RAPID REMOVAL OF PENTACHLOROPHENOL FROM SOIL BY LOW THERMAL WITH ZERO VALENT IRON

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ABSTRACT: *Zero valent iron (ZVI) has been widely used for remediation of chlorophenol contamination in aqueous phase. However, capability of this material for pentachlorphenol (PCP) contaminated soil is still limited. In this study, a thermally enhanced treatment coupled with ZVI was proposed to remove PCP from soil and to detoxify aqueous phase and soil. The results indicated that total PCP removal in soil and aqueous phases increased with ZVI dose. PCP distribution in aqueous phase was enhanced when PCP contaminated soil was remediated with ZVI. Dechlorination rate was enhanced from 2.26 to 6.84 h^{-1} as the temperature was increased from 25°C to 85°C. Dechlorination and PCP residual in soil were increased to 42% and decreased to 6%, respectively at 85°C and pH1. Dechlorination of PCP in this system preferred to occur at ortho> meta> para positions with the respect to OH group. This study has demonstrated the feasibility of applying ZVI for PCP remediation in soil.*

Keywords: Pentachlorophenol, low thermal, zero valent iron, aqueous phase, soil, intermediates.

1. INTRODUCTION

Pentachlorophenol (PCP) is used in a wide variety of agricultural and industrial applications as wood preservative, herbicide, pesticide, fungicide and broad-spectrum biocide over the world. Due to its recalcitrance and toxicity, PCP has been listed as one of the priority pollutants by the US EPA. Recently, zero valent iron (ZVI) has been widely studied for remediation of chlorinated aromatic compounds. Iron is also the cost-effective material for soil remediation. In general, three pathways for remediation of halogenated organic compounds have been identified: direct electron transfer, reduction by Fe^{2+} which comes from corrosion of Fe^o and the catalyzed hydrogenolysis of H_2 formed by iron metal reaction [1]. ZVI has been applied for the remediation of PCP contamination in liquid phase [2, 3]. However, remediation of PCP-contaminated soil with this material is not well addressed. Some studies investigated the remediation of ZVI on PCP contaminated soil [4, 5]. However, no result has been reported on byproducts and pathways of PCP removal from soil. In addition, the retention of PCP is strongly related to the natural organic matter content of soil to be treated. The sorption ability of PCP has been proved to increase with high humid acid content in soil [6, 7]. Consequently, higher natural organic matter of soil indicates that PCP will retain more favorably in soil, resulting in lower removal efficiency. The soil mineral fractions also play a role of adsorbent. If the contaminated soil with low soil organic matter exhibits an alkaline property, the majority of the PCP in the contaminated soil exists in ionized pentachlorophenolate form, which interacts mainly with mineral surface fraction. In addition, while PCP is retained in organic matter and strongly attached to soil colloid particles, ZVI is easily degraded due to formation of hydrates, oxides or complexions with other ligands present in soil if time of treatment is prolonged [8]. As a result, low removal efficiency of PCP from soil is obtained. So the dechlorination of PCP requires good contact with ZVI and is more challenging in soil than in water. Thus, enhancing desorption of PCP from contaminated soil is essential for a rapid dechlorination process. PCP is ionizable hydrophobic organic contaminant, which exists either as a protonated or deprotonated species. pH and temperature are two important factors affecting PCP desorption behavior from contaminated soil [9]. pH and thermal are also important in reductive dechlorination of chlorinated organic compounds using zero-valent iron [10-12]. Therefore, the thermally enhanced treatment coupled with ZVI seems to be a promising method to remove PCP from soil and to detoxify aqueous phase. A representative soil at a coastal site known for severe contamination with PCP (100 mg/kg) due to the chlorination activities was chosen as the primary study. In this study, individual and synergic effects of pH and temperature will be addressed. Byproducts of PCP in soil and aqueous phases will be identified to elucidate the mechanism of dechlorination, reduction or oxidation.

2. EXPERIMENTAL DETILES

PCP (purity > 95%) was purchased from AccuStandard Inc., USA. All other organic and inorganic reagents were of analytical grade. The average specific surface area (BET) of soil samples is 3 m^2/g The composition of the sandy soil was primarily sand with a low clay fraction. The nano Fe particles were synthesized in aqueous solutions via reduction of ferric ion ($FeSO_4.7H_2O$, 0.714 M) with sodium borohydride ($NaHB_4$, 5.172 M) under nitrogen condition. $NaBH_4$ solution was added dropwise to iron (II) solution at a rate of 0.625 mL/s while a tunable mechanical stirrer was employed at 300 rpm to stir solution in the reactor [13]. All solutions were purged with nitrogen for 1h to minimize the dissolved oxygen before use. The process is well known as described below:

$$Fe^{2+} + 2BH_4^- + 6\,H_2O \rightarrow Fe^0 + 2H_2BO_3 + 7H_2$$

The ratio of Fe^{2+}/BH_4^- was maintained at 1:8 to ensure the complete reduction of the iron in the solution and to avoid iron oxide accumulation on ZVI particle surface. The black solid particles were left for 15 min after the whole BH_4^- solution was dropped into the reactor. Thereafter, they were subjected to nitrogen vacuum filtration with 0.45 μm filter and washed three times with 25 mL ethanol to remove all water and the excess borate accumulating on ZVI particle surface. The black color of solid particle was visual evidence indicating no iron oxide was formed. The synthesized particles were weighed an appropriate amount for PCP removal from soil. Soil samples were pre-cleaned using n-hexane for 12 h to eliminate the organic contaminants in the soil. The soil was subsequently air-dried in a fume hood to completely remove hexane. The PCP-contaminated soil was prepared by spiking an appropriate amount of PCP in acetone solution into the pre-treated soil. The contaminated soil samples were homogenized vigorously for 15 min and then placed in the fume hood until the acetone was entirely evaporated for at least 1 day. Previous studies [14-16] have shown that 24 h is sufficient for the PCP in soil to reach an apparent equilibrium. Therefore, one day was chosen as the equilibrium time for the sandy soil. The soil was then placed into a brown glass vial and sealed with the cap for 1 day without shaking to allow the PCP to adsorb onto the soil matrix. The actual concentration of PCP in the soil was verified by Soxhlet extraction using acetone/hexane mixture with the ratio of 1/2 and subsequent analysis using Gas Chromatography/ Mass Spectroscopy (GC/MS). A batch experiment was carried out in 25 mL glass vials capped with Teflon-lined septa and aluminum caps. 5 mL of Milli-Q deionized water was poured into the vial containing 1g of PCP contaminated soil (100 mg/kg). Three levels of ZVI dosage (w/w), 2%, 5% and 10%, were used for PCP degradation experiments and then sealed up with Teflon-lined septum caps. Nitrogen was flown into all sealed vials to ensure anaerobic condition for 30 min before reaction. This step was very important to create an anaerobic condition. Control vials were prepared identically with samples but excluding ZVI. All vials were placed on a thermostatic orbital and shaked with the speed of 125 rpm. The orbital shaker was proposed to enhance the diffusion process of pollutant from soil to ZVI particles. At each experiment, samples and control vial were taken off and solid/liquid phases were separated with 0.45 μm filter for the analysis of residual PCP and byproducts. The sorption/co-precipitation of PCP and byproducts onto the non-reactive sites of ZVI surface of solid phase was washed with 1mL of acid HCl (0.5M), thus released into aqueous phase. PCP in aqueous phase was extracted by liquid-liquid extraction using n-hexane after pH adjustment to 1 and then Na_2SO_4 was used to eliminate water residual. PCP remaining on soil was extracted by acetone: hexane (1:2) under rotating shaker at 200 rpm for 9h and then filtered with 0.45 μm filter. All extracts were evaporated into 5mL with concentrator, continuously condensed to 0.5 mL under nitrogen flow, finally transferred into vials. The removal efficiencies and dechlorination are calculated as:

$$\text{PCP removal (\%)} = \frac{\left([PCP]_{initial\,mass} - \{[PCP]_{mass\ in\ liquid} + [PCP]_{massin\ soil}\}\right)*100}{[PCP]_{initial\ mass}}$$

$$\text{Dechlorination efficiency (\%)} = \frac{[\mathrm{Cl}^-]*100}{5*[\mathrm{PCP}]_o}$$

$[\mathrm{Cl}^-]$ is concentration of chloride measured in aqueous phase (mM); $[\mathrm{PCP}]_o$ is the initial PCP concentration (mM)

3. RESULTS AND DISCUSSION

3.1. Characterization of ZVI

BET and Langmuir surface area of ZVI particles in air condition were 13.69 m^2/g and 42.35 m^2/g, respectively, while BET and Langmuir surface area in nitrogen condition were 57.66 m^2/g and 80.035 m^2/g, respectively. The former BET result is comparable with other references such as 21.63 m^2/g [17], 33.5 m^2/g [18] and 29.67 m^2/g [19]. The latter is a little bit higher than other works, possibly due to the minimized oxygen before and during synthesis process, thus unstable oxides/hydroxides in the forms of Fe_2O_3, Fe_3O_4 and FeOOH were prevented and avoided oxidation of ZVI particles, resulting in the increased active sites for greater remediation capacity. XRD patterns of ZVI samples in nitrogen and air conditions are presented in Figure 1. The characteristic diffraction line at 44.7° 2 theta degrees indicates that zero-valent iron crytallinities are predominantly present in the samples and no signal for the iron oxides is observed for the freshly prepared samples. The smaller size of iron particles means larger specific area. The particles with larger specific surface area are supposed to provide more reactive sites and higher reactivity.

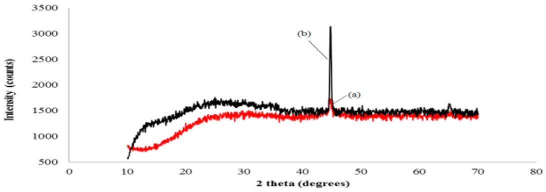

Figure 1: XRD patterns of nZVI particles: (a) Synthesis in N_2; (b) Synthesis in Air.

3.2. Effect of ZVI dose

The effect of ZVI dose (2%, 5% and 10%) on degradation and distribution of PCP in soil and aqueous phase are shown in Figure 2. In the control sample without the aid of ZVI, most of PCP (~74%) was transferred into aqueous phase under pH8. Since the pH value of soil is close to 8, the chlorophenolates is the predominant form in soil PCP in contaminated soil was found to decrease with increasing ZVI dose and only 8% of PCP remained in soil with 10% ZVI. It is evident that ZVI had noticeable effect on the removal of PCP. The higher ZVI dose is applied, the greater percentage of PCP is removed. The total removal of PCP in contaminated soil and aqueous phase increased linearly with ZVI dose. Most PCP removal is from PCP desorbed from soil into aqueous phase while the change of PCP remaining in soil is insignificant (~ 2%).

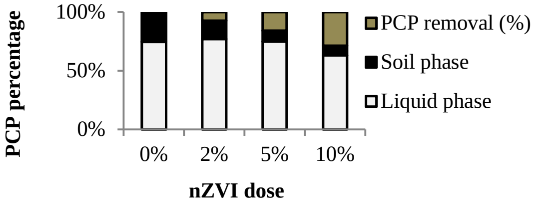

Figure 2: Effect of nZVI dose on PCP degradation and PCP distribution in soil and water. (Initial PCP contaminated soil: 100 mg/kg; reaction time: 60 min, room temperature: 25°C).

The pH value of vial containing PCP contaminated soil with 5% ZVI were adjusted to 1, 3, 5, 7, 9 and 12 using H_2SO_4 (0.5 M) or NaOH (0.5 M). Distribution of PCP in soil and aqueous phases at various pH values and ZVI doses are presented in Figure 3. For control sample (0% of ZVI), the amount of PCP in liquid increased with increasing pH. Only 48% of initial PCP was desorbed into liquid at pH 1 while almost 80% of PCP was desorbed into liquid and no much change PCP remained in soil at higher pH (pH >9). Small fraction of PCP remains in soil due to the stronger adsorption on soil surface than deprotonation of PCP at high pH.

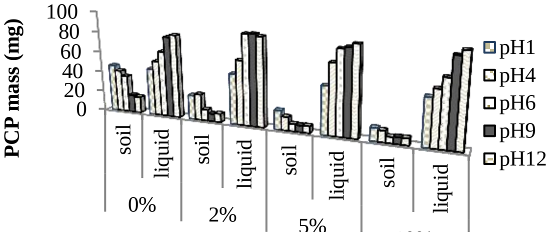

Fig. 3: Effect of pH value on PCP distribution in soil and liquid. (Initial PCP contaminated soil: 100 mg/kg; reaction time: 60 min, room temperature)

For the remediation of PCP-contaminated soil with ZVI, PCP distribution was enhanced in liquid phase and decreased in soil with increasing ZVI dose and pH compared with the control sample. At high pH (pH>4), ZVI particles were easily oxidized and covered by oxide and hydroxide while pentachlorophenolates, the predominant form of PCP in basic condition, were identified to be chemisorbed on iron oxide surface via inner-sphere coordination. However, at low pH (pH<4), the predominant form of pentachlorophenols was bonded to iron oxides by weak physical forces and preferred to sorption in natural organic matter. Therefore, over 80% of PCP was extracted into liquid with ZVI at pH above 6. This result supports the concept of applying iron oxides to enhance the extractable PCP from soil with water. The pH is also important in reductive dechlorination of chlorinated organic compounds using zero-valent iron. The effects of pH and ZVI dose on PCP dechlorination are shown in Figure 4. The lower pH allows more fresh iron surface available for reaction:

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

Under anaerobic condition, nZVI corrosion results in the release of H_2

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

Fe^{2+} and H_2 can further reduce PCP. However, dechlorination by reductive Fe^{2+} occurs very slowly and can easily be inhibited by the presence of other ligands in soil due to the formation of complexes with Fe^{2+} ion. Furthermore, H_2 is not an effective reductant without catalyst. Therefore, removal of PCP in contaminated soil and liquid was mainly attributed to reduction of Fe^{o} particles at acid condition which provided enough protons for dechlorination with increasing pH. In addition, the solution of low pH helped ZVI surface to remain fresh due to dissolution of oxide or hydroxide film. When pH reached to basic condition, the film of oxide or hydroxide irons quickly formed on the iron surface and decreased the surface reactivity, resulting in the low PCP removal efficiency. PCP desorption from soil predominated at high pH while PCP dechlorination occurred more easily and enhanced with higher ZVI dose at low pH. In terms of detoxification and real application, low pH and 5% of ZVI were chosen to further enhance dechlorination efficiency of PCP.

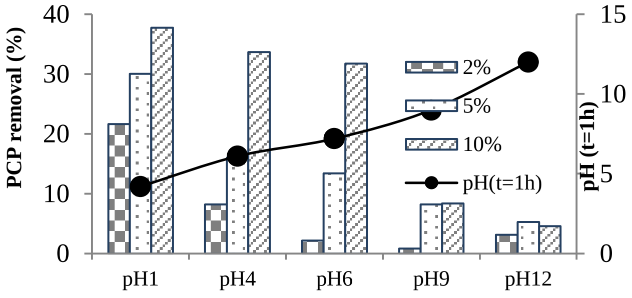

Figure 4: Effect of pH and nZVI dose on PCP removal from soil and liquid. (Initial PCP contaminated soil: 100 mg/kg; reaction time: 60 min, room temperature).

3.4. Effect of temperature

Organic matter (OM) contained in soil is responsible for PCP sorption and inhibits the contact between PCP and ZVI, thus reducing the amount of PCP degraded by ZVI particles. Therefore, ZVI coupled with thermal was employed to enhance mass transport of PCP from soil to iron surface as shown in Figure 5. Percentage of PCP dechlorination from soil was enhanced as PCP residual decreased with increasing temperature. Dechlorination efficiency increased to 15% without pH adjustment and 30% with pH 1 in the temperature of arange of 25-85°C. The increase of temperature led to the increase desorption of PCP from organic matter and solid surface of soil while the decrease in pH enhanced PCP dechlorination. At 85°C and pH1, 94% of PCP was removed from soil and 42% of PCP dechlorination was achieved. ZVI coupled with thermal in acid condition resulted in higher PCP dechlorination than that achieved with micro ZVI (Kim et al., 2000). However, the higher removal efficiency compared with dechlorination efficiency was observed and the gap between removal and dechlorination deficiency was increased with increasing temperature. An explanation is possibly due to the dechlorination reaction occurring in water-soil-iron interphase, which is limited by phase transfer mechanism. In addition, the increase of temperature may enhance other reactions of PCP with minor oxygen, PCP loss via evaporation and accumulation on vial wall/ septa in the system.

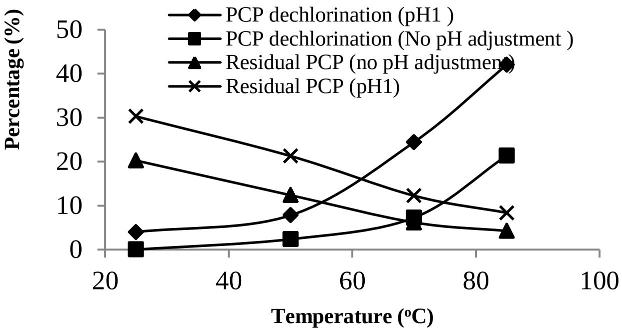

Figure 5: Effect of temperature on PCP removal from soil and dechlorination efficiency (nZVI dose: 5%; initial PCP contaminated soil: 100 mg/kg; reaction time: 60 min).

3.5. Identification of PCP byproducts

Chlorinated phenols with four, three and two chlorine atoms were all detected in liquid phase as shown in Figure 6. The presence of byproducts of PCP and increase of Cl^- obviously indicated the temperature and pH effect on the dechlorination rate of PCP from soil. Amount of byproducts increased with increasing temperature in acid condition. The presence of byproducts only in liquid phase indicated that the PCPs were desorbed from soil, adsorbed on the ZVI surface and finally reduced by ZVI. The amount of PCP byproducts appeared to increase with increasing temperature and followed the Gibbs energy calculation of chlorophenol formation [20]. The Gibbs energy of forming 2,3,4,5-tetrachlorophenol, 3,4,5-trichlorophenol and 3,4-dichlorophenol are the lowest in tetra-, tri- and di-chlorophenol groups, respectively. The reactivity of the C-Cl bond at the ortho- position is the highest, followed by the para- and meta- positions with respect to OH group. However, the final products of complete dechlorination are not observed in this system. Further research need to be carried out to enhance reactivity of nZVI on remediation of PCP-contaminated soil.

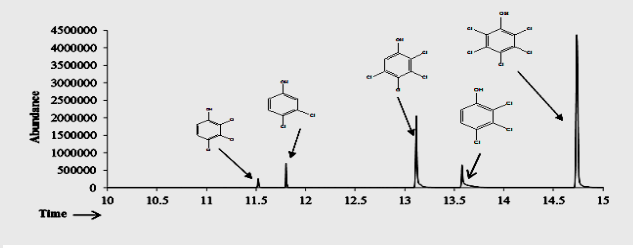

Fig.ure 6: Effect of pH and nZVI dose on PCP removal from soil and liquid. (Initial PCP contaminated soil: 100 mg/kg; reaction time: 60 min, room temperature).

5. CONCLUSIONS

For the purpose of the usage of thermally enhanced treatment coupled with ZVI, various temperatures (25-85°C), pH and ZVI doses were investigated to achieve the lowest PCP remaining in soil and to detoxify pollutants in aqueous phase. The higher PCP distribution (>80%) with ZVI was observed in aqueous phase compared with that of control sample (74%) in the same condition with no pH adjustment. The decrease in pH reduced the distribution due to the predominance of PCP molecules being adsorbed on organic matter of soil and increased PCP dechlorination. Dechlorination and PCP residual in soil were increased to 42% and decreased to 6%, respectively at the same operating condition. However, phenol as the final product of PCP dechlorination was not obtained by using this system. Further research needs to be carried out to enhance the reactivity of ZVI.

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