 V) shows the highest reactivity. Ni/Fe (0.19 V) has smaller difference in electrode potential than Cu/Fe (0.78 V) and Pt/Fe, but the dechlorination reactivity is reversed. It can be concluded that the reactivity is not exactly proportional to the difference in standard electrode potentials. Occasionally, the catalytic hydrogenation effect on dechlorination

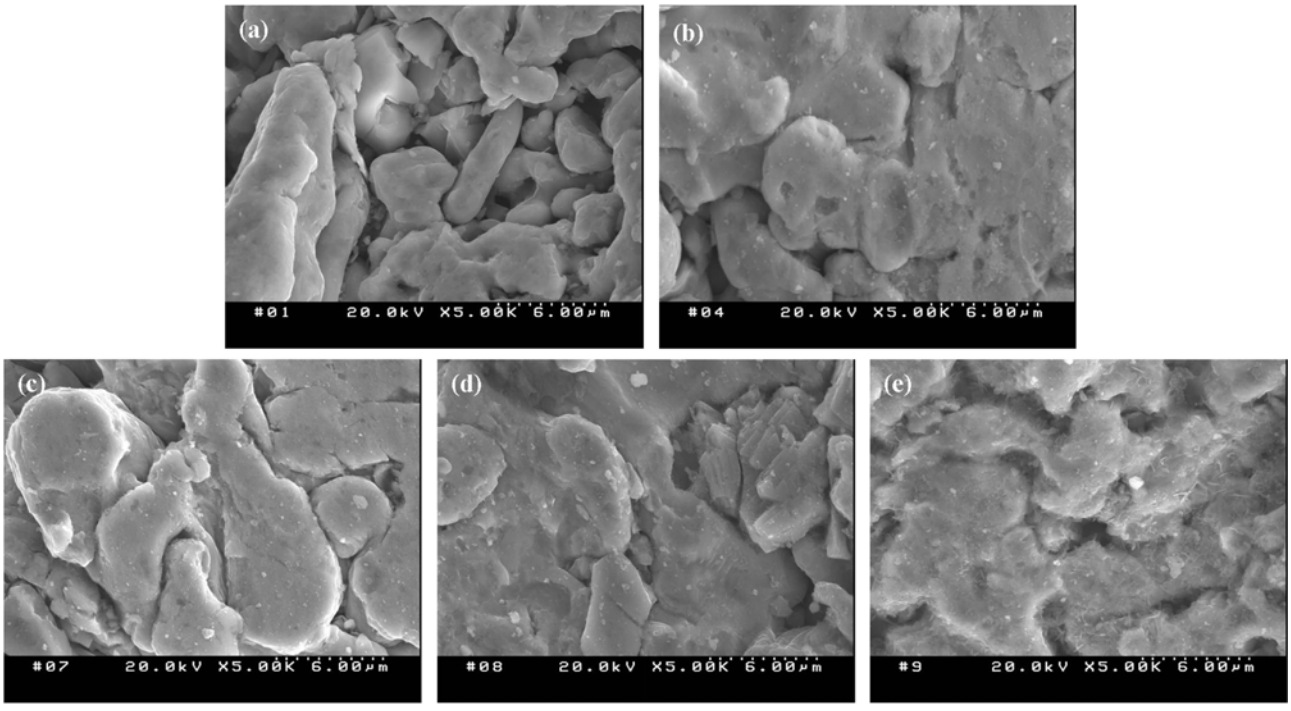

Fig. 6. SEM images of Fe^0 and catalyzed iron (×5,000): (a) Fe; (b) Pd/Fe (Pd content of 636 ppm); (c) Ni/Fe (Ni content of 1,269 ppm); (d) Cu/Fe (Cu content of 1,272 ppm); (e) Pt/Fe (Pt content of 887 ppm).

may be more important than the corrosion effect.

Palladium had better catalytic reactivity on the dechlorination of 2,4,6-TCP than nickel, copper, and platinum in this study. Previous study showed a similar trend, in that Pd/Fe showed higher reaction rate than Ni/Fe, Cu/Fe, and plain Fe (i.e., in the order of Pd/Fe>Ni/Fe>Cu/Fe>Fe) in TCE degradation [36]. Cheng et al. [1] hypothesized that hydrogen intercalated in a palladium lattice is the powerful reducing agent that reductively dechlorinates chlorinated organic compounds that are adsorbed on the surface of palladized electrodes. According to their experimental results, dechlorination of 4-chlorophenol to phenol occurred more rapidly on palladized electrodes than platinized ones. They suggested that palladium should be much more effective in promoting the dechlorination reaction than platinum, probably because of its ability to intercalate hydrogen in its lattice. There are more previous results related with hydrogen intercalation into palladium [52,53]. Wang and Zhang [33] reported that palladium could promote the dechlorination reaction by preventing the formation of iron oxides with some experimental results. The surface morphologies of the used iron metals obtained from SEM images are shown in Fig. 6. Bright spots found in the surface of catalyzed iron metals could be considered as the deposition of the catalytic metals such as Pd, Ni, Cu, and Pt based on EDS analysis (data not added) and a previous report [54].

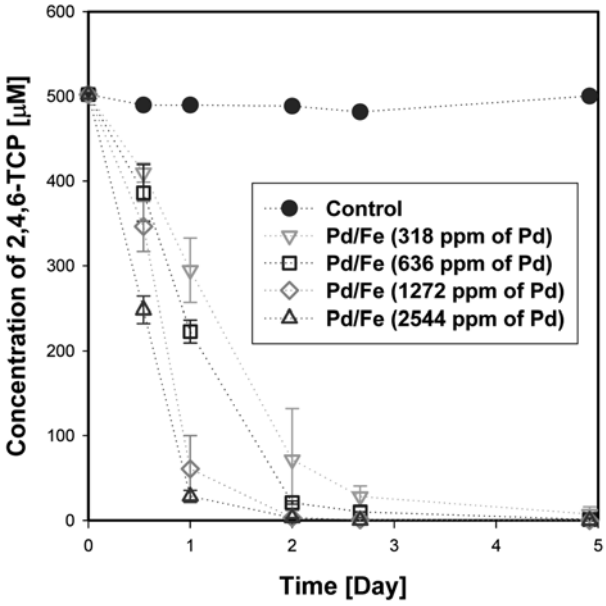

Fig. 7. Degradation of 2,4,6-TCP by Pd/Fe with various Pd contents (1.0 g of Pd/Fe per 10 mL of solution).

4. Dechlorination of 2,4,6-TCP by Pd/Fe with Various Pd Contents

Pd/Fe with various Pd contents of 318, 636, 1,272, and 2,544 ppm was applied to the dechlorination of 2,4,6-TCP, and the degradation results are shown in Fig. 7. The degradation rate of 2,4,6-TCP increased in proportion to the increase of Pd contents. According to the previous report, the conversion of chlorophenol to phenol by the Pd/Fe increased with increasing the Pd loading [14]. Pd/Fe with Pd content of 1,272 ppm degraded 500 mM of 2,4,6-TCP almost completely within 2 days. The degradation of 2,4,6-TCP and the generation of byproducts by using Pd/Fe with Pd content of 1,272 and 2,544 ppm are shown in Fig. 8. Approximately 90% of mass recovery efficiencies was achieved in all Pd/Fe systems and the dominant byproduct was phenol. Besides the phenol, a small amount of less chlorinated intermediates (e.g., 2,6-DCP, 2,4-DCP, 4-CP, and 2-CP) was generated and degraded during the reaction. Especially, cyclohexanone was detected in the Pd/Fe systems with Pd contents of 1,272 and 2,544 ppm indicating that even the benzene ring could be reduced by Pd-supported iron.

The degradation of 2,4,6-TCP by Pd/Fe with various Pd content was fit to a pseudo-first-order reaction model and the surface area-normalized rate constants (k_{SA}) under our experimental conditions are summarized in Table 2. The reaction rate constant (k_{SA}) increases with increasing Pd content. Possible explanations for the enhancement of reactivity with increasing Pd content may involve the increase of Pd concentration on the iron surface and increase of total

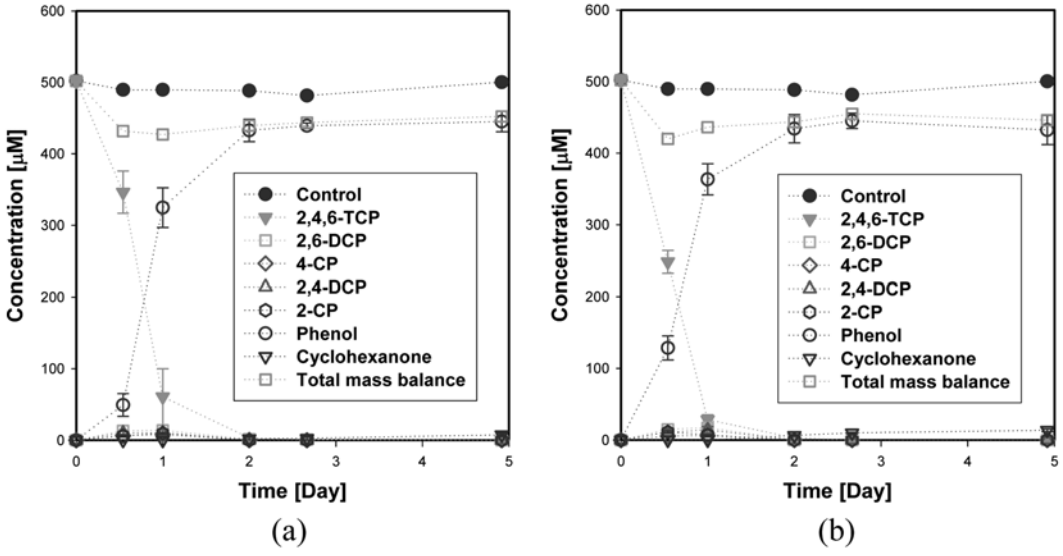

Fig. 8. Dechlorination of 2,4,6-TCP and byproducts by Pd/Fe with Pd content of (a) 1,272 ppm and (b) 2,544 ppm (1.0 g of Pd/Fe per 10 mL of solution).

Table 2. Surface area-normalized first-order reaction rate constants in 2,4,6-TCP degradation by Pd/Fe with various Pd contents

Catalyzed iron	Pd content [ppm]	k_{obs} [h^{-1}]	k_{SA} [L m^{-2} h^{-1}]	R^2
Pd/Fe	318	$4.05 (\pm 0.75) \times 10^{-2}$	$1.63 (\pm 0.30) \times 10^{-4}$	0.93
	636	$5.89 (\pm 0.05) \times 10^{-2}$	$2.54 (\pm 0.02) \times 10^{-4}$	0.94
	1,272	$9.82 (\pm 0.34) \times 10^{-2}$	$4.79 (\pm 0.17) \times 10^{-4}$	0.93
	2,544	$10.61 (\pm 0.38) \times 10^{-2}$	$5.52 (\pm 0.20) \times 10^{-4}$	0.96

Table 3. Summary of reaction rate constants in the degradation of several chlorinated aliphatics and aromatics by catalyzed and uncatalyzed iron

Compounds	Type of ZVM	Catalytic metal content [ppm]	k_{obs} [h^{-1}]	k_{SA} [L m^2 h^1]	R^2	References
2,4,6-TCP	Fe^0	-	-	-	-	[This study]
2,4,6-TCP	Pd/Fe	318	$4.05 (\pm 0.75) \times 10^{-2}$	$1.63 (\pm 0.30) \times 10^{-4}$	0.93	[This study]
2,4,6-TCP	Pd/Fe	636	$5.89 (\pm 0.05) \times 10^{-2}$	$2.54 (\pm 0.02) \times 10^{-4}$	0.94	[This study]
2,4,6-TCP	Ni/Fe	1,269	$1.08 (\pm 0.03) \times 10^{-2}$	$1.01 (\pm 0.03) \times 10^{-4}$	0.92	[This study]
2,4,6-TCP	Cu/Fe	1,272	$0.31 (\pm 0.10) \times 10^{-2}$	$2.24 (\pm 0.72) \times 10^{-5}$	0.90	[This study]
2,4,6-TCP	Pt/Fe	887	$0.24 (\pm 0.01) \times 10^{-2}$	$2.56 (\pm 0.11) \times 10^{-5}$	0.84	[This study]
PCP	Fe^0	-	$3.9 (\pm 0.7) \times 10^{-3}$	$3.2 (\pm 0.6) \times 10^{-4}$	0.97	[2]
PCP	Pd/Fe	500	$6.6 (\pm 2.8) \times 10^{-4}$	$5.4 (\pm 2.3) \times 10^{-5}$	0.88	[2]
PCP	Ni/Fe	240	$7.9 (\pm 4.0) \times 10^{-4}$	$6.4 (\pm 3.3) \times 10^{-5}$	0.83	[36]
PCP	Cu/Fe	200	$7.2 (\pm 4.1) \times 10^{-4}$	$5.8 (\pm 3.4) \times 10^{-5}$	0.80	[36]
PCP	Pt/Fe	180	$6.8 (\pm 3.7) \times 10^{-4}$	$5.5 (\pm 3.0) \times 10^{-5}$	0.81	[36]
PCE	Fe^0	-	-	$2.1 (\pm 2.7) \times 10^{-3}$		[43]
TCE	Fe^0	-	-	$3.9 (\pm 3.6) \times 10^{-4}$		[43]
1,1-DCE	Fe^0	-	-	$6.4 (\pm 5.5) \times 10^{-5}$		[43]
trans-1,2-DCE	Fe^0	-	-	$1.2 (\pm 0.4) \times 10^{-4}$		[43]
cis-1,2-DCE	Fe^0	-	-	$4.1 (\pm 1.7) \times 10^{-5}$		[43]
VC	Fe^0	-	-	$5.0 (\pm 1.5) \times 10^{-5}$		[43]

surface area due to the Pd deposition on the iron surface [14].

Reaction rate constants for the degradation of several chlorinated aliphatics and aromatics by catalyzed and uncatalyzed iron are summarized in Table 3. In contrast to the results of this study, uncatalyzed iron showed relatively high reaction rate constant in other researches [2,43]. In the PCP dechlorination investigated by Kim and Carraway [2,36], particularly, the reactivity of uncatalyzed iron is higher than that of catalyzed iron. Possible explanations for the differences in reaction rates between ZVI and catalyzed ZVI may involve the competitive sorption of chlorinated phenols and reactive hydrogen on iron and catalytic surfaces as well as effects of sorption on corrosion. Additionally, the pH-dependent behavior of chlorinated phenols and its effects on sorption must be considered [2]. The dechlorination rate of PCP by Fe^0 is similar to that of TCE by Fe^0 in Table 3. Pd/Fe, as compared to Fe^0, showed a retardation in the dechlorination of PCP but showed a enhanced reactivity in the dechlorination of TCE [36] and 2,4,6-TCP (this study). Therefore, it is possibly concluded that the reactivity of catalyzed iron is strongly dependent on structure of the compound to be dechlorinated and the degree of chlorination.

CONCLUSIONS

In order to evaluate the potential of plain ZVI and catalyzed ZVI for the treatment of contaminated groundwater and soils, electrochemical hydrodechlorination of 2,4,6-TCP was studied with a batch system. Even though dehalogenation of toxic organic compounds has been intensively studied during the last decade by using zero-valent iron (ZVI), the reactivity of iron is compound specific and ZVI showed very low reactivities for halogenated aromatic compounds including chlorophenols. For 2,4,6-TCP no degradation was observed with ZVI over the experimental period of 40 days indicating plain ZVI (Fe^0) was not active for chlorophenols. Catalyzed ZVIs successfully removed 2,4,6-TCP and Pd/Fe and Ni/Fe showed relatively enhanced reactivity, while Cu/Fe and Pt/Fe showed lower reactivities. The surface area normalized kinetic constants (k_{SA}) of Pd/Fe, Ni/Fe, Cu/Fe, Pt/Fe are 2.54×10^{-4}, 1.01×10^{-4}, 2.24×10^{-5}, 2.56×10^{-5} L m^{-2} h^{-1}, respectively.

The identification of less chlorinated phenols and phenol confirmed that the removal was dechlorination and phenol was the dominant product showing complete dechlorination was occurring in the Pd/Fe system. The high mass balance calculated as the sum of concentration of 2,4,6-TCP and daughter compounds confirmed that the acid modified liquid-liquid extraction was effective for the phenol system. The monitoring of pH in the Fe and Pd/Fe systems showed low pH in Pd/Fe system compared with ZVI system, and the low pH is favorable for the dechlorination. There are two expected roles of the catalytic metal coated on the iron; the first is the catalytic effect on the reaction as Pd, Ni, Cu, Pt are known as reduction catalyst. Another expected role of the secondary metal is to enhance the corrosion of ZVI and to keep the iron surface fresh, which is favorable for electron transfer from the ZVI surface to the

contaminants. Variable Pd content on the Pd/Fe was tested and the degradation rate of 2,4,6-TCP increased in proportion to the increase of Pd content.

The results of this study suggest that catalyzed ZVIs including Pd/Fe and Ni/Fe could be an alternative for the treatment of groundwater and soils contaminated with chlorophenols.

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