Effect of Degree of Chlorination on Chlorophenols Dechlorination Water Treatment with Zero Valent Iron

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Abstract— *Chlorophenols (CPs) are known for causing water pollution. Zero Valent Iron (ZVI) can be used to treat water via CP dechlorination. Incorporation (sorption, co-precipitation and/or physical entrapment) of CPs with iron oxides is a concurrent process occurring with dechlorination, which can be influenced by the physical-chemical properties of CPs and leads to concerns on CPs dechlorination with ZVI. This study aimed at investigating the effect of degree of chlorination on CPs incorporation and dechlorination when using ZVI. Pentachlorophenol (PCP), 2,3,4,6-Tetrachlorophenol (2,3,4,6-TeCP), 2,4,6-Trichlorophenol (2,4,6-TCP) and 2,4-Dichlorophenol (2,4-DCP) were chosen to study dechlorination and incorporation of CPs using ZVI. Experiments were carried out under identical settings in batch reactors under anoxic conditions. CP dechlorination was assessed using Gas chromatography-Mass spectrometry to quantify the respective CPs and all dechlorination products formed. Raman spectroscopy was used to identify the iron oxides formed on the ZVI. CPs dechlorination increased with increasing degree of chlorination except for with 2,4-DCP. The sequence of CPs dechlorination was PCP>2,3,4,6-TeCP>2,4-DCP>2,4,6-TCP with accumulation of lower CPs over 25 days reaction. CPs with lower degree of chlorination showed greater tendency for incorporation with the oxides. 2,4,6-TCP and 2,4-DCP concentrations in the solutions decreased over time but there was no increase in dechlorination products resulting in poor mass balance. Higher pKa values of 2,4,6-TCP (5.97-7.42) and 2,4-DCP (7.68) could lead to greater affinity of these CPs and/or their degradation products for incorporation with the oxides hindering dechlorination. The formation of oxides (akaganeite, hematite, lepidocrocite, goethite, wustite) observed with 2,4,6-TCP and 2,4-DCP could also limit the dechlorination and lead to greater incorporation of higher amount of these CPs with the oxides. This study demonstrated that CP dechlorination using ZVI increases with the increase in degree of chlorination of CPs. Further, the CPs tested showed increasing affinity for incorporation with the oxides and decreased dechlorination as the degree of chlorination decreases.*

Keywords— Chlorophenol, Dechlorination, Incorporation, Iron Oxides, Passivation, Sorption

I. INTRODUCTION

Chlorophenols (CPs) are manufactured organic compounds and used as disinfectants, pesticides, herbicides and wood preservatives. CPs have been detected as contaminants in groundwater, surface water, wastewater, air and soils as a result of improper disposal, accidental spills, leaching from landfills, evaporation from treated wood products and incineration of chlorinated wastes (ATSDR, 1999). Most of the CPs are listed as priority toxic pollutants by USEPA, becoming a threat to the water and soil environments and increasingly causing water pollution. Toxicity of chlorophenols (CPs) increases with increasing degree of chlorination (Czaplicka, 2004). PCP is identified as the most toxic CP (Tanjore and Viraraghavan, 1994) and is considered a possible human carcinogen from exposure via inhalation and dermal contact (USEPA, 2010). Removal of PCP has gained awareness in groundwater treatment but degradation of Tetrachlorophenol (TeCP), Trichlorophenol (TCP) and Dichlorophenol (DCP) have received little attention. Treating CPs is challenging due to their hydrophobic nature and aromaticity linked stability.

Zero valent iron (ZVI) is an effective treatment technique for chlorinated contaminants dechlorination due to its relatively high reactivity, cost effectiveness and low environmental impact (Choi et al., 2008, Gunawardana et al., 2011, Kim & Carraway, 2000). However, the application of ZVI for CP dechlorination is limited by (1) decrease in degradation rates over time as a result of reduced ZVI surface reactivity due to formation of surface passivating oxides and (2) the accumulation of lower degree chlorinated intermediates. Iron oxides are always present on the ZVI surface but different iron oxide phases form under different conditions. The formation of iron oxides and the characteristics of the phase that forms changes the ZVI surface properties and can dramatically affect CP dechlorination (Gunawardana et al., 2011). In addition, incorporation (sorption, co-precipitation and/or physical entrapment) of CPs with the iron oxides has been identified as another process occurring concurrently with dechlorination (Gunawardana, 2013). Incorporation could be influenced by the physical-chemical properties of CPs, which leads to concerns with efficiency of ZVI for CPs dechlorination. Previous research also provides evidence that ligands with a greater pKa value resulted in increased sorption onto iron oxides such as ferrihydrite (Song et al., 2008).

Based on this concept it may be expected that the tendency for incorporation will increase as the degree of chlorination decreases, given that the pKa of 2,4-DCP, 2,4,6-TCP, 2,3,4,6 TeCP and PCP are 7.68, 5.97-7.42, 5.22-5.62, 4.60-5.25, respectively. However, uncertainty remains related to the potential role of ZVI surface characteristics on reactivity for CP dechlorination, the possible relationship between iron oxide formation, CP dechlorination and/or incorporation as well as effect of degree of chlorination on CPs incorporation/dechlorination.

This study investigated the efficiency of ZVI for CP dechlorination and the effect of degree of chlorination on CPs incorporation and dechlorination when using ZVI. To gain insight into the effect of degree of chlorination on CPs dechlorination using ZVI, PCP, 2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP were chosen as the model contaminants and both dechlorination and incorporation processes of selected CPs were examined using ZVI.

II. MATERIALS AND METHODS

K. Materials

The ZVI used was electrolytic iron powder (<100 mesh, North American Höganäs), as received/without any modifications. Analytical grade solvents (ethyl acetate and acetone), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were obtained from Ajax Finechem. PCP powder (ACS grade, 98%), 2,3,4,6 Tetrachlorophenol (2,3,4,6-TeCP, Supelco, 98%), 2,4,6 Trichlorophenol (2,4,6-TCP, Aldrich, 98%), 2,4 Dichlorophenol (2,4-DCP, Aldrich, 99%), standard solutions of PCP, phenol, and chlorophenol isomers in methanol were purchased from Sigma-Aldrich. Deionised (DI) water (resistivity of 18.20 MΩcm, Millipore-Q system) was used in the experiments. Deoxygenated DI water was prepared by degassing DI water at 80^0C and 100 kPa for 1 hour and then sparging with oxygen free-nitrogen gas for half an hour. Stock solutions (5000 mg/L) of PCP, 2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP were prepared in ethyl acetate.

L. Iron Oxides Characterisation

Raman spectroscopy (Renishaw Raman system 1000 spectrometer) was used to identify the iron oxides present on ZVI particles pre- and post-exposure to CP solutions. Nine oxides commonly found on iron surfaces (akaganeite, maghemite, hematite, magnetite, wustite, lepidocrocite, goethite, feroxyhyte and ferrihydrite) were used as the reference iron oxides (Cornell & Schwertmann, 2003). Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) within MATLAB (Mathworks®) was used for quantification of iron oxides (Jaumot et al., 2005).

M. Experimental Procedure and Analysis

All experiments were carried out under identical experimental settings in batch reactors under anoxic conditions. Each CP was added to the solution and tested as a single compound in each vial. Batch tests were performed using Wheaton amber vials (30 mL) over 25 days reaction period. In each reactor, 1.00 (±0.01) g of ZVI (as received) was added, followed by 10 ml deoxygenated deionized water and 10 µl of respective CP stock solution was spiked. The initial concentration of each CP was 5 mg/L. After addition of CP solution, all vials were immediately sealed with aluminium caps and PTFE/silicone septa and agitated on a rotary shaker at 100 rpm at 23 (±1)°C until sampled. Control vials were prepared similarly, except that no solids were added. Experiments were done in duplicate.

At all sampling times the remaining total (i.e. dissolved plus incorporated) concentration of parent CPs and its degradation products as well as the aqueous (i.e. dissolved) concentrations of the parent CPs were determined using separate vials after extracting the iron/water mixture and filtered reaction solutions, respectively, with ethyl acetate and concentrated HCl. The acid modified liquid-liquid extraction method used in this study was based on Gunawardana (2013) and Kim & Carraway (2000) methodology. Extracted samples were analysed for parent CP and its degradation products concentrations using a Gas Chromatography-Mass Spectrometry (GC/MS) analysis with ZEBRON ZB5-msi capillary column (30 m L x 0.25 mm ID x 0.25 µm thickness) using the Selected Ion Monitoring (SIM) analysis method (Gunawardana, 2013).

The effects of different treatments on the concentration of CP degraded at 25 days of the experiment were compared using a two-way analysis of variance model using SPSS statistical software package (IBM SPSS Statistics version 20.0.0 [SPSS Inc., USA]). Significance was determined at the 95% level.

III. RESULTS AND DISCUSSION

N. Dechlorination of Chlorophenols using ZVI

The dechlorination of CPs using ZVI and the production of intermediate compounds are presented in Fig 1. In general, the reactivity of CPs with ZVI followed this sequence; PCP > 2,3,4,6-TeCP > 2,4-DCP > 2,4,6-TCP over the 25 days reaction (Fig 1). When comparing the dechlorination of the four CPs, after 25 days of reaction, PCP showed significantly higher dechlorination ($p<0.05$) whereas 2,4,6-TCP showed significantly lower dechlorination ($p<0.05$).

The dechlorination of each CP using ZVI resulted in accumulation of lower CPs (Fig 1). During PCP degradation, TeCPs were the end product (Fig 1a) while TCPs were the sole end product of 2,3,4,6-TeCP degradation (Fig 1b). Degradation of 2,4,6-TCP resulted in formation of DCPs and minute concentrations of MCPs (Fig 1c). When 2,4-DCP reacted with ZVI, small concentration of MCPs were detected as the end product (Fig 1d).

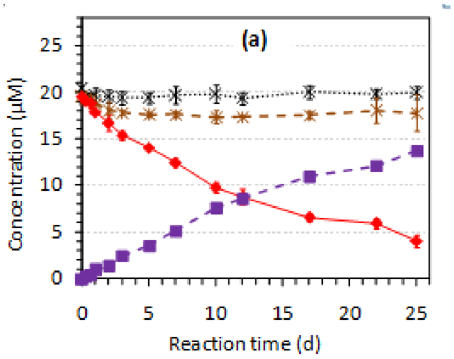

Figure 1. ZVI degradation of Pentachlorophenol (◆), 2,3,4,6-Tetrachlorophenol (■), 2,4,6-Trichlorophenol (▲) and 2,4-Dichlorophenol (●).

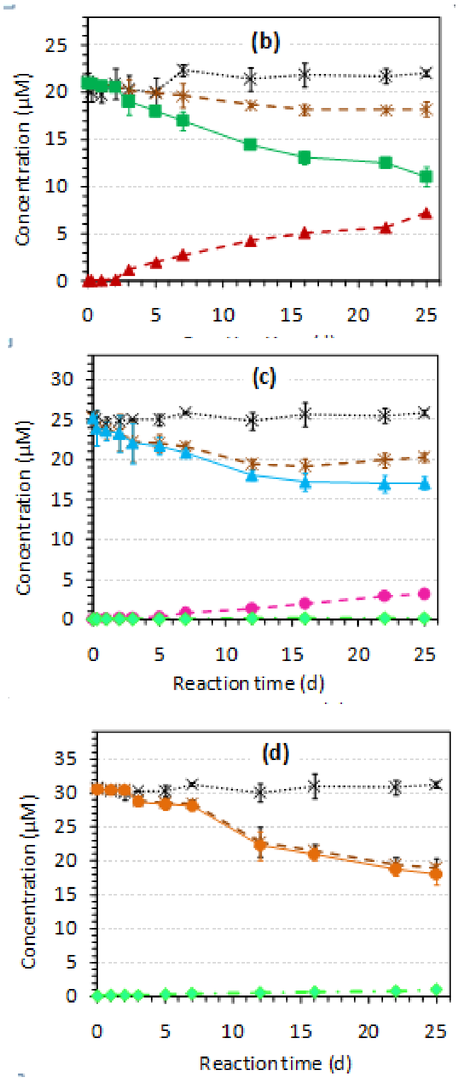

Figure 1. ZVI degradation of chlorophenols to lower CPs: (a) Pentachlorophenol (◆) and formation of TeCPs (■); (b) 2,3,4,6-Tetrachlorophenol (■) and formation of TCPs (▲; (c) 2,4,6-Trichlorophenol (▲) and formation of DCPs (●) and MCPs (◆) and (d) 2,4-Dichlorophenol (●)

and formation of MCP (◆); Control (✕); Mass balance (✳). Error bars indicate ± one standard deviation. Total TeCPs were the sum of all the TeCPs measured, total TCPs were the sum of all the TCPs measured, total DCPs were the sum of all the DCPs measured and total MCPs were the sum of all the MCPs measured.

The highest mass balance recovery was achieved with PCP (96%) during 25 days reaction (Fig 1a). The remaining three CPs (2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP) showed high mass balance recoveries during the initial reaction period (90% to 96%). However, the mass recoveries decreased appreciably to between 62% and 88% by the later stages of the reaction period (Fig 1). The incomplete recovery of the parent CPs and/or degradation products could possibly be attributed to the formation of various oxides (Section C), and incorporation of CP molecules with these oxides (Section B).

O. *Incorporation of Chlorophenols onto ZVI and Iron oxides*

CPs in the ZVI/water system could be, (1) in solution, (2) incorporated with the solid and extracted and (3) incorporated with the solid but non-extracted. The amount of extractable CPs incorporated in the solid phase was determined based on the total system and aqueous phase CP concentrations.

The amount of extractable CP incorporated per unit mass of ZVI (C_s, µmole CP/g of ZVI) was calculated as $C_S = [(C_T - C_W)*V_W)]/M_{ZVI}$, where C_T=total system CP concentration [µmole/L]; C_W=aqueous phase CP concentration [µmole/L]; V_W=volume of aqueous solution [L] and M_{ZVI}=initial amount of ZVI used in the batch reactor [g].

The amounts of extractable CP incorporated in the solid phase are shown in Fig 2. It should be noted that with some CPs a mass balance closer to 100% could not be achieved (Fig 1). In such instances, the poor mass balance could reflect an underestimate of the amounts of CPs incorporated on to the ZVI. However, the quantification of incorporated and extractable amounts of CPs provided information on the amount of CPs incorporated and unreacted with ZVI, without accounting for the possible incorporated and non-extracted CPs on the ZVI surface.

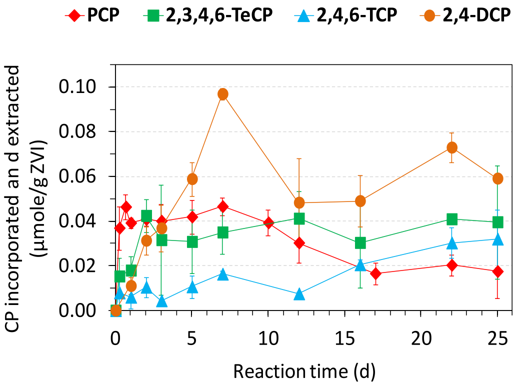

Figure 2. Incorporated and extracted CP concentrations on ZVI when reacted with ZVI.

Error bars indicate ± one standard deviation.

Initial amount of PCP (0.19 µmole/g ZVI), 2,3,4,6-TeCP (0.22 µmole/g ZVI), 2,4,6-TCP (0.25 µmole/g ZVI) and 2,4-DCP (0.31 µmole/g ZVI) was available in each system.

CP incorporation initially (days 0-5) increased rapidly followed by a slow decline or remained relatively constant for the rest of the reaction duration (Fig 2). The rapid increase in the incorporated CP amounts could be a result of physical entrapment and/or co-precipitation of CPs with the iron oxides and/or or sorption of CPs on to the reactive and/or non-reactive sites on the ZVI surface (Noubactep, 2008). The decline or the constant level of incorporated CP concentration could be attributed to, (1) strong incorporation of CPs with the oxides and lack of recovery of these incorporated CP molecules, (2) desorption of CPs and/or (3) dechlorination of CPs by ZVI. Further, the ZVI/water system is complex in nature and the CP compounds present in the solution along with the iron oxide phases on the ZVI surface continuously change during the reaction period. This could also result in variations in the amount of CPs incorporated during the reaction period.

A concern could be raised regarding the differentiation between CPs incorporation and dechlorination in the ZVI system when mass balance recovery was incomplete. However, if dechlorination was the predominant process, then detectable levels of lower CPs and/or phenol as end products would be expected to be present in the systems. As such, it could be suggested that CPs incorporation must have been a significant process of removal of 2,4,6-TCP and 2,4-DCP as only minute levels of CPs were detected in the ZVI systems.

Further, the detected minute levels of CPs as end provide evidence of dechlorination; however, a majority of these end products may have also been incorporated with the iron oxides during the reaction. While this study cannot identify the specific incorporation process, it is evident that the decrease in mass balance as the degree of chlorination decreases (Fig 1) is the expected trend based on decreasing sorption affinity of CPs for an iron oxide as the degree of chlorination increases. The low mass balances indicate that the extraction method, which was the method used by Kim and Carraway (2000), did not extract all CPs under all conditions. The fact that the lower degree CPs had the lowest recovery during extraction supports the possibility that oxide phases remaining after extraction are retaining some of the CPs.

P. Effect of Iron Oxides on Chlorophenols Dechlorination and Incorporation

The relative amounts of oxides present on the ZVI surface before and after reaction with respective CPs are presented in Table 1. Prior to reaction with CPs, a mixture of magnetite and wustite was observed on ZVI surface.

products in these systems

During and after 25 days of PCP reaction, magnetite was found to be the predominant oxide on the ZVI surface (Table 1). On the other hand, reaction of 2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP with ZVI resulted in formation of magnetite (relatively low amount compared to magnetite formed with PCP) along with a mixture of akaganeite, hematite, lepidocrocite, goethite and wustite on the ZVI surfaces during and after 25 days of the reaction (Table 1).

The electric conductivity of oxides on the ZVI surface is an important factor affecting the reactivity of ZVI material (Schlicker et al., 2000). Detection of magnetite as the primary iron oxide with the PCP/ZVI system (Table 1) is also consistent with the enhanced PCP dechlorination observed compared to other three CPs (Fig 1). Magnetite is electrically conductive and has the highest conductivity of all iron oxides thus allows electron transfer facilitating the dechlorination reaction (Ritter et al., 2002).

The lower dechlorination observed for 2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP compared to PCP dechlorination may be also associated with the various oxides being formed on the ZVI surface during the reaction with the respective CPs (Table 1).

A mixture of iron oxides (akaganeite, hematite, lepidocrocite, wustite, goethite, ferrihydrite) (Table

Table 1. Percentages of iron oxides present on the iron surface at the start, after 12 days and end of experiments (estimated by MCR-ALS analysis)

Treatment	**Type of CP**	**Type of iron oxide**						
		Akaganeite	**Hematite**	**Magnetite**	**Lepidocrocite**	**Goethite**	**Wustite**	**Ferrihydrite**
ZVI (UW)*		-	-	74	-	-	24	<5
ZVI+	PCP	-	-	93	-	-	7	-
	2,3,4,6-TeCP	-	-	85	5	<5	<5	-
	2,4,6-TCP	5	5	80	<5	<5	-	-
	2,4-DCP	5	<5	82	5	<5	-	-
ZVI§	PCP	-	-	100	-	-	-	-
	2,3,4,6-TeCP	-	-	92	-	<5	<5	-
	2,4,6-TCP	5	6	85	-	<5	-	-
	2,4-DCP	5	<5	85	5	<5	-	-

*The iron surface at the start of the experiment;
+ The iron surface after 12 days of reaction;
§ The iron surface after 25 days of reaction;
"-" : Respective iron oxide(s) were not detected on the metal surface(s)
"<5" : Percentage amount of respective iron oxide(s) detected on the metal surface(s) was less than 5%

1) along with magnetite (relatively small amounts compared to that with PCP) was detected during reaction of other three CPs (2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP) with ZVI (Table 1). Dechlorination of these three CPs could be limited by the formation of passive oxides (akaganeite, hematite, goethite, lepidocrocite and wustite) due to the low conductivities of these oxides at room temperature compared to the higher conductivity of magnetite (Cornell & Schwertmann, 2003). The passive oxides formed could decrease the number of redox reactive sites on the ZVI surface and impede the electron transfer and transport of CP molecules thereby hindering dechlorination of these CPs, but possibly increased CPs incorporation (especially, 2,4,6-TCP and 2,4-DCP) with the iron oxides. Based on the findings of this study, CPs with higher pKa values (2,4-DCP: pKa of 7.68 and 2,4,6-TCP: pKa of 5.97-7.42) seemed to have higher tendency for incorporation with the oxides hindering the dechlorination process. Furthermore, with the progressive growth of the oxides and their aging, the adsorbed CPs could be further entrapped in the oxides/oxyhydroxides structures and reduce desorption of such CP molecules limiting the availability of CPs in the aqueous phase for dechlorination. In addition, the review of literature provides evidence that the solubility of Fe^{II} oxides is higher than the solubility of Fe^{III} oxides and magnetite is more soluble than $Fe(OH)_2$ (Cornell & Schwertmann, 2003). Therefore, the incorporated CP and/or degradation products with the passive iron oxides seemed to be difficult to extract using HCl and ethyl acetate leading to poor CP mass balance (Fig 1).

IV. CONCLUSIONS

This study investigated the effect of degree of chlorination on dechlorination/incorporation of four CPs, (1) PCP, (2) 2,3,4,6-TeCP, (3) 2,4,6-TCP and (4) 2,4-DCP using ZVI. The ZVI treatment resulted in partial CPs dechlorination and formation of lower CPs as the end products. In general, using the ZVI resulted in higher CP dechlorination with increased degree of chlorination of the CP compounds except for 2,4-DCP. The reactivity of CPs with ZVI followed this sequence; PCP > 2,3,4,6-TeCP > 2,4-DCP > 2,4,6-TCP over the 25 days reaction. As the degree of chlorination of the CPs decreased, the CPs showed increased affinity for incorporation with iron oxides and decreased dechlorination. In particular, 2,4,6-TCP and 2,4-DCP demonstrated greater tendency for incorporation with the iron oxides which may be attributed to the higher pKa values of these two CPs leading to greater resemblance for incorporation with the oxides hindering the dechlorination. The reaction of PCP with ZVI resulted only in the formation of magnetite on the ZVI surface that facilitated electron transfer and PCP dechlorination. When the other CPs (2,3,4,6-TeCP, 2,4,6-TCP and 2,4-DCP) reacted with ZVI, a mixture of passive oxides (akaganeite, hematite, lepidocrocite, goethite and wustite) and relatively low amount of magnetite (compared to the ZVI systems with PCP) was detected. These passive oxides hindered the CPs dechlorination, but possibly increased CPs incorporation with the oxides.

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