Reduction of 2,4,6-trichlorophenol with zero-valent zinc and catalyzed zinc

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ABSTRACT

Reductive dechlorination of 2,4,6-trichlorophenol (2,4,6-TCP) was conducted with Zn and Zn bimetals, Pd/Zn, Ni/Zn, Cu/Zn, Pt/Zn. Zn showed relatively low reaction rate toward 2,4,6-TCP, while Pd/Zn had dramatically increased reactivity and other bimetals had higher reaction rates than that of plain zinc. Phenol and less chlorinated phenols were found as dechlorination products. Pd/Zn produced cyclohexanone which is a product of aromatic ring reduced. Surface area normalized kinetic constants and second metal contents normalized kinetic constants were calculated and compared. Two mechanisms, mainly catalytic activation and enhanced corrosion, were proposed for the reactivity enhancement.

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1. Introduction

In last decades, considerable attention has been given to the treatment of wastewater and groundwater contaminated by chlorinated organic compounds and inorganic compounds [1–10]. Chlorinated aliphatic compounds (e.g., TCE and PCE) have been widely used as organic solvents in various industrial processes and the solvent-contaminated wastewater has been also generated. Such chlorinated solvents released into subsurface environments may lead to extensive contamination of groundwater resources because of their widespread and mobile property [11–13].

Chlorophenols are also widely used as wood preservers, pesticides, herbicides, biocides, and dyes [3]. Because of their numerous origins, chlorophenols have been found in soil, groundwater, and even in the food chains [14–16]. Chlorophenols constitute a particular group of priority toxic pollutants listed by the US EPA [17–18] 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) [19].

Several physical, chemical, and biological methods such as activated carbon adsorption, incineration, and biological degradation have been proposed for the treatment of chlorinated phenols [20]. Generally, biological treatment is superior to physicochemical methods with high treatment costs and possibilities of secondary pollution. However, microorganisms may easily be inhibited by toxic chlorophenols to be treated when conventional biological treatments are used [3,20].

One cost-effective approach for the treatment of chlorinated organic compounds is reductive dechlorination using zero-valent metals (ZVMs). ZVMs such as iron, tin, and zinc have been moderately strong reductants that are capable of reducing many common environmental contaminants including halogenated organics, metals, nitrate, munition wastes, and pesticides. When chlorinated organics in solution come in contact with ZVMs, they undergo a thermodynamically favorable reductive dechlorination. Chloride is released into the solution and oxidized metal ions also dissolved in the solution or precipitated. Therefore, ZVM provides electrons in the reductive dechlorination reaction and oxidation of the ZVM is equivalent to metal corrosion [5,9,21]. Several research groups tried to treat halogenated hydrocarbons in wastewater and groundwater using ZVMs and halogenated aliphatics such as chlorinated methanes, ethanes, and ethenes were degraded successfully [6,8,22–26].

In several ZVMs, iron has been used most popularly for the dechlorination of chlorinated hydrocarbons in field studies as well as laboratory tests since it is relatively inexpensive (i.e., relatively low installation and operation costs) and environmentally acceptable (i.e., nontoxic) [3,4,6,27]. Zero-valent zinc has been also studied as a candidate metal for the degradation of chlorinated organics. Zero-valent zinc has high reactivity toward the chlorinated ethane, ethylene and acetylene [9,22,28]. Reduction of carbon tetrachloride (CCl_4) by zero-valent zinc has been also observed in several researches [26,29,30]. Octachlorodibenzo-p-dioxin (OctaCDD) was dechlorinated to hexa- and pentaCDD under basic and neutral conditions and the dechlorination of pentachlorophenol (PCP) on a zinc electrode in both propylene carbonate solvent and water was

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investigated [31,32]. In spite of the high reduction potential of zero-valent zinc (-0.76 V), it has not received as much attention as iron because the Zn(II) species released can be a concern in water contamination.

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

2. Experimental

2.1. Chemicals

Chlorophenols and other chemicals including 2,4,6-TCP (98%), 2,6-dichlorophenol (2,6-DCP, 99%), 2,4-DCP (99%), 4-chlorophenol (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 (37%, ACS grade), and sulfuric acid (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). Granular zinc (-30 +100 mesh, 99.8+%) was also from Aldrich Chemical Co., Inc. (Milwaukee, WI). All purchased 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.

2.2. Preparation of Zn bimetals

Bimetallic zinc was prepared by mixing acidic solutions of secondary metals with zero-valent zinc (e.g., granular zinc). The secondary metal stock solution was prepared by purchasing acidic solution (5.0 wt.% of palladium(II) chloride (PdCl$_2$)) or by dissolving metal salts into hydrochloric acid (5 wt.% of nickel, 5 wt.% of copper, and 2.5 wt.% of platinum). For the preparation of bimetallic zinc, 2.0 mL of the each secondary metal stock solution (but, 4.0 mL of Pt stock solution) was diluted to 100 mL with DI water and then added to 100.0 g of acid-washed zinc, respectively. The contents were placed on a shaking table and shaken at 180 rpm for 20 min before rinsed with purified water and acetone, and the prepared bimetals were completely dried in drying oven (60–65 °C) for 6–7 h. The bimetals were dark gray in color with no visual evidence of oxide formation on the surface.

Assuming that all of the secondary metals (e.g., Pd, Ni, Cu, and Pt) were reductively precipitated onto the zinc [4], the content of the Pd, Ni, Cu, and Pt was calculated to be 636, 1269, 1272, and 887 ppm (mg of catalytic metal/kg of base metal), respectively. The subsequent preparation of Zn bimetals and ICP analysis (ICP-OES, Optima$^{\text{TM}}$ 4300 DV, PerkinElmer) of the catalytic metals in the diluted stock solutions before and after exposure to zero-valent zinc showed that 90–98% of the catalytic metals were removed (data not shown). All of the metals and bimetals prepared for experiments were stored in amber vials after under nitrogen gas atmosphere.

The N$_2$-BET surface area of the metals was measured (Micromeritics ASAP-2010, quadruplicate measurements) and the specific surface areas (m^2/g) were: Zn; 0.0185 ($\pm$0.0062), Pd/Zn (Pd content = 636 ppm); 0.0676 ($\pm$0.0040), Ni/Zn (Ni content = 1269 ppm); 0.1765 ($\pm$0.0051), Cu/Zn (Cu content = 1272 ppm); 0.0595 ($\pm$0.0028), Pt/Zn (Pt content = 887 ppm);

0.3886 ($\pm$0.0028). Scanning electron microscopy (SEM, S-4200, HITACHI, Japan) images were obtained in an attempt to investigate bimetal and bare metal surfaces. Energy dispersive X-ray spectroscope (EDS) was also used to obtain the information about elemental composition and distribution of the secondary metals at the bimetal surfaces.

2.3. Reactor system

A stock solution (100,000 mg/L of 2,4,6-TCP in methyl alcohol) was prepared and diluted to 100–120 mg/L (506–608 μM of 2,4,6-TCP) with purified water before the degradation experiments. EPA VOA amber vials (40 mL, Fisher Scientific) were used as batch reactors. Diluted stock solution (10.00 ($\pm$0.05) mL) was added into a pre-washed glass vial containing ZVMs (2.00 ($\pm$0.01) g of Zn or Zn bimetal). Immediately after the addition of the diluted stock 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 (e.g. Zn or Zn bimetal). All vials were raped with aluminum foil to avoid photo catalytic degradation and were horizontally placed on an orbital shaker at room temperature (25 $\pm$ 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 using a Thermo Orion pH meter (model 720A$^+$). Two-point calibration (pH 4 and 7) was performed before the pH measurements.

2.4. Extraction and analysis

Chlorophenols were extracted by adding ethyl acetate as extraction solvent and followed by adding concentrated sulfuric acid in the purpose of achieving the a high extraction efficiency [4,33]. In the experimental results presented, control vials were always extracted using the same method as the samples and triplicate sample vials and duplicate control vials were tested.

p-Xylene (50 ppm) was added to the solvent before the extraction as an internal standard. 2,4,6-TCP and all of the byproducts were analyzed using 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 μm film thin and length 30 m). Split mode (20:1) injection of 1 μL 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 the 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. The target compound and expected dechlorination products (2,4,6-TCP, 2,6-DCP, 2,4-DCP, 4-CP, 2-CP, phenol, cyclohexanone, cyclohexanol) were analyzed for making calibration curves. The calibration curves were linear over the concentration range of interest.

3. Results and discussion

3.1. Dechlorination of 2,4,6-TCP by granular Zn and Zn bimetals

Granular zinc was applied to dechlorination of 2,4,6-TCP. A very slow dechlorination of 2,4,6-TCP was exhibited in zero-valent zinc system (Fig. 1). The degradation efficiency was less than 20% and 2,4-DCP was detected as the major intermediate for the reaction period of 40 days. The initial mass of the chlorophenol ($\approx$500 μM) was almost recovered through the modified liquid–liquid extraction by adding acid to enhance the recovery rate. The mass recovery of control was above 95% indicating no significant mass loss through volatilization or photodegradation.
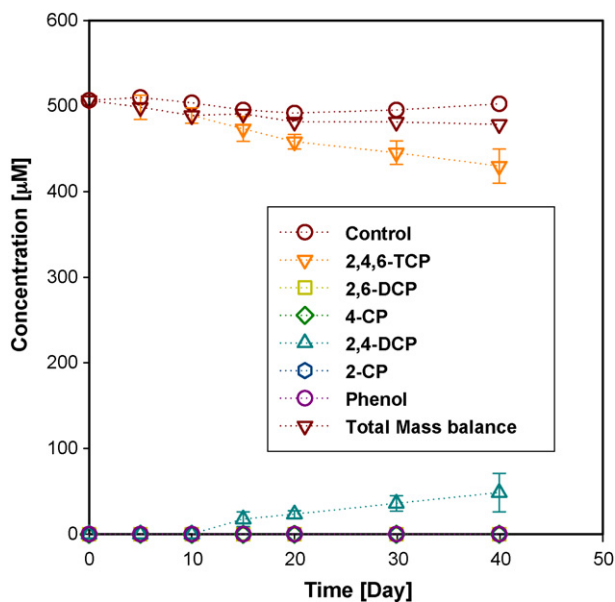
Fig. 1. Degradation of 2,4,6-TCP by Zn (2.0 g of Zn per 10 mL of solution). Error bars indicate 1 S.D. Some error bars are smaller than data symbols.

Four Zn bimetals (e.g., Pd/Zn, Ni/Zn, Cu/Zn, and Pt/Zn) were tested toward 2,4,6-TCP degradation. The results of dechlorination of 2,4,6-TCP in Zn bimetal systems, Pd/Zn (Pd content = 636 ppm), Ni/Zn (Ni content = 1269 ppm), Cu/Zn (Cu content = 1272 ppm), and Pt/Zn (Pt content = 887 ppm) are shown in Figs. 2–5. Over the reaction period of 20 days, a complete degradation of 2,4,6-TCP was observed only in Pd/Zn system (Fig. 2). The dechlorination of 2,4,6-TCP was confirmed by the appearance of the less chlorinated intermediates and the mass balance calculated. The mass recovery efficiency through the extraction was approximately 85%. The 2,4,6-TCP was degraded exponentially and two dichlorophenol (DCP) isomers (e.g., 2,4-DCP and 2,6-DCP), two chlorophenol (CP) isomers (e.g., 2-CP and 4-CP), phenol, and cyclohexanone were formed as byproducts. As 2,4,6-TCP disappeared, phenol was produced predominantly. Especially, the detection of cyclohexanone indicates that the reduction of the aromatic ring as well as the hydrodechlorination may occur in the reduction of chlorinated phenols. In Figs. 3–5, the decrease of 2,4,6-TCP and the production of total
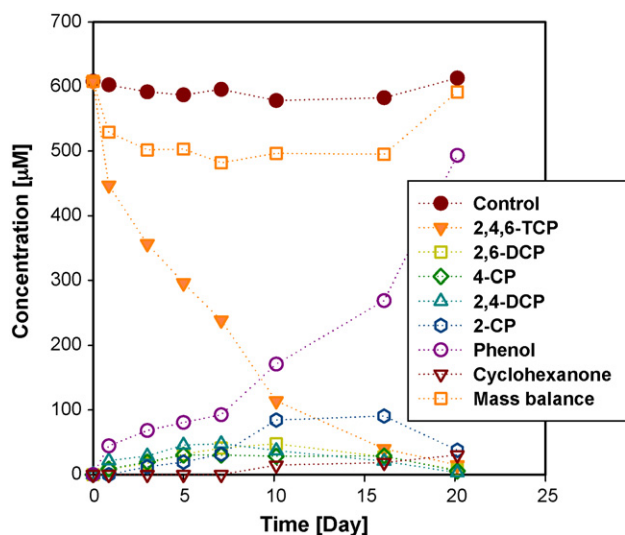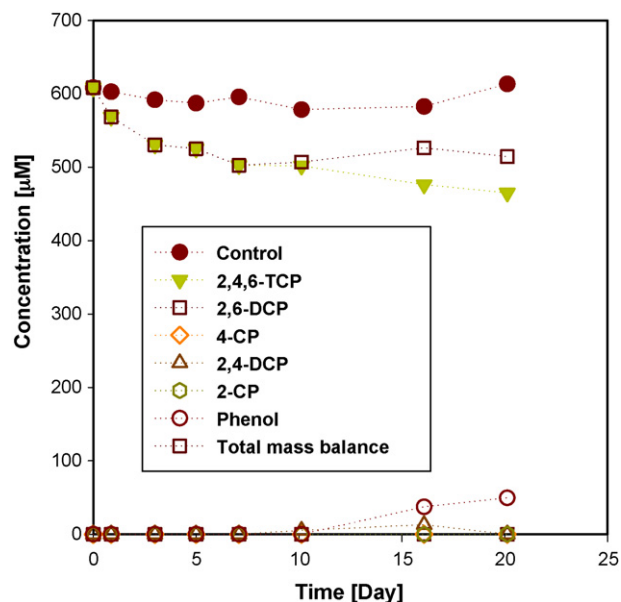

Fig. 3. Dechlorination of 2,4,6-TCP by Ni/Zn with Ni content of 1,269 ppm (2.0 g of Ni/Zn per 10 mL of solution).

daughter compounds are shown for Ni/Zn, Cu/Zn and Pt/Zn systems, respectively. Over the reaction period, the extent of removal of 2,4,6-TCP in Ni/Zn, Cu/Zn and Pt/Zn systems was much lower than that in Pd/Zn system. Trace amount of daughter compounds were observed in these reaction systems and the mass recovery were relatively poor in the reaction vials compared with the controls.

These results indicate that palladized zinc (Pd/Zn) can be an attractive candidate for the dechlorination of 2,4,6-TCP. Oxidation of zinc, however, often results in the release of harmful metal ions, such as Zn^{2+}, that limits the use of this metal in *in situ* barriers. To overcome this problem, a combination of zinc metal and hydroxyapatite has been proposed to remove the dissolved Zn^{2+} by precipitation of low solubility metal phosphates [34]. Additionally, the degradation of the byproducts (e.g., 2,4-DCP, 2,6-DCP, 2-CP, and 4-CP) formed during the dechlorination reaction must be consid-
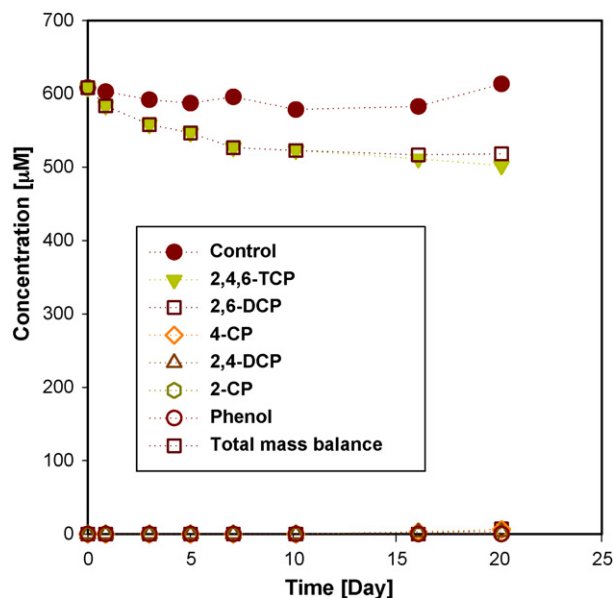

Fig. 2. Dechlorination of 2,4,6-TCP by Pd/Zn with Pd content of 636 ppm (2.0 g of Pd/Zn per 10 mL of solution).

Fig. 4. Dechlorination of 2,4,6-TCP by Cu/Zn with Cu content of 1272 ppm (2.0 g of Cu/Zn per 10 mL of solution).
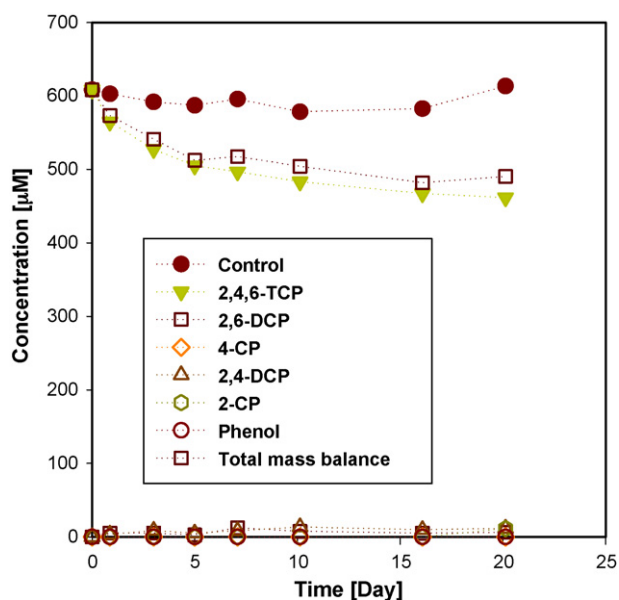
Fig. 5. Dechlorination of 2,4,6-TCP by Pt/Zn with Pt content of 887 ppm (2.0 g of Pt/Zn per 10 mL of solution).

ered because such of the less chlorinated intermediates are also harmful to the environment.

3.2. pH variation of the solution in Zn and Pd/Zn system

During the degradation experiments, the aqueous solution pH was monitored in Zn and Pd/Zn system for 20 days and the results are shown in Fig. 6. The pH variation range in Zn and Pd/Zn system without any pH buffer was 4.9–7.6 and 4.9–9.3, respectively. As compared with Fe system, the solution pH in Fe system with no pH buffer increased to near 10 [23,35]. The pH increase in Zn system was less than in Fe system. The trends show that the solution pH increased steeply at the initial period of the reaction and increased gradually after that. The increase of pH may be due to the consumption of protons by the hydrodechlorination reaction.. The solution pH increase commonly observed in previous studies
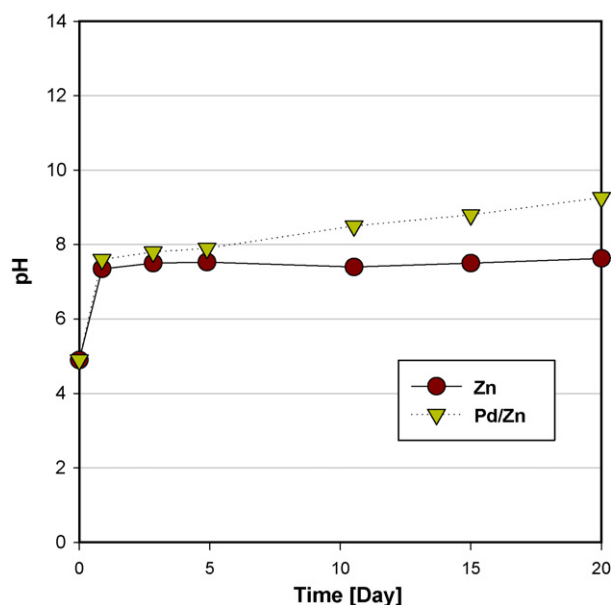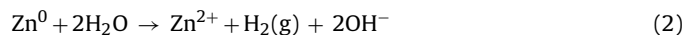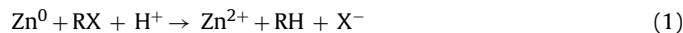

Fig. 6. pH variation of the solution in 2,4,6-TCP degradation by Zn and Pd/Zn.

with zero-valent iron for reductive degradation [2,5,6,8,23,35]. The hydrodechlorination and generation of hydrogen leads to the consumption of proton as shown in following equations (Eqs. (1) and (2)). Zinc also react with dissolved oxygen as a corrosion reaction (Eqs. (2) and (3)).

$$Zn^0 + RX + H^+ \rightarrow Zn^{2+} + RH + X^- \tag{1}$$

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

$$2Zn^0 + O_2 + 2H_2O \rightarrow 2Zn^{2+} + 4OH^- \tag{3}$$

The lower pH is favorable for dechlorination reactions and their applications because the hydrodechlorination reaction consumes protons. Increased pH lowers the reaction rate by making the metal surface inactive with metal (hydr)oxides deposition. 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 [23].

3.3. Kinetic analysis of the degradation of 2,4,6-TCP

The degradation of 2,4,6-TCP by Zn and Zn bimetals 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 [6,26,36–39]. Previous studies have shown that the rate of reduction by iron metal is first order with respect to the concentration of the chlorinated compounds and the amount of metal surface available. To describe this, the pseudo-first-order kinetic model used to determine k_{obs} can be expanded to

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

or

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

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 [37]. 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 current experimental conditions are shown in Table 1. Pd/Zn showed much higher k_{SA} in comparing with other bimetal systems. The k_{SA} of Pd/Zn was about two fold higher than that of Pd/Fe indicating zinc is as good as iron or a little better [33]. These rate constants also could be normalized by the bulk loading of the second metal (i.e., catalytic metal) under an assumption that the reaction rate is highly affected by the extent of primary metal surface coverage with a secondary metal. According to the previous study, metal surface area and surface concentration of Pd increased with the increase of bulk loading of Pd [40]. In this study, the reaction rate constants were normalized by the loading of the second metal, assuming that the reactivity depends on the mass of the second metal. First-order reaction rate constants normalized by the metal surface area per volume of aqueous solution (k_{SA}) and normalized to 100 ppm of mass loading of the second metal ($k_{SA,100}$) were also compared in Table 1. The order of reaction rate indicated by $k_{SA,100}$ is consistent with the order k_{SA}.

Other researchers have studied dechlorination reactions of several chlorinated aliphatics and aromatics using bimetals [5,7,28,41]. In all the cases, the presence of catalytic metals greatly enhanced the reaction rates. Kim [23] has proposed two expected roles of

Table 1
Surface area-normalized pseudo-first-order reaction rate constants of 2,4,6-TCP degradation by Zn and Zn bimetals.

| Type of ZVM	Second 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] (V)
Zn	–	$0.02\,(\pm0.00)\times10^{-2}$	0.96	$5.41\,(\pm0.00)\times10^{-5}$	–	–
Pd/Zn	636	0.72×10^{-2}	0.98	5.33×10^{-4}	8.37×10^{-5}	1.68
Ni/Zn	1269	0.11×10^{-2}	0.84	3.12×10^{-5}	2.46×10^{-6}	0.51
Cu/Zn	1272	0.07×10^{-2}	0.93	5.88×10^{-5}	4.62×10^{-6}	1.10
Pt/Zn	887	0.12×10^{-2}	0.85	1.54×10^{-5}	1.74×10^{-6}	1.96

[a] Second metal content based on mass.
[b] Uncertainties represent 95% confidence interval.
[c] Calculated from reference [53]. 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; Zn = −0.763 V).

the second (catalytic) metals coated on the base metal. The first is the promotion of catalytic hydrodehalogenation and hydrogenation reactions on the surface of the metal added. Noble metals such as Pt, Rh, Ni, and Pd are known as hydrodehalogenation and hydrogenation catalysts [42]. The catalytic hydrodechlorination of chlorophenols using palladium [43–47] and nickel [43] in the liquid phase has been reported. The gas phase hydrodechlorination of several halogenated aromatics (e.g., chlorobenzene, chlorotoluenes, chlorophenols, and bromobenzene) using the nickel supported catalyst, Ni/SiO$_2$, has also been studied [48,49]. Cheng et al. [1] have proposed that hydrogen generation by hydrogenation at palladium catalyst surfaces plays an important role in the catalytic hydrodehalogenation reaction. The other expected role of the second metal is to enhance the corrosion of the primary metal. When two metals contact, the corrosion of one metal increases and that of the other decreases. This system has been used to protect metal structures by coupling with easily corrosive metals. The extent of corrosion is related to the difference in standard electrode potential between the metal pair, but other factors also affect the corrosion process [50]. Enhanced corrosion through this mechanism supplies electrons to the second metal coatings on which the electron transfer occurs. The dechlorination reaction using ZVMs requires metallic corrosion to complete electron transfer.

The difference of standard electrode potentials between the primary metal and the secondary metal composing the each bimetal are calculated and presented in Table 1. Although Pt/Zn have the biggest differences (1.96 V) in electrode potential among the bimetallic combinations, Pd/Zn (1.68 V) shows the highest reactivity. Therefore, it can be concluded that the reactivity is not exactly proportional to the difference in standard electrode potentials and the catalytic hydrogenation effect may be more important than the corrosion effect.

Palladium had better catalytic reactivity for dechlorination of 2,4,6-TCP than nickel, copper, and platinum in this study. Previous study showed 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 [23]. The reduction and subsequent deposition of Pd onto iron surfaces from PdCl$_2$ are spontaneous processes via the following reaction [1,51,52]:

$$Fe^0 + PdCl_2 \rightarrow Fe^{2+} + 2Cl^- + Pd^0\downarrow \qquad (6)$$
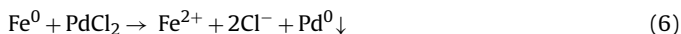
Cheng et al. [1] hypothesized that hydrogen intercalated in a palladium lattice is the powerful reducing agent that reductively dechlorinates chlorinated organic compounds that are adsorbed on the surface of palladized electrodes. According to their experimental results, dechlorination of 4-chlorophenol to phenol occurred 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. Additionally, they proposed three mechanisms for the hydrodehalogenation of chlorophenol to phenol (Fig. 7). One is direct reduction at metal surface (A); another is hydrogenation at palladium catalyst sur-
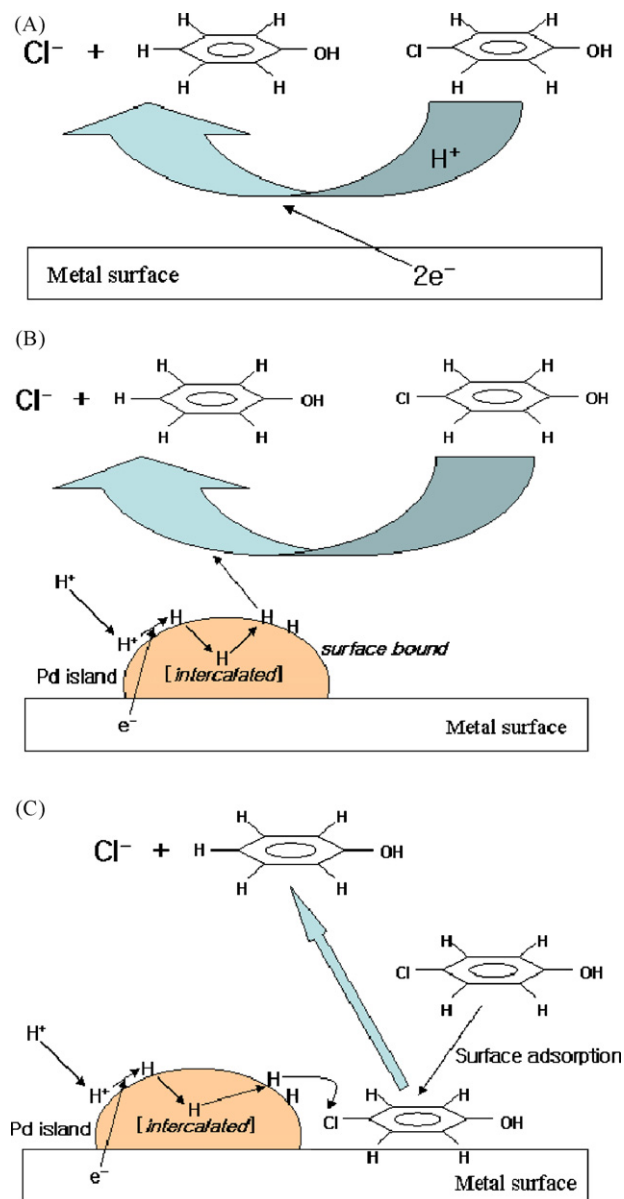

Fig. 7. Proposed mechanisms for the hydrodehalogenation of chlorophenol to phenol [1].

face (B); the third is adsorption of chlorophenol at metal surface followed by hydrogenation at palladium island/metal surface (C). The reactions on the palladized ZVMs depend on the adsorption of the chlorinated organic compound on the metal surfaces and the reaction with hydrogen at the palladium/metal interface [1]. Wang and Zhang [52] reported that palladium could promote the dechlorination reactions by preventing the formation of iron oxides. Their experiments have confirmed that the nanoscale iron particles exposed to air reacted more slowly with PCE and TCE than the freshly prepared iron particles. Palladium coated onto iron surfaces, however, significantly reduced the oxidation of iron with preserving the reactivity of the zero-valent iron. In this study the enhancement will be due to the catalytic effect rather than the protection of base metal surface from oxide formation.

3.4. SEM images and EDS spectra of used Zn metals

SEM images were obtained in an attempt to investigate the bare Zn and bimetallic Zn surface. The surface morphology of the used Zn metals is shown in Fig. 8. Bright spots found in the surfaces of bimetallic Zn could be considered as the deposition of the catalytic metals. Additionally, rougher surfaces were shown in the catalyzed Zn than the plain Zn. Energy dispersive X-ray spectroscope (EDS) was also used to obtain the information about elemental composition at the bimetal surfaces and the representative EDS spectra of Cu/Zn and Pt/Zn are shown in Fig. 9. Particular bright spots on the metal surface showed relatively high intensity of the catalytic metal used. However, some bright spots showed very low (or no) intensity of the catalytic metal, indicating not all of the bright spots are catalytic metal.
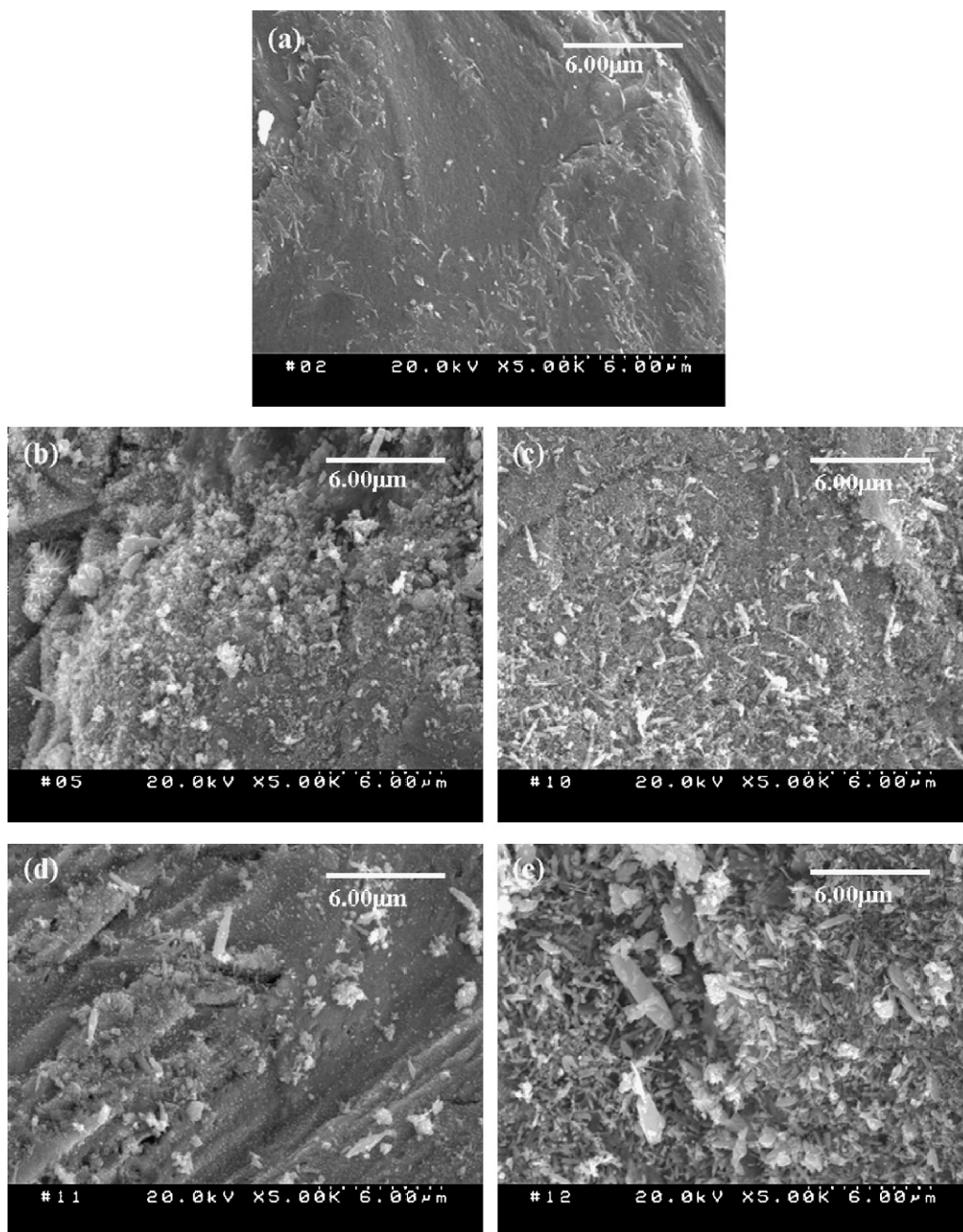

Fig. 8. SEM images of Zn and Zn bimetals (5000×): (a) Zn; (b) Pd/Zn (Pd content of 636 ppm); (c) Ni/Zn (Ni content of 1269 ppm); (d) Cu/Zn (Cu content of 1272 ppm); (e) Pt/Zn (Pt content of 887 ppm).
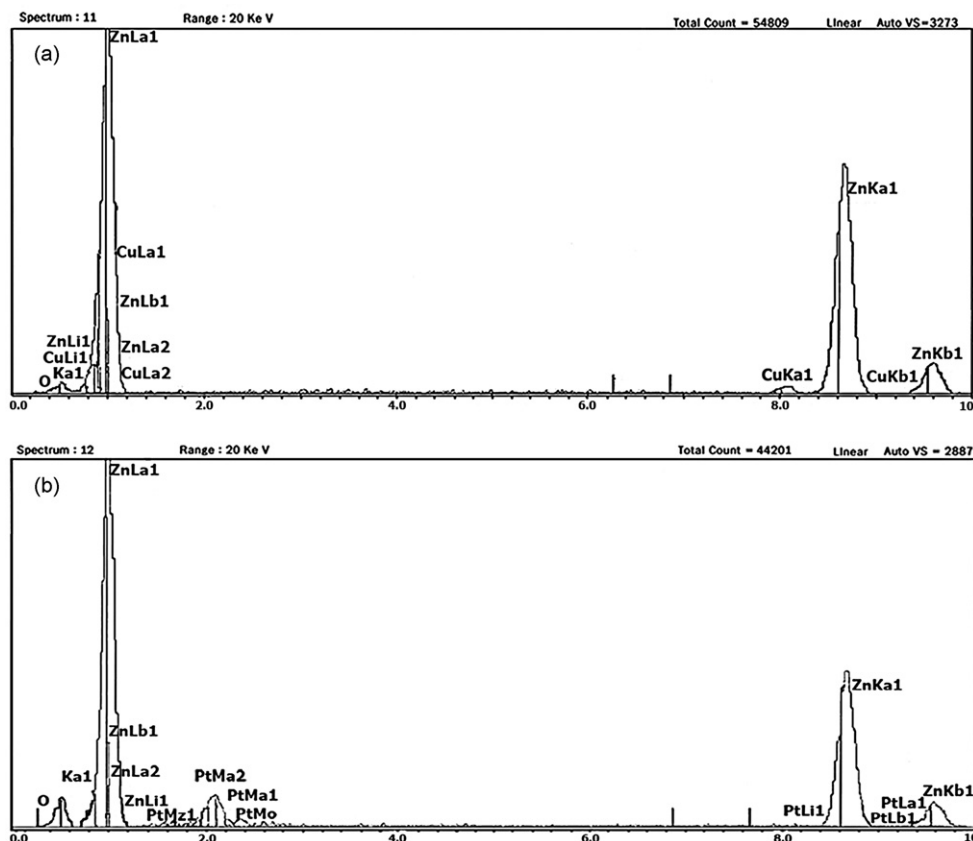
Fig. 9. EDS spectra of (a) bright spot on Cu/Zn surface, (b) bright spot on Pt/Zn surface.

4. Conclusions

The reductive dechlorination of 2,4,6-TCP in aqueous phase was investigated. Zinc-bimetals (Pd/Zn, Ni/Zn, Cu/Zn, Pt/Zn), which were prepared by coating the secondary metal on zinc surface, were evaluated against 2,4,6-TCP. Plain Zn showed relatively low reactivity toward 2,4,6-TCP, while bimetals showed very increased reactivity and Pd/Zn had dramatically increased reactivity. Phenol was the major products indicating all chlorines could be removed from the target compound and less chlorinated phenols also were found as dechlorination products. Cyclohexanone, a non-aromatic product, was found as a reduction product showing the Pd/Zn reduced aromatic ring after dechlorination. Surface area normalized kinetic constants and s metal contents normalized kinetic constants were calculated and compared. Two mechanisms, catalytic activation and enhanced corrosion, were proposed for the reactivity enhancement and the catalytic activation turn out the major enhancement mechanism. Even if the toxicity of zinc ion released from zinc metal and the high price compared with iron could be limitations to use the metal in environmental application, zinc can be an alternative metal for reductive detoxification with higher reduction potential, bimetal formation, and keeping relatively lower pH during the reaction periods.

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