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# Liquid-liquid Extraction Methods to Determine Reductive Dechlorination of 2,4,6-trichlorophenol by Zero-valent Metals and Zero-valent Bimetals

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**Abstract:** The reductive dechlorination of 2,4,6-trichlorophenol (2,4,6-TCP) was studied using zero-valent metals (ZVMs) and bimetals. A reliable extraction method was required to distinguish the removal by chemical transformation from the removal by physical adsorption on the ZVMs or bimetal. Three liquid–liquid extraction methods with ethyl acetate were evaluated by conducting mass recovery tests in the ZVM-chlorophenol systems. A typical liquid–liquid extraction showed low recoveries for 2,4,6-TCP and the reaction products while the modified liquid–liquid extraction involving acid addition gave increased recoveries. The Mg system needed an additional modification since the modified extraction method was not working on the Mg and Pd/Mg system. Pd/Fe and Pd/Zn gave the highest reaction rate for 2,4,6-TCP dechlorination, producing less or no chlorinated daughter compounds while the plain metals such as Fe and Zn showed much slower degradation rates for 2,4,6-TCP.

**Keywords:** Adsorption, chlorinated phenols, extraction, reductive dechlorination, zero-valent metals (ZVMs)

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## INTRODUCTION

Groundwater and soils contaminated with toxic organic compounds such as chlorinated solvents have been a major issue in environmental cleanup efforts and posed technical challenges in many ways. Permeable reactive barriers (PRB) that utilize various reactive materials have been developed more than a decade ago as an alternative to cost-demanding pump-and-treat techniques and applied to a number of sites to treat contaminated groundwater. The increasing popularity of PRB technology, despite some limitations, is largely due to its economical and technical advantages compared to conventional techniques.

A number of studies have examined potential utilities of zero-valent metals (ZVMs) as a reactive material for PRBs to treat halogenated hydrocarbons in groundwater (1–4). In particular, zero-valent iron (ZVI) received a great deal of attention because of high reactivity, low cost, and low environmental impact. Researchers have worked several years to improve the performance of ZVI, including amended iron (e.g. Pd/Fe, Ni/Fe) and nanoscale iron (5–11). Reductive dehalogenation was found to be the main mechanism of the degradation of halogenated hydrocarbons although there is large variation in reaction rate among different classes of compounds (1–3). For example, the disappearance of chlorinated organics from aqueous phase occurs mainly through the dechlorination reaction on the metal surfaces. However, the chlorinated hydrocarbons and their dechlorination products could be adsorbed on the metal or metal hydroxide surfaces, and in some cases, the sorption is so strong that the adsorbed compound is not readily extracted with a simple liquid-liquid extraction (12). Contaminant removal by sorption has been demonstrated for tetrachloroethene (PCE) and trichloroethene (TCE) with iron metal filings (13,14). In order to properly assess the true reactivity of a ZVM system, the removal of contaminant by adsorption has to be distinguished from the removal by chemical reaction.

Measurement of phenolic compounds, including chlorinated phenols, in aqueous solution usually involves GC or HPLC analysis. Although HPLC is a preferred method for its simplicity in sample preparation, it is not suitable for trace analysis of phenolic compounds because of high detection limit. When GC is utilized, solvent extraction is needed to separate the compound from aqueous phase. However, in the presence of solid particles, single solvent extraction may not be sufficient to extract the phenolic portion associated with the solid surfaces. Therefore, a standardized extraction method to minimize the mass loss (e.g., adsorption) is required in quantitative analyses of phenolic compounds in reaction with ZVMs.

The physicochemical properties of phenolic compounds such as the water solubility, the octanol-water partition coefficient ($K_{ow}$), and the dissociation constant (p$K_a$) play an important role when phenol and chlorophenols are extracted from water phase to organic solvent phase (15). $K_{ow}$ of phenolate ($-O^-$) is much lower than that of the corresponding phenol ($-OH$) (16). The solution pH is also an important factor because the extraction efficiency is influenced by acid dissociation of phenolic compounds (i.e., $-O^-$ form/$-OH$ form).

In this study the reduction of 2,4,6-trichlorophenol (2,4,6-TCP) was investigated to examine performance of several ZVMs and bimetals and to address the role of adsorption in the overall removal of 2,4,6-TCP. Simple liquid–liquid extraction using ethyl acetate and two modified extraction methods were tested to compare extraction efficiency. The effect of pH was also examined by measuring the solution pH during extraction.

## MATERIALS AND METHODS

### Chemicals

Ethyl acetate (99.8%, HPLC grade), methanol (99.93%, HPLC grade), p-xylene (anhydrous, $> 99\%$), phenol (loose crystals, $> 99\%$, ACS reagent), cyclohexanol (99%), and cyclohexanone (99.8%) were obtained from Sigma-Aldrich (St. Louis, MO). Hydrochloric acid (37%, ACS grade), sulfuric acid (95–98%, ACS grade), palladium(II) chloride (5 wt% solution in 10 wt% HCl), 2,4,6-TCP (98%), 2,6-dichlorophenol (2,6-DCP, 99%), 2,4-dichlorophenol (2,4-DCP, 99%), 4-chlorophenol (4-CP, $> 99\%$), and 2-chlorophenol (2-CP, $> 99\%$) were obtained by Aldrich Chemical (Milwaukee, WI). The ZVI was iron metal powder (electrolytic, finer than 100 mesh) obtained from Fisher Scientific (Fair Lawn, NJ). Granular zinc 0.15–0.59 mm, $>99.8\%$) and granular magnesium (0.84 mm, 98%) were from Aldrich (Milwaukee, WI). All chemicals were used as received without further purifications. Deionized water (DI water) was generated by a Barnstead water purification system (resistivity $\geq$ 17.5 MΩ·cm and total organic carbon $<$ 1.0 mg/l).

### Preparation of Bimetals

Bimetallic ZVMs were prepared by mixing acidic Pd(II) solution with ZVMs (5,6,17). $PdCl_2$ stock solution (2 ml) was diluted to 100 ml with DI water and then added to 100.0 g of acid-washed ZVMs (100 ml of 0.05 M HCl solution per 100 g of ZVM for 10 min). The contents were placed on an orbital shaker (NB-101M, N-Biotech) and shaken at 180 rpm for 20 min. After that, the mixtures were rinsed with DI water and acetone and dried completely in drying oven (60–65°C) for 6–7 h, followed by storing in $N_2$ atmosphere until use. The prepared bimetals were dark gray in color with no visual evidence of oxide formation and stored in $N_2$ atmosphere. ICP-OES analysis (Optima™ 4300 DV, Perkin Elmer) of Pd in the Pd solutions before and after exposure to ZVMs showed that 98–100% of the Pd was removed (data not shown) and the content of Pd in the bimetals was about 636 ppm.

## Reactor System

Stock solution of 2,4,6-TCP (100,000 mg/l in methanol) was diluted to 100 mg/l (506–550 μM) with purified water. EPA VOA amber vials (40 ml, Fisher Scientific) were used as batch reactors. To each pre-washed vial, 1.00 ( ± 0.01) g of ZVMs (or bimetals) and 10.00 ( ± 0.05) ml of diluted 2,4,6-TCP solution were added. Immediately after addition of 2,4,6-TCP solution, the vials were capped with Teflon lined silicone septa and open-top screw caps. Control vials were prepared identically but without ZVMs (or bimetals). All vials were placed on the orbital shaker at room temperature (25 ± 0.5°C) and shaken at 180 rpm. After 42–72 hours of reaction time, triplicate reaction vials and duplicate control vials were taken and sacrificed 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 $720A^+$).

## Extraction

Three types of liquid–liquid extraction methods using ethyl acetate as the extracting agent were tested in this study. The first method was a typical liquid–liquid extraction. In this extraction, 5 ml of ethyl acetate were injected to 10 ml of the reacted solution through the septa, and the vials were shaken for 10 min, which was determined to be sufficient for complete extraction of 2,4,6-TCP in the preliminary test. This method was referred to as "Extraction A". The second method was a modified liquid–liquid extraction of Extraction A by adding 0.25 ml of concentrated sulfuric acid to promote protonation of phenolates and desorption of chlorophenols from ZVM surfaces. Different amounts of sulfuric acid (0.10–0.50 ml) were also tested with 72 h samples containing 10 ml of 2,4,6-TCP solution (100 mg/l) and 1.0 g of ZVM. The third method (Extraction C) was applied only to the magnesium systems. At the end of each reaction time, all of the supernatant in the reaction vial was transferred to another vial free of metals. The supernatant was extracted with 5.0 ml of ethyl acetate and 0.25 ml of concentrated sulfuric acid on the orbital shaker (180 rpm) for 10 min. This method could minimize the acid consumption by eliminating acid reaction with the metal (Mg). All standard samples were prepared by injecting an aliquot of the stock solution into purified water and extracting with the Extraction B.

Chlorinated phenols and byproducts were determined using a GC (Agilent Technology 6890 N) with a mass selective detector (Agilent 5973 MS Detector) and a HP-5MS capillary column (Agilent Technology Inc.). *p*-Xylene (50 ppm) was added as an internal standard before the extraction. 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.

## RESULTS AND DISCUSSION

### Effect of Adding Acid on the Extraction Efficiency

The recovery efficiencies of 2,4,6-TCP from reaction and control vials with and without adding sulfuric acid can be compared from Fig. 1. The initial concentration of 2,4,6-TCP was 506 μM. Addition of 0.25 ml of $H_2SO_4$ with 5 ml of ethyl acetate in extraction (Extraction B) increased the mass recovery of 2,4,6-TCP compared to the extraction by ethyl

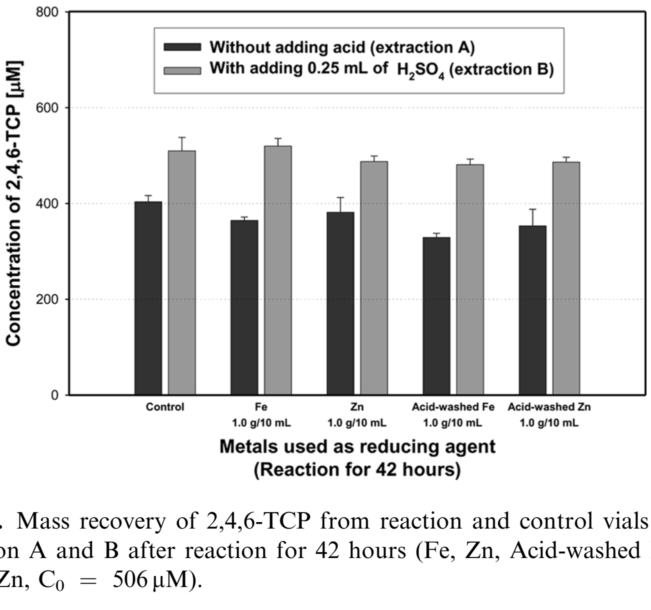

***Figure 1.*** Mass recovery of 2,4,6-TCP from reaction and control vials through Extraction A and B after reaction for 42 hours (Fe, Zn, Acid-washed Fe, Acid washed Zn, $C_0 = 506\,\mu M$).

acetate only (Extraction A) in all tested vials. No reaction product was detected during 42 h reaction, indicating dechlorination of 2,4,6-TCP did not occur with the plain ZVMs such as Fe and Zn, It has been expected that the ZVMs could dechlorinate the chlorophenols because the ZVMs were successfully applied in the dechlorination reaction for chlorinated ethenes (3,13,18). In Extraction A, additionally, the total extracted mass of 2,4,6-TCP in the presence of metals was less than that in control vials with the amount of extracted mass of control (403 μM) $>$ Zn (382 μM) $>$ Fe (364 μM) $>$ acid-washed Zn (353 μM) $>$ acid-washed Fe (329 μM). This mass loss of 5–18% compared to the control in the metal systems may be due to the adsorption of 2,4,6-TCP on the metal surfaces and/or the more formation of anionic 2,4,6-TCP ($-O^-$) with the increase of solution pH after reaction. Further discussion related to pH effect is provided in the following section. There was no significant difference in the recoveries between untreated and acid-washed Fe and Zn,. This implicates that the acid-washing, which has been used for the reactivating purpose of the metal surface, is not effective on the dechlorination of 2,4,6-TCP and no effect on the recovery rates.

The extraction results of Pd/Fe and Pd/Zn system after reaction for 42 h are shown in Figs. 2 and 3, respectively. As 2,4,6-TCP was dechlorinated, less chlorinated products including 2,6-DCP, 4-CP, 2,4-DCP, 2-CP, and phenol were detected with Extraction A and Extraction B. This

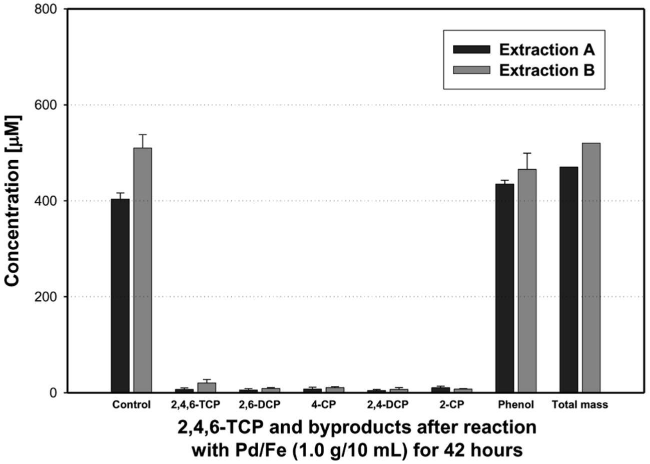

***Figure 2.*** Reductive dechlorination of 2,4,6-TCP by Pd/Fe and production of chlorinated phenols extracted through Extraction A and B (Reaction for 42 hours, $C_0 = 506\,\mu M$).

indicates that the palladium coated iron or zinc are effective in the dechlorination of chlorophenols and it appears the reaction mechanism involves stepwise reaction since the less chlorinated compounds are found. In the Pd/Fe system (Fig. 2), phenol was detected as a dominant reaction product after the 42 h of reaction. The reactivity enhancement of the palladium coated Fe was previously reported for several chlorinated compounds (5,9,10). Since the p$K_a$ value of phenol (9.89) is higher than that of 2,4,6-TCP (6.15), the extent of acid dissociation (i.e., $[-O^-]/[-OH]$) is lower in the phenol-dominated solution than that in the 2,4,6-TCP solution. Therefore, with Extraction A, the total extracted mass in the sample (Pd/Fe) vials (470 μM) could be larger than that of the plain metal systems and control (discussed more in the following section). The extraction efficiencies increased with adding acid (i.e., Extraction B) in both Pd/Fe and Pd/Zn system and the total extracted mass (520 μM, 515 μM in Pd/Fe and Pd/Zn system, respectively) was shown to be similar to the measured concentration in control (510 μM). On the other hand, Extraction A Pd/Zn system (Fig. 3) yield much smaller total extracted mass (228 μM) than that in the controls (403 μM). Possible explanations for this low extracted mass may be that there was the more formation of phenolate ($-O^-$) after reaction due to pH increase and/or the adsorption of phenolic compounds on the Pd/Zn surfaces. However, it appears that the mass loss by adsorption is a more important factor for

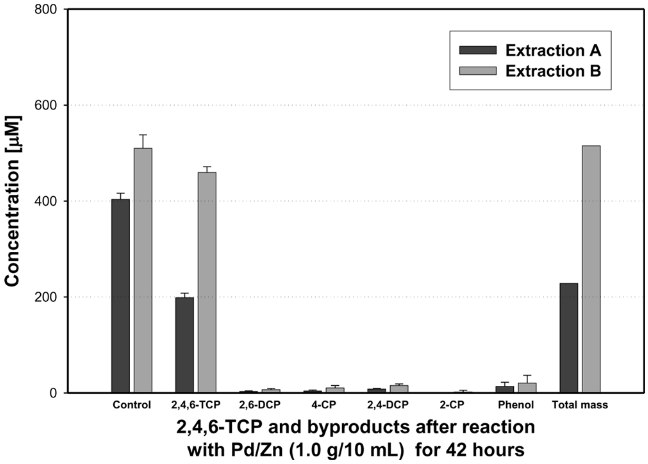

***Figure 3.*** Reductive dechlorination of 2,4,6-TCP by Pd/Zn and production of chlorinated phenols extracted through Extraction A and B (Reaction for 42 hours, $C_0 = 506\,\mu M$).

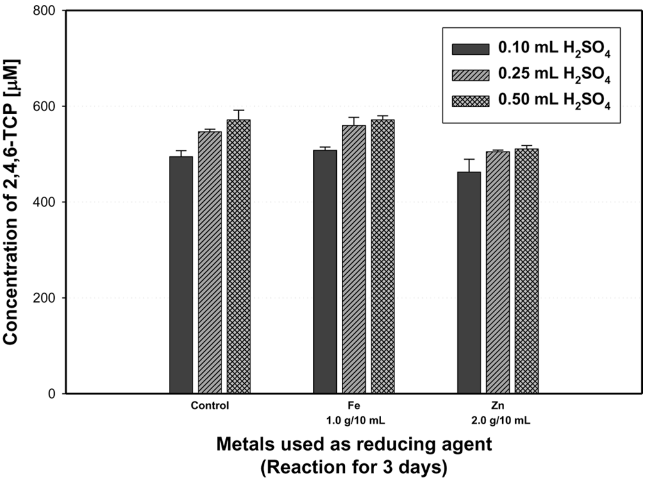

***Figure 4.*** Mass recovery of 2,4,6-TCP from reaction and control vials through Extraction B with variable amounts of $H_2SO_4$ after reaction with Fe and Zn for 72 hours (No dechlorination products were detected after the reactions, $C_0 = 550\,\mu M$).

the low recovery of Pd/Zn system considering the similar pH of Pd/Zn system to other systems (discussed more in the following section).

Variable amount of $H_2SO_4$ was tested for the 72-h samples Fe and Zinc systems (Fig. 4). Relative percentage of recoveries of 2,4,6-TCP obtained with triplicate samples with varying amount of 0.10 ml, 0.25 ml, and 0.50 ml of concentrated $H_2SO_4$ were 90% (0.10 mL), 99% (0.25 mL), and 104% (0.50 mL) in conrols,: 92% (0.10 mL), 102% (0.25 mL), and 104% (0.50 mL) in the Fe system, and 84% (0.10 mL), 92% (0.25 mL), and 93% (0.50 mL) in the Zn system, respectively. With the more acid, the higher extraction efficiency was observed in each reactor system. However, relatively small increases of the extraction efficiency were exhibited when the acid increased from 0.25 ml to 0.50 ml.

## Extraction Efficiencies by Various Extraction Methods in Mg and Pd/Mg System

As shown in Figs. 1–3, more than 90% of the initial mass was recovered through Extraction B in all plain metal and bimetal systems. Figure 5 shows mass recoveries of 2,4,6-TCP by different extraction methods used in Mg and Pd/Mg systems. In contrast to other metals, the mass recovery efficiencies of Mg and Pd/Mg systems were signigicantly low, giving

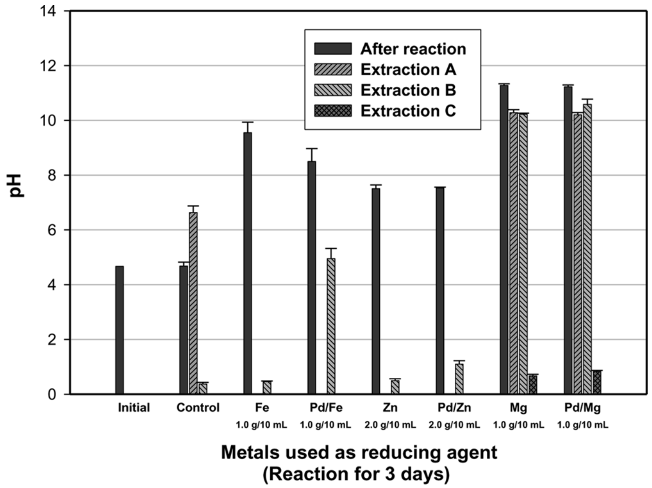

***Figure 5.*** Mass recovery of 2,4,6-TCP and daughter products extracted through Extraction A, B, and C after reaction with Mg (1.0 g/10 ml) and Pd/Mg (1.0 g/10 ml) for 72 hours (No dechlorination products were detected after reaction with Mg, $C_0 = 506\,\mu M$).

recoveries of 2 and 24% with Extraction A and 33 and 36% with Extraction B, respectively, after reaction for 72 hours. These poor extraction efficiencies, especially for Extraction B, may be due to the failure to protonate the chlorophenolates and phenolate prior to the extraction. As shown in Fig. 6, the pH of the Mg and Pd/Mg system was around 10 even after acid addition. Magnesium has much higher reduction potential (−2.37 V) than iron (−0.44 V) and zinc (−0.76 V) and it reacted with the added sulfuric acid very intensely with the generating hydrogen gas. Therefore, an alternative method in which acid was added into the decanted solution (i.e., Extraction C) was applied to the extraction in Mg and Pd/Mg system.

As shown in Fig. 6, the addition of ethyl acetate (5.0 ml) and sulfuric acid (0.25 ml) to the decanted supernatant (Extraction C) could lower the solution pH below 1.0 in both Mg and Pd/Mg system. This pH is low enough to protonate the dissociated (or anionic) chlorophenols and phenol to the protonated ones (i.e., neutral form). The mass recovery through Extraction C (Fig. 5) was 93% and 46% respectively. About 6% of mass loss in Extraction C may be due to the adsorption of 2,4,6-TCP on the Mg surfaces. In Pd/Mg system, however, the total mass recovery efficiency was relatively poor in spite of lowered pH through the Extraction C. Adsorption of 2,4,6-TCP and less chlorinated daughter compounds onto the Pd/Mg particles and/or metal hydroxides is

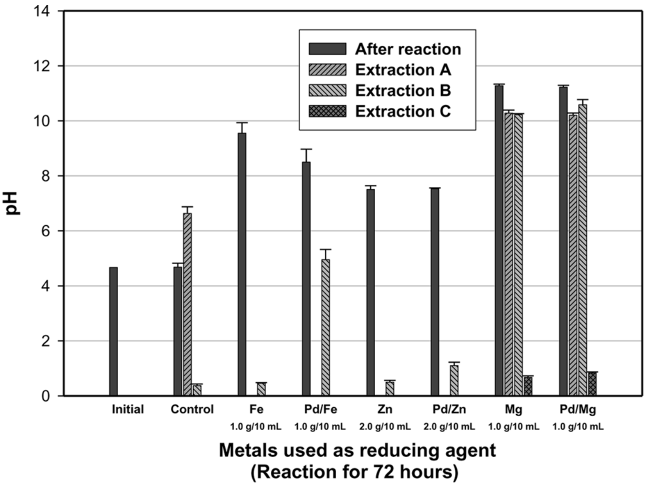

***Figure 6.*** Solution pH after reaction for 72 hours and extraction through Extraction A, B, and C in various metal systems (The solution pH after Extraction A was not measured in Fe, Pd/Fe, Zn, and Pd/Zn system).

considered to be a major sink for the mass loss. Even if mass recovery was less than 50%, the identification of daughter products indicates that the Pd/Mg is able to dechlorinate 2,4,6-TCP. One of the most interesting results is the detection of cyclohexanone and cychlohexanol which are the aromatic ring reduced and dechlorinated products. This implicates that the Pd/Mg system can reduce the aromatic compounds to corresponding aliphatic ring compounds. Trace amount of cyclohexanone was also found in the Pd/Fe and Pd/Zn system.

## Relationship between Solution pH and the Extraction Efficiency

After reaction for 72 hr the solution pH was measured in the aqueous phase before and after extraction and the results are shown in Fig. 6. In the controls, the initial pH of the 2,4,6-TCP solution was $4.6 \pm 0.1$ and increased to $6.6 \pm 0.2$ after adding ethyl acetate. This increase in pH may be due to the proton consumption of dissociated 2,4,6-TCP ($-O^-$ form) to reach a new equilibrium following mass transfer of non-dissociated chlorophenol ($-OH$ form) to the ethyl acetate phase and then formation of non-ionic (or neutral) form with consuming protons to make a new equilibrium. When the solution pH is higher than the $pK_a$ value ($pK_a$ of 2,4,6-TCP $= 6.15$), chlorophenolates ($-O^-$ form) are dominant in the solution. As described above, the octanol-water partition coefficient ($K_{ow}$) of chlorophenolate is lower than that of the corresponding chlorophenol. Consequently, the low mass recovery with Extraction A in the controls is mainly due to the increase in solution pH after adding ethyl acetate. The solution pH of the controls was lowered to $0.37 \pm 0.06$ by addition of sulfuric acid and the extraction efficiency was improved as shown in Figs. 1, 2, and 3.

In the reaction vials, the solution pH was higher than the p$K_a$ of most chlorophenols after reaction with the various ZVMs. Both the hydrodechlorination and the corrosion reaction by oxygen and water consume protons and/or produce hydroxide ions, as shown in the following equations, where RCl is chlorinated organics:

$$Fe^0 + RCl + H^+ \longrightarrow Fe^{2+} + RH + Cl^- \qquad (1)$$

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

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

The increased pH could induce the precipitation of metal hydroxides, which results in lower reactivity of metal surfaces (18). The pH increase could also induce the adsorption of phenolic compounds from solution to metal (hydr)oxides. Kung and McBride reported that adsorption of chlorophenols from solution to metal oxide under moderately acidic conditions was controlled in part by the extent of dissociation of the chlorophenol and the anionic chlorophenolate was much more likely to be chemisorbed on metal oxide surfaces (19). Therefore, it can be possibly concluded that the total extractable mass could be reduced by both the adsorption and the lower $K_{ow}$ of the anionic forms of chlorophenols at the higher solution pH than the p$K_a$ of the chlorophenols. In all the tested metal systems, the solution pH was higher than the $pK_a$ indicating 2,4,6-TCP and reaction products mainly existed as anionic forms.

## CONCLUSIONS

Accurate quantification of the target compound and its secondary products is needed to properly evaluate the performance of treatment systems involving ZVMs. Three extraction methods (Extraction A, B, and C) were investigated in various ZVM-chlorophenol systems. The use of ethyl acetate only (Extraction A) as an extraction solvent could not fully extract the initial mass of 2,4,6-TCP. The mass loss of chlorophenols during extraction may result from formation of anionic form ($-O^-$) with the increase of solution pH after reaction and the adsorption of phenolic compounds on the metal surfaces. Extraction B (i.e., adding sulfuric acid with ethyl acetate) increased the extracted mass compared to single ethyl acetate extraction in all the tested metal systems. The increase of extraction efficiency in this method is attributed to the increase of chlorophenols with neutral form (–OH) relative to the anionic form ($-O^-$) and/or the acid-mediated desorption of adsorbed phenolic compounds from the metal surfaces. Pd/Fe and Pd/Zn successfully dechlorinate the 2,4,6-TCP producing less chlorinated phenols and phenol as daughter products over the reaction periods while plain ZVMs such as Fe and Zn showed very slow degradation rates.

In Mg and Pd/Mg system the mass recovery efficiency was low in spite of the addition of sulfuric acid. The failure to protonate the chlorophenolates and phenolate caused the poor extraction efficiency. Lowering pH using Extraction C recovered the lowered pH increased significantly the extraction efficiency in Mg system. In Pd/Mg system, however, the total mass recovery efficiency was relatively poor with Extraction C, and the adsorption of phenolic compounds onto the Pd/Mg related surfaces was considered as the major reason of the mass loss. A significant amount of cyclohexanone and cyclohexanol derived from the aromatic ring reduction was found in the Pd/Mg system.

Our experimental results also indicate that more reduction of 2,4,6-TCP and more formation of phenol with a higher p$K_a$ could increase the mass recovery through Extraction A. Consequently, the disappearance of chlorophenols by sorption onto ZVM-related surfaces has to be distinguished from the disappearance by reductive dechlorination reaction in ZVM-chlorophenol systems. The solution pH and the p$K_a$ of phenolic compounds play an important role in the extraction efficiency. Extraction B or C could be an effective extraction method in degradation systems with ZVMs.

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