REMOVAL OF SELECT CHLORINATED HYDROCARBONS BY NANOSCALE ZERO-VALENT IRON SUPPORTED ON POWDERED ACTIVATED CHARCOAL

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By

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ABSTRACT


Nanoscale Zero Valent Iron (NZVI) has shown limited effectiveness in degrading chlorinated hydrocarbons (CHCs), like 1,1,1-Trichloroethane (1,1,1-TCA) and Trichloroethene (TCE), in aqueous solution. A rapid agglomeration behavior of NZVI particles due to van der waals and magnetic forces can negatively impact its overall effectiveness due to increase in particle size, and decline in CHC degradation kinetics. Different support materials, such as clays and activated carbon, have been used to stabilize NZVI particle and reduce agglomeration in aqueous solution. In this bench-scale study, NZVI supported on Powdered Activated Charcoal (PAC) was selected to prepare a composite, called PAC/NZVI, for a more effective treatment of 1,1,1-TCA and TCE in aqueous solution. The study shows that PAC/NZVI has both adsorption and degradation capability toward 1,1,1-TCA and TCE. PAC exhibited high porosity to accommodate NZVI as a suitable support in order to keep NZVI in suspension in aqueous medium and to minimize agglomeration. Bench-scale experiments with variable concentrations of PAC (0.1–0.8 g/L) and NZVI (0.2–0.6 g/L) showed that PAC/NZVI composite can be highly efficient in rapid 1,1,1-TCA removal by adsorption, and effective in overall degradation leading to production of non-chlorinated daughter products. Increase in PAC concentration in the composite was correlated with greater removal of 1,1,1-TCA by sorption whereas lower PAC concentration yielded greater degradation kinetics and higher
byproduct yields. PAC/NZVI was found to be active for more than three months presumably because NZVI embedded within hydrophobic pore spaces of PAC did not get oxidized. Cu amendment to NZVI as a secondary/catalysts metal showed faster degradation and higher byproduct yields.
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Chapter 1

INTRODUCTION

1.1 Groundwater contamination

Studies have shown that a large number of drinking water aquifers in the U.S. have become contaminated by synthetic organic chemicals due to past disposal practices of industrial wastewater and accidental spills (Pye & Patrick, 1983; GAO, 2005; Gómez et al., 2015). Chlorinated hydrocarbons (CHCs) constitute a class of organic chemicals that has impacted groundwater quality in the U.S. and other parts of the world. Despite decades of treatment activities, more than 126,000 sites remain in the U.S. requiring soil and groundwater contamination remediation, with an estimated cost as much as $110-127 billion (GAO, 2005). According to a report from the U.S. Government Accountability Office (Gómez, 2015), more than 45,000 contaminated sites are currently being managed by different government agencies, including ~38,800 sites by the Department of Defense that allocated ~$30 billion during 1986-2008 for the treatment of contaminated aquifers.

1.2 Groundwater remediation

The level of CHCs in contaminated soil and groundwater can be attenuated or degraded by various naturally occurring physical, chemical and microbiological processes in the soil as well as in groundwater, which are collectively termed “natural attenuation”. In the saturated zone of the aquifer, the CHCs tend to partition between liquid and solid phases.
The increase in the soil organic matter content, expressed as a fraction of organic carbon ($f_{oc}$), can result in an increase of partitioning/adsorption of CHCs to aquifer solids due to their hydrophobic nature (Gómez, 2015).

Groundwater contamination can be treated either *ex situ* or *in situ*. Pump-and-treat used to be a popular *ex situ* groundwater treatment approach, which involves extracting contaminated groundwater from the subsurface aquifer followed by treatment in an above-ground facility. The treated water is often discharged to a surface water reservoir to allow natural infiltration to recharge the aquifer. But achieving aquifer remediation goals by pump-and-treat methods is often time-consuming and difficult to accomplish. Gomez (2015) reported that pump-and-treat was applied at 77 contaminated sites during 1994-2005, but only 7 sites have achieved the remedial goals to date. The remediation of aquifers contaminated with CHCs by pump-and-treat is difficult and challenging as CHCs often enter into low permeability soil units and their recovery by pumping is ineffective.

### 1.3 Nanoscale Zero-Valent Iron (NZVI)

Nanoscale Zero Valent Iron (NZVI) is a relatively new technology for *in situ* treatment of contaminated groundwater. Its small particle size (10-100 nm) makes NZVI an injectable material for *in situ* groundwater treatment (Song & Carraway, 2006). NZVI can also be an efficient remediation option for source zone treatment in a contaminated aquifer. NZVI has been successfully used for treating a wide variety of organic and inorganic contaminants, such as CHCs, pesticides, arsenic, chromium. Recent investigations have shown that NZVI can completely reduce CHCs to benign byproducts (Liu & Zhang, 2010; Zhang et al., 2010; Shih et al., 2011). However, due to van der waal and magnetic forces, NZVI particles tend to agglomerate (He & Zhao, 2005) in aqueous solution. Furthermore,
NZVI can become oxidized rapidly by reaction with oxidizing species (Xiao et al., 2015) including water, thus diminishing its reactivity and longevity (He & Zhao, 2005; Phenrat et al., 2007). Polyelectrolytes, such as carboxymethylcellulose (CMC), polyacrylic acids, and certain surfactants, have been used as stabilizers for NZVI to reduce nanoparticle agglomeration (Kadar et al., 2011; Zhang et al., 2011). NZVI also can be stabilized using different support materials, such as clays, porous activated carbon or charcoal (Su et al., 2013; Sunkara et al., 2010; Üzüm et al., 2009), which can prevent rapid NZVI agglomeration and oxidation, and extend its longevity as a reactive material to treat contaminated aquifers. NZVI supported on activated carbon (AC) can offer dual property (for adsorption and degradation) in removing CHCs from aqueous solution (Sunkara et al., 2010). While AC-supported NZVI composite (NZVI deposited on AC, referred to as AC/NZVI henceforth) can destroy a wide range of organic contaminants by chemical reduction, AC also acts as an adsorbent for other contaminants that are difficult to degrade (Zhu et al., 2009). AC/NZVI composites have been successfully used to treat recalcitrant CHCs like perchloroethene, trichloroethene, trihalomethanes, polychlorinated biphenyls, nitrobenzene, heavy metals, etc. (Choi et al., 2009; Kadar et al., 2011; Sunkara et al., 2010).

Although a number of studies have been completed to better understand the behavior AC/NZVI composites, many questions still remain unanswered. Two important questions are: (1) what is the role of AC support on pollutant degradation behavior by NZVI and the distribution of degradation byproducts? (2) what is the relative significance of AC and NZVI in the composite and their combined effect on the removal of various pollutants? NZVI stabilized with CMC has been shown to reduce its agglomeration and
improve dispersion in the aqueous solution but the role of CMC on AC/NZVI dispersion requires further study. The published procedures for synthesizing AC/NZVI composites often also vary significantly among studies (Xiao et al., 2015). Further, the role of AC/NZVI synthesis procedure on its longevity has not been studied yet. The addition of secondary metals, such as Nickel, Palladium and Copper has shown enhanced reduction of CHC by NZVI (He et al., 2007) but the effect of adding a secondary metal to AC/NZVI composite is yet to be examined.

1.4 Research objectives

This study attempts to address the questions mentioned above and offers new insight into the removal mechanisms (adsorption vis-a-vis degradation) of CHCs by AC/NZVI composites. In this study, powdered activated charcoal (PAC) was chosen as support, which is prepared by the mechanical crushing/milling of activated wood charcoal (from coconut husks) into a very fine powder. Due to its small particle size (0.4-44 micron), PAC has a greater external specific surface area (1500 m²/g) than that for granular activated charcoal (GAC) however, the difference between overall surface area (external and internal) of PAC and GAC is not significant. The application of PAC/NZVI composites for organic pollutant removal has not been studied thus far. This study investigates the degradation of select CHCs by PAC/NZVI composite, and examine the effect of a secondary metal, Copper (Cu), to PAC/NZVI composite on CHCs removal. This includes estimating degradation kinetics, and characterizing byproduct distribution and carbon mass balance for select chlorinated hydrocarbons, particularly 1,1,1-trichloroethane (1,1,1-TCA) and trichloroethene (TCE), as model organic pollutants. The study makes improvements and optimizes synthesis procedure for PAC/NZVI composite.
and NZVI-PAC mixture to minimize the loss in NZVI reactivity in the long term. The specific objectives of this study are identified below:

I. Evaluate degradation of 1,1,1-TCA and TCE with unsupported NZVI, PAC/NZVI composite and NZVI-PAC mixture in terms of degradation kinetics and byproduct distribution.

II. Examine the effect of amending PAC/NZVI composite with zero-valent copper in PAC/Cu- NZVI composite in 1,1,1-TCA and TCE degradation, and compare with PAC/NZVI in terms of removal by adsorption and degradation, and byproduct distribution.

III. Evaluate the reactivity of PAC/NZVI composites prepared with varying PAC and NZVI loadings (concentrations), expressed in terms of CHC degradation kinetics and byproduct distribution, and removal mechanisms (adsorption vs. transformation).

IV. Evaluate the long-term reactivity of PAC/NZVI composites towards model CHCs with insight into its longevity.
Chapter 2

MATERIALS AND METHODS

2.1 Chemicals

Ferric chloride hexahydrate (ACS grade; Ricca Chemical Company), sodium borohydride (98%; Sigma-Aldrich), copper chloride dihydrate (CuCl₂.2H₂O; 99+%; Arcos Organics), TAPSO or 3-[[1,3-Dyhydroxy-2-2(hydroxymethyl)-2-propanyl]]-2-hydroxy-1-propanesulfonic acid (99+%), carboxymethylcellulose (99+%), and 1,1,1-trichloroethane (1,1,1-TCA, 99%) was also purchased from Sigma-Aldrich. Trichloroethene (TCE, 97%) was purchased from Acrose Organics. Powdered Activated Charcoal (PAC) was purchased from Charcoal House, USA.

2.2 Batch experiment setup

Experiments were carried out in 160 mL borosilicate glass serum bottles sealed with Teflon-lined butyl rubber stopper and aluminum crimp. NZVI was freshly synthesized by chemical reduction of aqueous ferric chloride by sodium borohydride reagent (borohydride reduction method) in individual bottle reactors. This was accomplished inside an anaerobic chamber to avoid NZVI oxidation by oxygen in order to simulate anoxic groundwater condition during CHC degradation experiments. The atmosphere inside of the anaerobic chamber was nominal ~1-2% hydrogen with the balance being nitrogen. Two approaches for NZVI synthesis were used: (i) in the first approach, ferric
chloride reagent solution was added to the pre-weighed amount of PAC followed by addition of sodium borohydride to prepare a composite, called PAC/NZVI; (ii) in the second approach, NZVI was synthesized before adding fixed amount of PAC to prepare NZVI-PAC mixture. The reactor bottles containing either PAC/NZVI composite or NZVI-PAC mixture was spiked with aqueous CHC solution. After CHC injection, the batch reactors were mixed continuously on an end-over-end rotary mixer at ~45 rpm at STP. Headspace samples from the sealed batch reactors were withdrawn using a gastight syringe (Hamilton) typically at pre-determined time intervals and analyzed immediately by gas chromatography. While sampling, the reactor bottles was taken off the rotator for ~30-45 seconds. The duration of the experiment varied depending upon its objective. The synthesis procedure was carefully devised to accomplish the objectives of this study. While synthesizing unsupported NZVI, PAC was not added to the solution, PAC/NZVI composite was synthesized by mixing ferric chloride solution to PAC before adding sodium borohydride to facilitate NZVI deposition on PAC (Figure 1) While synthesizing NZVI/PAC mixture, sodium borohydride reagent was added to ferric chloride solution in presence of CMC to form unsupported NZVI first, before mixing it with predetermined amounts of PAC.

2.3 **Synthesis of PAC/NZVI and PAC/Cu-NZVI composites**

The following was accomplished outside the anaerobic chamber:

1. Add 20 mg of PAC in two reactor bottles which make PAC concentration 0.2 g/L in the reactors.
2. Add 3.44 mL of 100 mM FeCl₃*6H₂O reagent solution to each reactor bottle. After synthesis, this will become equivalent to 0.2 g/L of NZVI in the reactor.

3. Add 25 mL of 30 mM TAPSO buffer (adjusted to pH 8) in each bottle.

4. Seal the bottles with Teflon-lined grey butyl rubber stopper and aluminum crimp.

5. Equilibrate the bottles on a rotator for two hours (end-over-end mixing at 45 rpm).

6. After equilibration, transfer the reactor bottles to the anaerobic chamber after removing their seals.

The following steps were accomplished inside the anaerobic chamber:

1. Add 4.12 mL of freshly prepared 500 mM NaBH₄ reagent to each reactor bottle while swirling gently (borohydride/Fe³⁺ stoichiometric ratio = 6:1).

2. Allow 10 minutes for ferric chloride reaction with borohydride to be complete, in which Fe³⁺ will get chemically reduced to NZVI (Equation 1 below; Sun et al. 2007).

3. Add deoxygenated deionized (DDI) water to make total liquid volume in the reactor to 96 mL.

   \[
   4\text{FeCl}_3(aq) + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^0(s) + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+(aq) + 6\text{H}_2(g) \quad (1)
   \]

   \[
   \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{BO}_2^- + 4\text{H}_2(g) \quad (2)
   \]

   \[
   \text{Fe}^0(s) + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^- + \text{Fe}^{2+} \quad (3)
   \]

Cu amended NZVI was synthesized by adding 150 μL of 100 mM CuCl₂·2H₂O solution to NZVI and PAC solution before adding TAPSO buffer while all the other steps were same.
2.4 Synthesis of NZVI, Cu-NZVI and NZVI-PAC mixture

In this procedure, ferrous sulfate heptahydrate (FeSO₄·7H₂O) was used to synthesize 0.2 g/L NZVI by borohydride reduction method (similar to the procedure described earlier) but with TAPSO buffer adjusted at pH 7 and with 4 g/L CMC as a stabilizer. PAC was added to the reactor (0.2 g/L) after NZVI synthesis is complete. While all experiments with PAC/NZVI composite experiments were completed at pH 8, the experiments with NZVI-PAC mixture experiments were completed at pH 7 to compare with NZVI only control. Sodium borohydride is a strong reductant that reduces Fe(III) to Fe⁰(s). However, borohydride can react with water also (Equation 2). NZVI is very reactive with water and can get oxidized to form Fe²⁺ (Equation 3).

![Conceptual model of PAC/NZVI complex](image)

Figure 1: Conceptual model of PAC/NZVI complex

2.5 Chemical Analysis

CHC and its degradation products were monitored by a gas chromatograph (model 7890; Agilent Technologies) equipped with electron capture (ECD) and flame ionization (FID) detectors HP 624 (30m x 0.32 mm x 0.25 µm, Agilent technologies) and GasPro column
30m x 0.32 mm x 0.25 μm, Agilent technologies) were installed and connected to ECD and FID. All the CHCs peaks were visible on ECD whereas all the other hydrocarbon peaks were visible on FID. Helium served as a carrier gas at a constant flow of 2.5 mL/min and the GC method was, split/splitless inlet = 250°C, oven temperature = 150°C (isothermal). Nitrogen gas (N₂) was used as make up gas for ECD at a flow rate of 2.5 mL/min. The flow rate for H₂ and air was 450 and 30 mL/min respectively for FID. A 50 μL of reactor headspace was extracted using 250 μL gastight syringe (Hamilton, Reno, NV) from sealed batch reactors for each sampling and manually injected into the gas chromatograph. The sampling interval varied depending on the retention time and degradation kinetics of the compounds.

2.6 Data treatment

The chromatograms generated for each sampling was integrated and the peak area under the curve for the individual chemical was recorded in Microsoft Excel worksheets and converted to moles and mole fraction using calibration curves. Dimensionless Henry’s constant was utilized to calculate the amount of CHC in aqueous phase and headspace of the reactor bottles. Averages of the chemical amounts and sampling times for the two reactors was taken for further data analysis and chart preparation showing CHC remaining and byproduct yields (mole fractions) vs. time for estimating pseudo first-order degradation rate constant ($k_{obs}$).

The data for CHC removal from the initial ~30 to 60 minutes was be used for estimating pseudo first-order degradation rate constant ($k_{obs1}$). Further, the long-term degradation rate constant ($k_{obs2}$) was also be estimated for experiments lasting for several weeks and months. Additional charts were prepared to summarize the results of
experiments in order to examine the effect of PAC loading, NZVI loading and synthesis procedure.
Chapter 3

RESULTS AND DISCUSSION

3.1 Degradation of 1,1,1-Trichloroethane with unsupported NZVI and Cu-NZVI

The degradation of 1,1,1-TCA with 0.2 g/L NZVI stabilized with 4 g/L CMC was rapid ($k_{obs1} = 0.23 \text{ hours}^{-1}$, first 45 min) with the production of ethane and ethene as only reaction byproducts (Figure 2). The degradation kinetics slowed considerably afterward ($k_{obs2} = 0.03 \text{ hours}^{-1}$, after 1 hour). After ~3 hours, the 1,1,1-TCA mole fraction remaining ($m/m_0$) was 0.73, and ethane and ethene mole fraction yields ($m/m_0$) were 0.03 and 0.01, respectively. The carbon mass balance ($m/m_0$) at 3 hours was 0.77, where most of the 1,1,1-TCA degraded in the first one hour of the experiment. In order to understand the long-term degradation of 1,1,1-TCA with CMC-stabilized 0.2 g/L NZVI, the reactors were further analyzed at 24 hours and at ~500 hours (Figure 2C). The 1,1,1-TCA remaining ($m/m_0$) at 24 hours and 500 hours were 0.68 and 0.64 respectively. Ethane and ethene yields ($m/m_0$) at 500 hours were 0.04 and 0.02, where the balance of the degraded 1,1,1-TCA produced some unknown byproducts. No significant loss in 1,1,1-TCA was observed in control reactors (without NZVI) over the experiment period.

The degradation of 1,1,1-TCA with Cu-NZVI (0.2 g/L NZVI modified with 5 wt% Cu stabilized with 4 g/L CMC) was much more effective (Figure 3). Within 1.5 hours, almost all of 1,1,1-TCA degraded (remaining $m/m_0 < 0.01$). Ethane was the key byproduct
of degradation with a yield \((m/m_0)\) of 0.23 at 1.5 hours. The two minor byproducts were 1,1-DCE and ethene \((m/m_0 = 0.05 \text{ and } 0.04 \text{ at } 1.5 \text{ hours})\) and the carbon mass balance \((m/m_0)\) was 0.32. The rest of 1,1,1-TCA degraded into some unidentified byproducts. \(k_{\text{obs}1}\) was 1.6 fold faster than \(k_{\text{obs}2}\) \((k_{\text{obs}1} = 6.1 \text{ hour}^{-1}, k_{\text{obs}2} = 3.72 \text{ hour}^{-1})\). In comparison to CMC stabilized NZVI, the pseudo first-order rate-constant of 1,1,1-TCA degradation with Cu-NZVI was much greater \((k_{\text{obs}1} \text{ and } k_{\text{obs}2} \text{ were } \sim 25\text{-fold and } 100\text{-fold larger, respectively})\).

The production of ethane and ethene from 1,1,1-TCA degradation with NZVI and Cu/NZVI may suggest multiple pathways of degradation. In one scenario, ethane can be produced through hydrogenolysis reactions that involve sequential dehalogenation \((1,1,1\text{-TCA} \rightarrow 1,1\text{-dichloroethane} \rightarrow \text{chloroethane} \rightarrow \text{ethane})\). However, Fennelly and Roberts (1998) have shown that 1,1 dichloroethane \((1,1\text{-DCA})\) hydrogenolysis to ethane with zero-valent iron is slow and unlikely, which excludes 1,1-DCA as an intermediate to ethane formation. However, ethane production by sequential hydrogenolysis of 1,1,1-TCA with Cu-NZVI is more likely. The formation of 1,1-DCA in this study, if any, was below detection limit. However, the formation of ethene \((\text{Figures 3})\) as an intermediate with NZVI and 1,1-dichloroethene \((1,1\text{-DCE})\) and ethene as intermediates with Cu/NZVI \((\text{Figures 3})\) may suggest the following pathway: (i) 1,1,1-TCA degradation to 1,1-DCE via dehydrochlorination, followed by (ii) 1,1-DCE degradation to ethene via hydrogenolysis \((\text{Vogel and McCarty; 1987})\). Ethane production may have been either by sequential hydrogenolysis of 1,1,1-TCA, or by hydrogenation of ethene. Production of 1,1-DCE and ethene as intermediates thus confirms dehydrochlorination and hydrogenolysis pathways.
3.2 Removal of 1,1,1-Trichloroethane with PAC/NZVI composite

Rapid initial adsorption followed by degradation of 1,1,1-TCA was observed with 0.2 g/L PAC-0.2 g/L NZVI composite (Figure 4). The initial loss of 1,1,1-TCA in ~20 min was near complete \((m/m_0)\) remaining ~0.06, which may be attributed to its adsorption to PAC in the PAC/NZVI composite. This was followed by a slower 1,1,1-TCA loss due to degradation during 20-60 min \((k_{obs1} = 0.30 \text{ hour}^{-1})\). Long-term degradation during 100-500 hours was significantly slower \((k_{obs2} = 0.01 \text{ hour}^{-1})\). After 500 hours, further 1,1,1-TCA degradation and byproduct generation nearly stopped. Ethane and ethene were the only byproducts detected at ~500 hours and their respective yields \((m/m_0)\) were 0.08 and 0.01. No other chlorinated intermediates were detected. The carbon mass balance \((m/m_0)\) was 0.09 at ~500 hours, which suggests that most of the 1,1,1-TCA adsorbed initially to PAC/NZVI composite either did not degrade or the degraded products did not desorb into the aqueous phase.

Effect of Increasing PAC loading on 1,1,1-TCA Degradation: The degradation of 1,1,1-TCA with varying PAC loadings in PAC/NZVI composites (0.2 g/L NZVI with increasing PAC loadings at 0.1, 0.2, 0.4, 0.6, and 0.8 g/L) showed systematic behavior in results (Figures 4-8). With PAC-NZVI composite containing 0.2 g/L NZVI deposited on 0.1 g/L PAC, the initial removal of 1,1,1-TCA by adsorption was the smallest of all PAC loadings (1,1,1-TCA remaining, \(m/m_0\), was 0.17 in ~30 min; Figure 5). In other experiments with higher PAC loading in PAC/NZVI composites, 1,1,1-TCA remaining \((m/m_0)\) due to rapid initial loss by adsorption in the first 30 min was progressively smaller (0.06, 0.02, 0.01 and 0.01 at 0.2, 0.4, 0.6 and 0.8 g/L PAC in the composites, respectively). The short-term rate constants of 1,1,1-TCA degradation \((k_{obs1})\) increased systematically with increasing
PAC loading in PAC-NZVI composites, as follows: 0.16, 0.30, 0.41, and 0.64 hour\(^{-1}\) at 0.1, 0.2, 0.4 and 0.6 g/L PAC in PAC/NZVI, respectively. However, the long-term degradation rate constants (\(k_{\text{obs2}}\)) decreased somewhat with increasing PAC loading, as follows: 0.11, 0.10, 0.01, 0.01 hour\(^{-1}\) at 0.1, 0.2, 0.4, 0.6 g/L PAC in PAC/NZVI, respectively. The ethane yields (\(m/m_0\)) also decreased with increasing PAC loading, as follows: 0.12, 0.08, 0.029 and 0.025 at 0.1, 0.2, 0.4, 0.6 g/L PAC in PAC/NZVI, respectively. Further, ethene yields (\(m/m_0\)) were <0.01 and were not affected by increasing PAC loading.

**Effect of Increasing NZVI loading on 1,1,1-TCA Degradation:** The degradation of 1,1,1-TCA with varying NZVI loadings in PAC/NZVI composites (0.2, 0.4, and 0.6 g/L NZVI, each with 0.2 g/L PAC) showed systematic results (Figures 4, 9 and 10). In all cases, the initial loss of 1,1,1-TCA due to adsorption to PAC/NZVI was rapid and high (1,1,1-TCA remaining, \(m/m_0 < 0.10\)). Ethane yields declined with higher NZVI loadings, as follows: \(m/m_0\) values were 0.08, 0.04, and 0.02 at 0.2, 0.4, and 0.6 g/L NZVI in PAC/NZVI composite, respectively. Further, ethene yields were in trace amounts (\(m/m_0 < 0.01\)) at 0.2, 0.4 and 0.6 g/L NZVI. The increase in NZVI loading in PAC/NZVI showed a minor increase in initial degradation kinetics (\(k_{\text{obs1}}\)), as follows: 0.28, 0.34, and 0.33 hour\(^{-1}\) at 0.2, 0.4 and 0.6 g/L NZVI in PAC/NZVI, respectively. The long-term degradation kinetics (\(k_{\text{obs2}}\)) of 1,1,1-TCA also did not show significant change, as follows: 0.10, 0.01, and 0.01 hour\(^{-1}\) at 0.2, 0.4, and 0.6 g/L NZVI, respectively. Such increase in \(k_{\text{obs1}}\) together with a decline in ethane yields show a loss in PAC/NZVI reactivity that may be due to potential NZVI agglomeration on the PAC surface.
3.3 Long term removal of 1,1,1-TCA with PAC/NZVI Composites

Multiple injections of 1,1,1-TCA to batch reactors containing PAC/NZVI in four successive cycles over a period of ~3 months showed good 1,1,1-TCA removal by adsorption and degradation (Figure 11). A PAC/NZVI composite with 0.2 g/L PAC-0.2 g/L NZVI showed high initial removal by adsorption in the first 3 consecutive cycles (1,1,1-TCA remaining, \( m/m_0 < 0.10 \) at 1 hour in cycles 1 to 3), but in cycle 4 the removal declined (1,1,1-TCA remaining, \( m/m_0 < 0.5 \) at 1 hour). The short-term kinetics did not change much in 4 consecutive cycles except 3\(^{rd}\) cycle, as follows: \( k_{\text{obs1}} \) values were 0.28, 0.29, 0.05, and 0.25 hour\(^{-1}\) in cycles 1, 2, 3 and 4, respectively. A lower \( k_{\text{obs1}} \) value in cycle 3 may have been due to unintended lower initial 1,1,1-TCA concentration in the reactors.

No significant change in the long-term degradation kinetics was observed (\( k_{\text{obs2}} \) values was \( ~0.01 \) hour\(^{-1}\) in all 4 cycles). For the first 2 cycles, the ethane yields were similar (\( m/m_0 = 0.13 \) each in cycles 1 and 2) but ethane yields increased to 0.32 and 0.33 in cycles 3 and 4, respectively. The greater amount of ethane yields in cycles 3 and 4 may be attributed to 1,1,1-TCA adsorption to PAC approaching its capacity, thus facilitating its greater interaction with NZVI leading to degradation. Ethene yields in all 4 cycles remained low (\( m/m_0 < 0.1 \)) as it simultaneously formed and further degraded to ethane. Overall, the result showed that PAC/NZVI composite remained active for at least 3 months (each cycle lasted \( ~500 \) hours).

Three consecutive cycles of 1,1,1-TCA degradation with a PAC/NZVI composite containing 0.4 g/L PAC and 0.2 g/L NZVI showed a slightly greater initial removal at 1 hour (Figure 12) by adsorption, as follows: 1,1,1-TCA remaining, \( m/m_0 < 0.02 \) in cycles 1, 2 and 3, in comparison to 0.2 g/L NZVI in PAC/NZVI composite described earlier.
The short-term degradation kinetics showed a modest decline from cycle 1 to 2, but did not change further in cycle 3 ($k_{obs1} = 0.41, 0.12$ and $0.11 \, \text{hour}^{-1}$ in cycles 1, 2 and 3, respectively). Long-term degradation kinetics was much slower but did not vary much in consecutive cycles ($k_{obs2} = 0.01 \, \text{hour}^{-1}$ in all three cycles). Ethane yields ($m/m_0$) progressively increased in three consecutive cycles (0.05, 0.14, and 0.35 in cycles 1, 2 and 3, respectively). Progressively higher amount of ethane yields in 3 consecutive cycles again may be attributed to gradually declining sorption of 1,1,1-TCA to PAC, which in turn allows greater 1,1,1-TCA interactions with NZVI. Ethene yields were small and they are not included for individual cycles. The duration of each cycle was $\sim 400$ hours.

Similar long-term experiment conducted with PAC/NZVI composite containing 0.6 g/L PAC and 0.2 g/L NZVI showed similar adsorption behavior, as follows: 1,1,1-TCA remaining, $m/m_0 < 0.1$ in all 3 cycles (Figure 13). Short-term degradation kinetics decreased significantly from cycle 1 to 2 and 3 ($k_{obs1}$ values were 0.54, 0.2 and 0.15 hour$^{-1}$ in cycles 1, 2 and 3, respectively; data not shown) whereas the long-term kinetic remained unchanged ($k_{obs2}$ values were <0.01 hour$^{-1}$ for all 3 cycles). Significant yet gradual increase in net ethane yield ($m/m_0$) was observed from cycle 1 to 3, as follows: 0.044, 0.08 and 0.17 in cycles 1, 2 and 3, respectively). The duration of the experiment in cycle 1 was $\sim 1000$, and $\sim 400$ hours in cycles 2 and 3.

Similar long-term experiment conducted with PAC/NZVI composite prepared with 0.8 g/L PAC and 0.2 g/L NZVI showed similar adsorption behavior, as follows: 1,1,1-TCA remaining, $m/m_0 < 0.02$ and < 0.1 in cycle 1 and 2 respectively (Figure 14). Short-term degradation kinetics decreased significantly from cycle 1 to 2 ($k_{obs1}$ values were 0.54 and 0.14 hour$^{-1}$ in cycles 1 and 2; data not shown) whereas the long-term kinetic remained
unchanged ($k_{obs2}$ values were <0.01 hour$^{-1}$ in cycles 1 and 2). An increase in the net ethane yield ($m/m_0$) was observed from cycle 1 to 2, as follows: 0.03 and 0.11 in cycle 1 and 2 respectively). The experiment duration in cycles 1 and 2 were ~200 hours.

Consecutive cycles of 1,1,1-TCA amendment to batch reactors containing 0.2 g/L PAC-0.4 g/L NZVI composite (Figure 15). High adsorption in the first cycle was observed whereas a modest drop in the initial adsorption was noticed in the second cycle (1,1,1-TCA remaining, $m/m_0$ <0.10 and <0.2 in cycles 1 and 2, respectively). Short-term kinetics also decreased significantly from cycle 1 to cycle 2 as follows: $k_{obs1} = 0.35$ and 0.18 hour$^{-1}$ in cycle 1 and 2. Further, no significant change in the long-term degradation kinetics was observed in two consecutive cycles ($k_{obs2}$ values were <0.01 hour$^{-1}$ in cycles 1 and 2). However, ethane yield ($m/m_0$) doubled from cycle 1 to 2 as follows: 0.04 and 0.1 in cycles 1 and 2 respectively). Experiment duration in both cycles was similar (~450 hours).

Consecutive cycles of 1,1,1-TCA removal with PAC/NZVI composite containing 0.2 g/L PAC-0.6 g/L NZVI showed significant adsorption in consecutive cycles (1,1,1-TCA remaining, $m/m_0$ < 0.05 and 0.1 in cycles 1 and 2; Figure 16). A significant decrease in the short-term 1,1,1-TCA removal kinetics was observed as follows: $k_{obs1}$ declined from 0.334 to 0.155 hour$^{-1}$ from cycle 1 to 2. Minor increase in the long-term kinetics was observed as follows: $k_{obs2}$ increased 0.009 to 0.013 hour$^{-1}$ from cycle 1 to 2. Ethane yields ($m/m_0$) also increased in consecutive cycles from 0.05 to 0.01 in cycle 1 to 2).

3.4 Removal of 1,1,1-Trichloroethane with PAC/Cu-NZVI composite

The degradation of 1,1,1-TCA with PAC/Cu-NZVI containing 0.2 g/L PAC-0.2 g/L NZVI with 5%wt Cu showed its rapid initial removal (Figure 17); the 1,1,1-TCA remaining
(m/m₀) at 1 hour was ~ 0.01, which is smaller than that for 0.2 g/L PAC-0.2 g/L NZVI composite (1,1,1-TCA remaining, m/m₀ ~0.05; Figure 4). The initial rate constant of 1,1,1-TCA degradation with PAC/Cu-NZVI was significantly greater than that for PAC/NZVI composite with same PAC and NZVI concentrations but without Cu (k_{obs1} was 0.91 and 0.30 hour⁻¹ in the first hour for PAC/Cu-NZVI and PAC/NZVI, respectively; Figures 4B and 17B). The rate constant of 1,1,1-TCA degradation with PAC/Cu-NZVI slowed down ~2 fold during 2-6 hour (k_{obs2}: 0.37 hour⁻¹; Figure 17). Although 1,1,1-TCA was totally removed in 1 day, ethane and ethene production continued for about ~1 week. The ethane and ethene yields (m/m₀) after a week with PAC/Cu-NZVI were 0.25 and 0.08, respectively; in comparison, the ethane and ethene yields after 2 weeks with PAC/NZVI were <0.01, each.

Total byproduct yield (sum of ethane and ethene) was greater for 5% Cu and 0.2 g/L NZVI Cu/NZVI (m/m₀ = 0.23) in comparison to 0.2 g/L PAC and 0.2 g/L NZVI composite (m/m₀ = 0.14). While the ethane yield did not change significantly due to Cu amendment, ethene yield increased (m/m₀, 0.04, Cu/NZVI; 0.05, PAC/Cu-NZVI). A considerable amount of 1,1-DCE was produced with Cu/NZVI (m/m₀ = 0.04) however no such harmful byproduct was observed with PAC/NZVI.

The reactivity of the PAC/Cu-NZVI composite changed significantly with increase in NZVI concentration to 0.4 g/L (i.e., 0.2 g/L PAC-0.4 g/L NZVI with 5% Cu). Very good initial removal was observed (1,1,1-TCA remaining, m/m₀, <0.05 at ~1 hour; Figure 18A) with rapid short-term removal kinetics (k_{obs1} = 1.13 hour⁻¹; Figure 18B), which is better than that for PAC/Cu-NZVI composite with 0.2 g/L NZVI concentration (k_{obs1} = 0.91 hour⁻¹). At 0.4 g/L NZVI concentration in PAC/Cu-NZVI, the long-term degradation
kinetics \( (k_{\text{obs2}}) \) was also modestly greater \( (0.48 \text{ hour}^{-1} \) with 0.4 g/L NZVI vs. 0.37 hour\(^{-1}\) 0.2 g/L NZVI). Ethene and ethane yields \( (m/m_0) \) at \( \sim 1 \) day were 0.08 and 0.1 with 0.4 g/L NZVI in PAC/Cu-NZVI composite, which was comparable to that with 0.2 g/L NZVI in PAC/Cu-NZVI composite.

Comparison of performance of the PAC/Cu-NZVI composites prepared with the varying amount of copper (2.5 vs. 5 wt% Cu with 0.2 g/L PAC and 0.4 g/L NZVI) shows minor difference in initial 1,1,1-TCA removal \( (1,1,1\text{-TCA remaining, } m/m_0, \sim 0.15 \text{ at 1 hour with 2.5 wt% Cu; Figure 19B vs. } \sim 0.1 \text{ at 1.5 Hour with Cu 5 wt% Cu; Figure 18B}). No significant difference was noticed in the short term kinetics \( (k_{\text{obs1}} \text{ was } 0.93 \text{ and } 1.128 \text{ hour}^{-1} \) with 2.5 and 5 wt% Cu, respectively; see Figures 19B and 18B). Further, the long-term degradation kinetics \( (k_{\text{obs2}}) \) showed a modest change with increasing Cu loading \( (0.35 \text{ and } 0.48 \text{ hour}^{-1} \) with 2.5 and 5 wt% Cu, respectively; Figures 19C and 18C). Further, while increase in Cu loading modestly increased initial 1,1,1-TCA removals and degradation kinetics, it did not affect byproduct amounts after \( \sim 1 \) day (ethane yields were 0.14 and 0.11 with 2.5 and 5 wt% Cu respectively; ethene yields were 0.08 each with both 2.5 and 5 wt% Cu; Figures 19A and 18A).

3.5 Comparison of 1,1,1-TCA degradation with NZVI-PAC mixtures and PAC/NZVI composite

The degradation of 1,1,1-TCA with NZVI-PAC mixture (0.2 g/L PAC mixed in with 0.2 g/L NZVI after NZVI synthesis) shows its rapid initial removal by adsorption \( (1,1,1\text{-TCA remaining, } m/m_0, \sim 0.077 \text{ at } \sim 1 \text{ day; Figure 20A}). \) The short-term removal kinetics of 1,1,1-TCA \( (k_{\text{obs1}}) \) with NZVI-PAC mixture was 0.23 hour\(^{-1}\) (Figure 20B), which is less than 0.30 hour\(^{-1}\) with PAC/NZVI composite (Figure 4B). However, the long-term degradation
kinetics \( (k_{\text{obs2}}) \) was quite comparable \((\sim 0.01 \text{ hour}^{-1})\) with both PAC/NZVI composite and NZVI-PAC mixture. Further, ethane yield was smaller with NZVI-PAC mixture \((m/m_0, \sim 0.03; \text{Figure 20A})\) in comparison to PAC/NZVI composite \((m/m_0, \sim 0.08; \text{Figure 4A})\), whereas ethene yields with both materials were quite similar.

At higher NZVI loadings \((0.4 \text{ and } 0.6 \text{ g/L})\) in the NZVI-PAC mixture (Figures 21 and 22) the rapid initial removal of 1,1,1-TCA due to adsorption was similar \((1,1,1-\text{TCA remaining}, m/m_0, \sim 0.07 \text{ and } 0.05 \text{ at 1 hour with 0.4 and 0.6 g/L NZVI, respectively; Figures 21B and 22B})\), which was comparable with 1,1,1-TCA remaining \((m/m_0 \sim 0.06; \text{Figure 20B})\) with 0.2 g/L NZVI in NZVI-PAC mixture (described above). Further, the short-term degradation kinetics of 1,1,1-TCA increased systematically with increasing NZVI loading \((k_{\text{obs1}} \text{ was } 0.21, 0.31 \text{ and } 0.45 \text{ hour}^{-1} \text{ at 0.2, 0.4 and 0.6 g/L NZVI})\). However, the long-term kinetics of 1,1,1-TCA remained \(~0.01 \text{ hour}^{-1} \text{ at 0.2, 0.4 and 0.6 g/L NZVI in the NZVI-PAC mixture. Long-term ethane yield (m/m_0) shows minor increase with increasing NZVI content as follows: 0.03, 0.04, and 0.05 with 0.2, 0.4 and 0.6 g/L (Figure 20A, 21A and 22A) with NZVI in the mixture whereas long-term ethene yields (m/m_0) were <0.03, 0.04 and 0.05 with 0.2, 0.4 and 0.6 g/L with NZVI in the mixture.}

### 3.6 Trichloroethene degradation with NZVI, Cu/NZVI, PAC/NZVI and PAC/Cu-NZVI

*Trichloroethene degradation with NZVI*: TCE degradation with unsupported 0.2 g/L NZVI stabilized with CMC at pH 7 (Figure 23) shows modest degradation with ethene and ethane as byproducts. The initial TCE degradation kinetics \((k_{\text{obs1}})\) in the first hour was 0.24 hour\(^{-1}\) but it declined afterward to 0.01 hour\(^{-1}\) during 1-3 hours. After \(~3\) hours of the
experiment, the TCE remaining ($m/m_0$) was 0.70 and ethane and ethene yields ($m/m_0$) were 0.01 and 0.04, respectively (Figure 23A).

*Trichloroethene degradation with Cu/NZVI:* The degradation of TCE with unsupported Cu-NZVI (0.2 g/L NZVI with 5 wt% Cu) shows ethene and ethane as byproducts (Figure 24). The initial rate constant of TCE degradation ($k_{obs1} = 0.3$ hour$^{-1}$) in the first hour was significantly greater than long-term degradation kinetics ($k_{obs2} < 0.02$ hour$^{-1}$, Figures 24B and 24C). After 2 hours, TCE remaining ($m/m_0$) was 0.80, whereas ethane and ethene yields ($m/m_0$) were 0.007 and 0.013 (Figure 24A). No further degradation was observed over 24 hours.

*Trichloroethene degradation with PAC/NZVI composites:* The degradation of TCE with various NZVI concentrations in PAC/NZVI composites offered key insight into the effect of NZVI loading on TCE adsorption and degradation behavior (Figure 25). PAC/NZVI composite with 0.2 g/L NZVI and 0.2 g/L PAC showed excellent removal of TCE by adsorption (TCE remaining, $m/m_0$, ~0.02; Figure 25A) within 15 min. Very high initial removal kinetics was observed in the first hour of the experiment ($k_{obs1} = 1.55$ hour$^{-1}$), which declined considerably in the second hour ($k_{obs2} = 0.41$ hour$^{-1}$). After 2 hours, almost all of the TCE was removed ($m/m_0 = 0.003$). While, ethane and ethene yields ($m/m_0$) in the first 2 hours were ~0.01 (Figure 25A), yet their production continued for 500 hours. In the long-term, ethene and ethane yields ($m/m_0$) after ~500 hours were ~0.08 and 0.03, respectively.

The degradation of TCE with a higher NZVI concentration in PAC/NZVI composite (0.4 g/L NZVI supported on 0.2 g/L PAC) showed (Figure 26) results similar to 0.2 g/L PAC-0.2 g/L NZVI composite described above (Figure 25). Most of the TCE was
removed within 20-30 minutes of the experiment (TCE remaining, $m/m_0$, <0.10, Figure 26A). Faster initial removal kinetics was observed ($k_{\text{obs1}} = 0.62 \text{ hour}^{-1}$, Figure 26C) in the first hour of the experiment that declined 2 folds in the second hour ($k_{\text{obs2}} = 0.32 \text{ hour}^{-1}$). After 2 hours of the experiment, the TCE remaining ($m/m_0$) was <0.001, whereas ethane and ethene yields ($m/m_0$) were ~0.01 each, which did not show much change much in comparison to the experiment with 0.2 g/L NZVI in PAC/NZVI composite (described above). After more than 1000 hours, significant amount of ethane and ethene yields ($m/m_0$) were 0.015 and 0.04 respectively (Figure 26B).

TCE degradation at a higher NZVI concentration in PAC/NZVI composite with 0.6 g/L NZVI supported on 0.2 g/L PAC) showed results similar to composites prepared with lower NZVI concentrations (described above). Almost all the TCE was removed in first 10 minutes (TCE remaining, $m/m_0$, <0.01) Figure 27). The initial ethane and ethene yields after 2 hours ($m/m_0$) were 0.004 and 0.015, respectively. After ~1500 hours, ethane and ethene yields ($m/m_0$) were 0.035 and 0.10 respectively (Figure 27B). Overall, increasing NZVI concentrations on PAC-NZVI composite showed that the variation of initial ethane yields ($m/m_0$) were 0.01, 0.01, 0.003 for 0.2, 0.4 and 0.6 g/L NZVI, respectively. Further, ethene yields ($m/m_0$) were 0.01, 0.01, 0.015 for 0.2, 0.4 and 0.6 g/L NZVI respectively (Figure 25A, 26A and 27A).

**Trichloroethene removal with PAC/Cu-NZVI:** The degradation of TCE was much more effective with PAC/Cu-NZVI (0.2 g/L PAC-0.2 g/L NZVI and 5 wt% Cu), where initial TCE removal in the first 15 minutes was near complete (TCE remaining $m/m_0$ ~0.01; Figure 28). All the TCE was removed within first 2 hours of the experiment. Initial ethane and ethene yields ($m/m_0$) were 0.004 and 0.012, respectively, which was modestly greater
in comparison to their yields with a similar PAC/NZVI composite (0.2 g/L PAC-0.2 g/L NZVI) but without Cu were 0.003 and 0.004, respectively. The long-term ethane and ethene yields at ~1500 hours were 0.09 and 0.24, respectively (Figure 28B). The kinetics of TCE degradation ($k_{\text{obs1}}$) in the first hour was 1.46 hour$^{-1}$, which declined modestly in the second hour to 0.63 hour$^{-1}$; Figure 28C)
Chapter 4

CONCLUSIONS

1. Comparison of unsupported NZVI vs. PAC/NZVI composite: Unsupported NZVI appeared to be much less effective in degrading for 1,1,1-TCA and TCE in comparison to PAC/NZVI composites. The PAC/NZVI composite displayed complete removal of 1,1,1-TCA and TCE by the synergy of adsorption and degradation whereas unsupported NZVI showed partial degradation of 1,1,1-TCA and TCE. PAC/NZVI also displayed favorable byproduct (ethane and ethene) distribution, with no chlorinated intermediates.

2. Effect of PAC and NZVI loading in PAC/NZVI composite: A modest increase in 1,1,1-TCA adsorption was observed with the increase in PAC loading in PAC/NZVI composite. The initial $k_{obs1}$ increased with increasing PAC loading whereas the long-term $k_{obs2}$ decreased a little. A minor decline in ethane yield was observed with increasing PAC loading.

The increase in NZVI loading in PAC/NZVI composite did not show increase in initial or long-term degradation kinetics. The slight decrease in ethane yield was observed with higher NZVI loading. A minor decrease in ethene production was also observed. Based on byproduct yields, 0.2 g/L PAC-0.2 g/L NZVI displayed better
performance, which might indicate an optimum NZVI concentration that can be supported on PAC.

3. Long-term Performance of PAC/NZVI composite: PAC/NZVI showed excellent potential for 1,1,1-TCA removal by adsorption and degradation in the long term. Significant rapid initial removal of 1,1,1-TCA was observed in three consecutive cycles, followed by a somewhat smaller decline in 4th cycle. A significant increase in ethane production observed in the 4th cycle may be attributed to less overall adsorption of 1,1,1-TCA. Ethene production and build up was observed in four consecutive cycles, which may indicate its greater desorption due to gradual reduction in PAC effectiveness as a sorbent. No significant effect of PAC and NZVI loading was observed in the consecutive removal of 1,1,1-TCA. Experiment conducted with varied PAC and NZVI loading displayed similar 1,1,1-TCA removal capacity.

4. Effect of Cu amendment to PAC/NZVI (i.e., comparison of PAC/NZVI and PAC/Cu-NZVI): The initial rapid removal of 1,1,1-TCA due to adsorption by PAC/NZVI composite and PAC/Cu-NZVI composite was comparable for same PAC and NZVI concentrations. In other words, the initial removal of 1,1,1-TCA within 30 minutes of the experiment with PAC/NZVI and PAC/Cu-NZVI composites were comparable. However, a complete degradation of 1,1,1-TCA was achieved by PAC/Cu-NZVI within 7 hours, whereas it took ~500 hours to achieve similar 1,1,1-TCA removal with PAC/NZVI. Although the degradation of 1,1,1-TCA by PAC/Cu-NZVI was complete in 7 hours, the production of ethane and ethene continued for 600 hours suggesting slow desorption. Further, the total byproducts yields were significantly higher with PAC/Cu-NZVI ($m/m_0 = 0.33$) in comparison to PAC/NZVI ($m/m_0 = 0.14$).
5. The effect of Cu loading in PAC/Cu-NZVI: The short and long-term 1,1,1-TCA degradation kinetics increased at higher NZVI concentration in PAC/Cu-NZVI composite. The increase in Cu loading from 2.5 to 5 wt% in the PAC/Cu-NZVI composite, however, did not exhibit any significant change in the amount of initial removal by adsorption, short and long-term degradation, or byproduct yields.

6. Comparison of Unsupported NZVI and PAC/NZVI composite in TCE degradation: Unsupported NZVI displayed very limited degradation capacity in degrading TCE with very small amount of byproduct generation. Cu/NZVI displayed the similar result with partial removal of TCE. On the other hand, PAC/NZVI composite displayed significant adsorption and degradation capacity towards TCE. Most of the TCE was removed within half an hour. Ethene was major degradation byproduct and ethane was a minor byproduct. Although the TCE was removed from within half an hour the byproduct generation continued for more than ~1,000 hours. The increase in NZVI concentration exhibited an initial increase in ethane production although the long-term byproduct generation did not change significantly due to increased NZVI loading. Cu amendment to the PAC/NZVI composite displayed a significant increase in the initial byproducts yields, which continued for about 1,500 hours. The byproduct yields were significantly higher than the byproduct yields for PAC/NZVI composite.

7. Comparison of PAC/Cu-NZVI and unsupported Cu-NZVI performance shows that a considerable amount of 1,1-DCE formed with Cu/NZVI whereas no harmful byproducts were observed with PAC/Cu-NZVI. Further, the total byproduct yield of 1,1,1-TCA degradation by PAC/Cu-NZVI composite is also higher ($m/m_0 = 0.33$) than that by unsupported Cu/NZVI ($m/m_0 = 0.27$).
8. Comparison of NZVI-PAC mixture with PAC/NZVI composite: Further, NZVI-PAC mixtures also performed better than unsupported NZVI in terms of complete removal of 1,1,1-TCA and a favorable byproduct distribution (ethane and ethene). However, in comparison with NZVI-PAC mixture, PAC/NZVI composites displayed better performance in terms of mole fraction recovery of ethane and but not ethene. Yet, no significant difference was observed between PAC/NZVI composite and NZVI-PAC mixture in their adsorption behaviors, and both showed a slight decline in the short and long term removal kinetics in consecutive cycles. Significant reduction in ethane production was observed with NZVI-PAC mixture whereas ethene production remained similar.
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Figure 2: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI prepared with 4 g/L CMC at pH 7. Initial 1,1,1-TCA ~0.62 µmoles (~200 µL of 419 mg/L stock solution). (B) 1,1,1-TCA degradation constants $k_{obs1}$ and $k_{obs2}$. (C) Long-term 1,1,1-TCA degradation over 3 weeks.
Figure 3: (A) 1,1,1-TCA degradation and byproduct distribution with 0.2 g/L NZVI prepared with 4 g/L CMC at pH 7 with 5wt% Cu. (B) 1,1,1-TCA degradation constant $k_{obs1}$ and $k_{obs2}$ with Cu/NZVI. Initial 1,1,1-TCA ~0.62 µmoles
Figure 4: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI supported on 0.2 g/L PAC with at pH 8. Initial 1,1,1-TCA ~0.62 µmoles. (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 5: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI supported on 0.1 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 μmoles. (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 6: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI supported on 0.4 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 μmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 7: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI supported on 0.6 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles. (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 8: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI supported on 0.8 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles. (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 9: (A) 1,1,1-TCA degradation and product distribution with 0.4 g/L NZVI supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 μmoles. (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 10: (A) 1,1,1-TCA degradation and product distribution with 0.6 g/L NZVI supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles. (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 11: (A) Sustained degradation of 1,1,1-TCA and ethane production for four consecutive cycles, with 0.2 g/L NZVI supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) Long-term 1,1,1-TCA degradation constant, $k_{obs2}$. (C) Long-term ethene production.
Figure 12: (A) Sustained degradation of 1,1,1-TCA and ethane production for three consecutive cycles, with 0.2 g/L NZVI supported on 0.4 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 μmoles (B) Long-term 1,1,1-TCA degradation constant, $k_{\text{obs,2}}$. (C) Long-term cumulative ethene production.
Figure 13: (A) Sustained degradation of 1,1,1-TCA and ethane production for three consecutive cycles, with 0.2 g/L NZVI supported on 0.6 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) Long-term 1,1,1-TCA degradation constant, k_{obs2}. (C) Long-term cumulative ethene production.
Figure 14: (A) Sustained degradation of 1,1,1-TCA and ethane production for three consecutive cycles, with 0.2 g/L NZVI supported on 0.8 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) Long-term 1,1,1-TCA degradation constant, $k_{obs2}$. (C) Long-term cumulative ethene production.
Figure 15: (A) Sustained degradation of 1,1,1-TCA and ethane production for three consecutive cycles, with 0.4 g/L NZVI supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) Long-term 1,1,1-TCA degradation constant, $k_{obs2}$. (C) Long-term cumulative ethene production.
Figure 16: (A) Sustained degradation of 1,1,1-TCA and ethane production for two consecutive cycles, with 0.6 g/L NZVI supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) Long-term 1,1,1-TCA degradation constant, \( k_{\text{obs}} \). (C) Long-term ethene production.
Figure 17: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI and 5 wt% Cu supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 μmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 18: (A) 1,1,1-TCA degradation and product distribution with 0.4 g/L NZVI and 5 wt% Cu supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 19: (A) 1,1,1-TCA degradation and product distribution with 0.4 g/L NZVI and 2.5 wt% Cu supported on 0.2 g/L PAC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 20: (A) 1,1,1-TCA degradation and product distribution with 0.2 g/L NZVI mixed with 0.2 g/L PAC with 4 g/L CMC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 21: (A) 1,1,1-TCA degradation and product distribution with 0.4 g/L NZVI mixed with 0.2 g/L PAC with 4 g/L CMC at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) 1,1,1-TCA degradation, respectively.
Figure 22: (A) 1,1,1-TCA degradation and product distribution with 0.6 g/L NZVI mixed with 0.2 g/L PAC with 4 g/L CMC at pH 8. Initial 1,1,1-TCA ~0.62 μmoles (B) and (C) show pseudo first-order rate constants for short-term \((k_{obs1})\) and long term \((k_{obs2})\) 1,1,1-TCA degradation, respectively.
Figure 23: (A) Degradation of TCE and byproducts distribution with 0.2 g/L unsupported NZVI with 4 g/L CMC at pH 7. Initial TCE ∼0.38 µmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) TCE degradation, respectively.
Figure 24: (A) Degradation of TCE and byproducts distribution with 0.2 g/L unsupported NZVI and 5 wt% Cu with 4 g/L CMC at pH 7. Initial TCE ~0.38 μmoles (B) and (C) show pseudo first-order rate constants for short-term ($k_{obs1}$) and long term ($k_{obs2}$) TCE degradation, respectively
Figure 25: (A) TCE degradation and product distribution with PAC/NZVI composite (0.2 g/L NZVI and 0.2 g/L PAC) at pH 8. Initial TCE ~0.38 μmoles. (B) and (C) show reaction byproduct yields TCE degradation rate constants ($k_{obs1}$ and $k_{obs2}$), respectively.
Figure 26: (A) TCE degradation and product distribution with 0.2 g/L PAC and 0.4 g/L NZVI at pH 8. Initial TCE ~0.38 µmoles (B) and (C) show reaction byproducts generation. TCE degradation rate constants ($k_{obs1}$ and $k_{obs2}$), respectively.
Figure 27: (A) TCE degradation and byproduct distribution with 0.2 g/L PAC and 0.6 g/L NZVI at pH 8. Initial TCE ~0.38 μmoles. (B) and (C) show reaction byproducts generation and TCE degradation rate constants ($k_{obs1}$ and $k_{obs2}$), respectively.
Figure 28: (A) TCE degradation and product distribution with 0.2 g/L NZVI and 5 wt% copper supported on 0.2 g/L PAC at pH 8. Initial TCE ~0.38 μmoles. (B) and (C) show byproduct generation and short term TCE degradation kinetics, respectively.
Figure 29: (A) Comparison of 1,1,1-TCA adsorption by with 0.2 g/L PAC at pH 7 and 8 (B) 1,1,1-TCA degradation with 10.47 mM NaBH₄ alone at pH 8. Initial 1,1,1-TCA ~0.62 µmoles (C) 1,1,1-TCA loss by adsorption to 0.2 g/L PAC at pH 8 in 4 consecutive cycles.
Table 1: Degradation of 1,1,1-TCA with (A) unsupported NZVI and Cu-NZVI prepared with 4 g/L CMC, (B) PAC/NZVI composites prepared with variable PAC and (C) PAC/NZVI composites prepared with variable NZVI concentrations. Other conditions include pH 8 and initial TCA ~0.62 μM.

<table>
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<tr>
<th>NZVI (g/L)</th>
<th>PAC (g/L)</th>
<th>1,1,1-TCA remaining (m/m₀)</th>
<th>Byproducts yields (m/m₀)</th>
<th>k_{obs1}</th>
<th>k_{obs2}</th>
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</thead>
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<td></td>
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<td>1,1,1-TCA</td>
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<td>1,1-DCE</td>
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<tr>
<td></td>
<td></td>
<td>remaining (m/m₀)</td>
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<td>(A) With unsupported NZVI and Cu-NZVI (figures 2-3)</td>
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<td>(C) With variable NZVI concentrations (figures 2 and 9-10)</td>
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Table 2: Long-term performance of PAC/NZVI composites with multiple cycles of 1,1,1-TCA reinjection. Effects of: (A) PAC concentration and (B) NZVI concentrations in PAC/NZVI composite. Conditions include pH 8 and initial TCA \(\sim 0.62 \, \mu\text{M}\).

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<th>NZVI (g/L)</th>
<th>PAC (g/L)</th>
<th>Cycle Id</th>
<th>1,1,1-TCA remaining (m/m₀)</th>
<th>Ethane yields (m/m₀)</th>
<th>(k_{\text{obs2}})</th>
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<td>(B) Effect of NZVI concentrations in PAC/NZVI composite on ethane yields and reaction kinetics (figures 15-16)</td>
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Table 3: Degradation of 1,1,1-TCA with (A) PAC/Cu-NZVI composites with variable NZVI and Cu concentrations. Other conditions include pH 8 and initial TCA ~0.62 µM.

(A) PAC/Cu-NZVI composites with variable NZVI and Cu loadings (figures 17-19).

<table>
<thead>
<tr>
<th>NZVI (g/L)</th>
<th>PAC (g/L)</th>
<th>Cu (%wt)</th>
<th>1,1,1-TCA remaining (m/m₀)</th>
<th>Byproducts yields (m/m₀)</th>
<th>k&lt;sub&gt;obs1&lt;/sub&gt;</th>
<th>k&lt;sub&gt;obs2&lt;/sub&gt;</th>
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<tbody>
<tr>
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<td>Ethane</td>
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(B) NZVI-PAC mixture with variable NZVI loadings (figures 20-22).

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<th>NZVI (g/L)</th>
<th>PAC (g/L)</th>
<th>Cu (%wt)</th>
<th>1,1,1-TCA remaining (m/m₀)</th>
<th>Byproducts yields (m/m₀)</th>
<th>k&lt;sub&gt;obs1&lt;/sub&gt;</th>
<th>k&lt;sub&gt;obs2&lt;/sub&gt;</th>
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Table 4: Degradation of TCE degradation with: (A) unsupported NZVI and Cu-NZVI (5 wt% Cu) (B) PAC/NZVI composites with variable NZVI concentrations, and (C) PAC/Cu-NZVI composite (5 wt% Cu). Other conditions include pH 8 and initial TCE ~0.38 µM (see figures 23-28)

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<th>NZVI (g/L)</th>
<th>Cu (wt%)</th>
<th>TCE remaining (m/m₀)</th>
<th>Byproducts yields (m/m₀)</th>
<th>kₚₙ₁</th>
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<td>(A) UnsUPPORTED NZVI and Cu-NZVI with 5 wt% Cu (figures 23-24)</td>
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<td>(B) PAC/NZVI composites with variable NZVI concentrations (figures 25-27)</td>
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<td>PAC (g/L)</td>
<td>TCE remaining (m/m₀)</td>
<td>Byproducts yields (m/m₀)</td>
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<td>kₚₙ₂</td>
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<td>(C) PAC/Cu-NZVI composite with 5 wt% Cu (figure 28)</td>
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