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DEGRADATION OF 1,2-DICHLOROETHANE WITH NANO-SCALE ZERO VALENT IRON PARTICLES

(Spine Title: Degradation of 1,2-DCA with nZVI Particles)

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A thesis submitted in partial fulfilment of the requirements for the degree of

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THE UNIVERSITY OF WESTERN ONTARIO
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ABSTRACT

The application of nanoscale zero-valent iron particles (nZVI) for abiotic remediation of chlorinated compounds is proving among the most viable technologies for environmental remediation. However, although most polychlorinated C2 compounds are easily dechlorinated by nZVI, 1,2-dichloroethane (1,2-DCA), has shown resistance to dechlorination by this nanomaterial. The present contribution shows how a combination of a catalyst and nZVI together with the addition of a hydrogen donor can be used to achieve dechlorination of 1,2-DCA under aqueous conditions similar to those found in the field. The best results for dechlorination were observed using formic acid as a H_2 donor and Pd as catalyst doped onto CMC stabilized nanoscale zero-valent iron particles at a temperature of 45°C. This leads to significant degradation (close to 18%) of 1,2-DCA at the end of seven days. As degradation products, evolution of ethane and propane were observed from the very first day of reaction.

Keywords: nZVI, nano-scale zero valent iron, hydrogen donor, catalyst, 1,2-DCA.

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1,1-DCA	: 1,1-dichloroethane
1,1-DCE	: 1,1-dichloroethylene
1,2-DCA	: 1,2-dichloroethane
Ag	: Silver
cis-DCE	: cis-dichloroethylene
CMC	: Carboxymethyl Cellulose
COCs	: Chlorinated Organic Compounds
DI	: De-ionized Water
E_0	: Standard Reduction Potential
HCA	: Hexachloroethane
HCOOH	: Formic Acid
IPA	: Isopropanol
Ni	: Nickel
NZVI	: Nano-scale Zero Valent Iron
PAA	: Poly Acrylic Acids
PCA	: Pentachloroethane
PCBs	: Polychlorinated biphenyls
PCE	: Tetrachloroethylene
Pd	: Palladium

PRBs	: Permeable Reactive Barriers
Pt	: Platinum
PVP	: Polyvinylpyrrolidone
RDX	: Hexahydro-1,3,5-trinitro-1,3,5-triazine
Rh	: Rhodium
Ru	: Ruthenium
SDBS	: Sodium Dodecylbenzene Sulfonate
TCE	: Trichloroethylene
TNT	: 2,4,6-trinitrotoluene
trans-DCE	: trans-dichloroethylene
VC	: Vinyl Chloride
ZVI	: Zero Valent Iron

1.0 INTRODUCTION

1.1 BACKGROUND

Groundwater contamination problems caused by halogenated organic compounds, heavy metals and energetic materials such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) are increasing in Canada. This is mainly due to the large number of toxic compounds utilized in agriculture and industry (Zhang et al, 1998; Environment Canada, Groundwater). Among these, chlorinated ethylenes such as tetrachloroethylene (PCE), trichloroethylene (TCE), trans-dichloroethylene (t-DCE), cis-dichloroethylene (c-DCE), 1,1-dichloroethylene (1,1-DCE), vinyl chloride (VC) as well as chlorinated ethanes such as hexachloroethane (HCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,1-dichloroethane (1,1-DCA) and 1,2-dichloroethane (1,2-DCA) are the most prevalent contaminants in soils and aquifers and have been listed as priority pollutants by both the US Environmental Protection Agency and the Superfund National Priority List (Zhang et al, 1998; Song and Carraway, 2005; Lien and Zhang, 2005). These chemicals are used in dry cleaning, wood preservation, pesticide manufacturing, metal cleaning, and paint removal. Accumulation of these chlorinated solvents in the sub-surface results from leaking underground or above-ground storage tanks, storage areas or buried chemical distribution pipelines, spillage at chemical loading and off-loading facilities or even from intentional disposal into the sub-surface. Once these solvents are spilled in aquifers in sufficient quantities, they have the capacity to penetrate below the water table and thus serve as a long-term source of contamination. The length of time required to dissolve a solvent source zone can be hundreds of years under natural conditions. When groundwater is used as a source of drinking water, the presence of these compounds becomes a serious risk to human health. These risks include liver or kidney damage and spontaneous abortions; moreover, some of these compounds are considered carcinogenic. Therefore, a great deal of time and effort has been put into the development of remediation techniques to treat contaminated sites (Geiger et al, 2009).

Depending on the type and location of the contaminants, both in-situ and ex-situ remediation options are being used for their removal from soil and groundwater. Electroreclamation, enhanced volatilization, vitrification, bioventing, biostimulation and natural attenuation are some of the commonly used in-situ treatment technologies, whereas, chemical extraction, dehalogenation, redox reactions, incineration and pyrolysis can be classified as ex-situ treatment technologies (Lodolo, 2007). However, the application of some of these techniques is hampered due to specific drawbacks associated with their implementation such as- high costs, incomplete decontamination resulting in formation of more toxic intermediates, slow outputs and complex process control (Lodolo, 2007).

One of the most promising technologies for the remediation of subsurface contamination involves the use of zero-valent metallic materials (Zhang et al, 1998; Wang et al, 2008; Sakulchaichareon et al, 2010), specifically zero-valent iron. In this case, groundwater flows through an iron rich reactive zone, resulting in chemical transformations of the contaminants into benign compounds (Wang and Zhang, 1997; Zhang et al, 1998; Schrick et al, 2002). Equation 1.1 can be used to express the reactions between chlorinated organic compounds and iron in aqueous solution. Here, iron acts as an electron donor (reductant) to remove chlorine.

$$C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zFe^{2+} + zCl^- \qquad \text{(Equation 1.1)}$$

Despite the promising use of iron fillings in permeable reactive barriers (PBRs), there still exist some challenges. For instance, the lower reactivity of zero-valent iron powder with lightly chlorinated compounds may produce and accumulate by-products such as, 1,2-dichloroethylene and vinyl chloride which are of even more toxicological concern than their parent compounds (Zhang et al, 1998; Wang et al, 2008). To address the above-mentioned shortcomings researchers have proposed nanoscale zerovalent iron (nZVI) as an alternative. (Zhang et al, 1998; Schrick et al, 2004, Li et al, 2006). Indeed, the use of nZVI for the treatment of sub-surface chlorinated hydrocarbons is of significant interest due to its low toxicity and significant contaminant degradation capabilities (Zhang et al, 1998; Schrick et al, 2004; He and Zhao, 2005; Sakulchaicharoen et al, 2010)

The very small dimension, high surface area to volume ratio, high surface energy as well as high surface reactivity is the reason behind the high reactivity of nZVI particles with environmental contaminants (Zhang et al, 1998; Zhang, 2003). As opposed to PBR technologies, instead of installing metal walls, nanoparticles, in the form of water slurry, can be injected into the contaminated plume requiring treatment by means of pressure or gravity or both. Their nanoscale size makes it possible to transport them to a certain extent by groundwater flow (Zhang, 2003; Li et al, 2006). Furthermore, the addition of promoters in the form of catalytic metals such as palladium (Pd), platinum (Pt), silver (Ag) or nickel (Ni) can lead to accelerated dechlorination rates and therefore, lead to the formation of benign hydrocarbons (Lien and Zhang, 2001; He and Zhao, 2005) rather than undesirable chlorinated byproducts. Nevertheless, these doped Fe nanoparticles tend to react rapidly with dissolved oxygen or even water, due to their extremely high reactivity, leading to quick loss in reactivity (He and Zhao, 2005). Another consideration is magnetic and van der Waals attractive forces between nZVI particles which cause agglomeration and the formation of larger particles or flocs (Sakulchaicharoen et al, 2010; He and Zhao, 2007). This agglomeration decreases available nZVI surface area for reaction (Sakulchaicharoen et al, 2010; He and Zhao, 2007). To prevent agglomeration, stabilizers such as Carboxymethyl Cellulose (CMC), polyvinylpyrrolidone (PVP) and guar gum can be added with iron nanoparticles. The addition of these stabilizers enhances dispersion of particles through electrostatic repulsion and/or steric hindrance (Sakulchaicharoen et al, 2010). Particle size reduction and the resulting gain in surface area leads to more reactive nanoparticles for the degradation of chlorinated solvents.

Despite the successful application of nZVI particles for remediation of chlorinated hydrocarbons, nitroaromatics and polychlorinated biphenyls, 1,2-dichloroethane (1,2-DCA) is found so far to be totally resistant to degradation using nZVI (Zhang et al, 1998; Song and Carraway, 2005; De Wildeman and Verstraete, 2003; Kopinke et al, 2004). 1,2-DCA is a chlorinated hydrocarbon that affects human liver and kidneys, neurological, cardiovascular, and immune systems (De Wildeman and Verstraete, 2003). Metal-based reduction has been found to be marginally successful in 1,2 DCA chemical dechlorination whereas catalytic hydrodechlorination and bioremediation are reported to be successful. However, the high temperature and molecular H_2 requirements make catalytic hydrodechlorination inconvenient for field application, whereas the very slow anaerobic bioremediation process is unsuited for the rapid dechlorination rate usually required in field applications (Ukisu et al, 1998; Klecka et al, 1998). An alternative and effective approach for successful dechlorination of 1,2-DCA at field scale is therefore required. Though to date iron has been unsuccessful in dechlorinating 1,2 DCA (Larson and Weber; De Wildeman and Verstraete, 2003), the process is thermodynamically possible. This makes the remediation of 1,2-DCA by nZVI particles through the application of an appropriate methodology of huge interest.

1.2 RESEARCH OBJECTIVES

The goal of this research work is to find a nZVI-based formulation able to degrade 1,2-dichloroethane (1,2-DCA) and to optimize degradation conditions. As presented in the following chapters 1,2-DCA dechlorination is a significant challenge for nZVI based remediation technologies. Optimization of the experimental conditions and investigation of the degradation pathways are the two other main objectives of this work.

1.3 THESIS OUTLINE

This thesis is written in "Integrated Article Format". A brief description of each chapter is presented below.

Chapter 1 introduces some general background information and states the objectives of the study.

Chapter 2 reviews previous research work focused on the degradation of 1,2-DCA. In addition, nanoparticle structure, synthesis and application for remediation of chlorinated organic compounds are also discussed.

Chapter 3 presents the experimental methodology as well as the results and discussion of the experiments carried on this research work.

Chapter 4 summarizes the research conducted in this study, and presents conclusions and recommendations for future work.

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CHAPTER 2

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

Chlorinated Organic Compounds (COCs) have caused widespread environmental contamination in both groundwater and soil since they are persistent in the environment over relatively long time periods and are difficult to directly degrade under most natural or abiotic conditions. Consequently, the environmental engineering community has devoted significant efforts to the degradation of these chlorinated organic compounds. Both in-situ and ex-situ approaches comprising of thermal, biological, physical and chemical treatments are commonly used to remove these contaminants (Wang et al, 2008).

Thermal treatments utilize high temperature to volatilize, burn and degrade contaminants. Specifically, in-situ thermal treatments such as soil vapour extraction, vitrification and ex-situ thermal treatments like incineration and pyrolysis have been used for remediation purposes. Nevertheless, incomplete combustion giving rise to dioxins and furans and high cost and fugitive emissions such as dust and particulates often make their application less attractive (Lodolo, 2007). Biological treatment requires optimal conditions and selective microorganisms to decompose COCs by metabolic processes (Wang et al, 2008). Bioventing, biostimulation, natural attenuation are some of the proposed in-situ biological treatments, whereas, contaminants are treated ex-situ in bioreactors (Lodolo, 2007). However, this is a relatively slow procedure and COCs often inhibit degradation through their toxic effects (Wang et al, 2008). Physio-chemical treatments are a combination of physical and chemical treatments. Here phase transfer of the pollutants is induced and chemical structure is altered by chemical reactions to produce less toxic compounds (Lodolo, 2007; Wang et al, 2009). Electroreclamation and enhanced volatilization are two examples of in-situ physio-chemical treatments. Although these technologies have been widely used for volatile organic compound degradation, heterogeneities in the treated zone and high concentration of contaminants heavily influence their activity (Lodolo, 2007). On the other hand, chemical extraction, dehalogenation and redox reactions have been proposed as ex-situ treatments. Chemical extraction is less effective for high molecular weight compounds and incomplete decontamination may form more toxic compounds (Lodolo, 2007). Therefore, a more convenient technology is required that can be used to remediate the contaminant in-situ with the maximum benefits.

Recently, the degradation of COCs by direct reduction using zero-valent iron (ZVI) technology has received great interest (Zhang et al, 1998; Wang et al 2008; Sakulchaichareon et al, 2010). Microscale zero-valent iron, usually applied in permeable reactive barriers (PRBs), reacts with contaminants like chlorinated aliphatics, aromatics and polychlorinated biphenyls to produce mostly benign compounds: hydrocarbons, chloride and water (Zhang et al, 1998; Schrick et al, 2002). However, the implementation of zero-valent metal technology in the sub-surface still faces various challenges, such as the low reactivity of iron particles towards less chlorinated hydrocarbons, in turn leading to the production of chlorinated by-products, which are sometimes even more toxic than the parent compounds. Moreover, the time required to complete the dechlorination is often very long (Wang et al, 2008). Furthermore, the construction of walls in aquifers at depths more than 30m poses engineering difficulties.

Current research indicates that nano-scale zero-valent iron (nZVI) can be a very good alternative to PRBs (Wang and Zhang, 1997; Zhang et al, 1998; Nurmi et al, 2005). Their very tiny dimensions allow them to be injected in the form of water slurry into the contaminated plume requiring treatment. The injection is done through pressure, gravity, or both. The nZVI-water slurry reacts more rapidly to dechlorinate organic contaminants in the sub-surface than the larger ZVI particles (Li et al, 2006). The ability to deliver nanoparticles directly to the contaminated zone in the sub-surface, even in areas where many conventional methods are inaccessible (such as beneath buildings and airport runways) make nZVI a very attractive remediation technology (Elliot and Zhang, 2001).

2.2 NANOSCALE ZERO-VALENT IRON TECHNOLOGY

The structure of iron nanoparticles is important for their environmental remediation function. These nanoparticles are generally spherical in shape, colloidal in nature and have a strong tendency to aggregate (Li et al, 2006) (Fig 2.1). The very small dimensions (~1-100 nm), relatively high specific surface area (~30 m^2/g) and greater density of reactive sites are responsible for the high intrinsic reactivity of nZVI particles (Zhang et al, 1998; Elliot and Zhang, 2001; Nurmi et al, 2005). Under aqueous conditions, iron nanoparticles contain a Fe^0 core, which is a moderate reducing agent and is slowly oxidized in air or water (equations 2.1, 2.2) (Li et al, 2006). This core is surrounded by a shell of iron oxides, hydroxides or oxyhydroxides (Eqns 2.3, 2.4, 2.5) (Fig 2.1) with a shell thickness approximately 5 nm (Liu et al, 2005a). It has been reported that oxidation of the Fe^0 core causes transportation of electrons through the iron oxide shell that in turn reduces organic contaminants (Yan et al, 2010). The mixed valence iron oxide shell protects the Fe^0 core from further oxidation (Li et al, 2006).

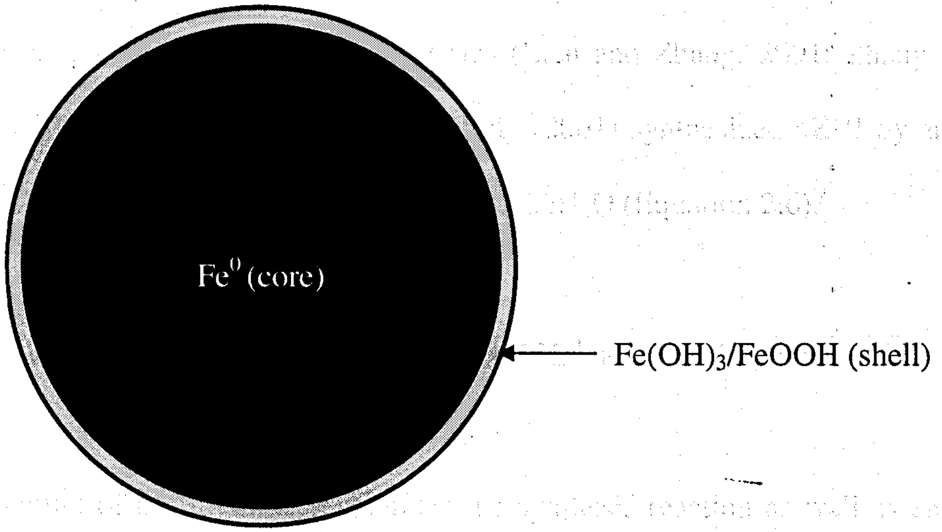


Fig 2.1- Core-Shell Structure of nZVI

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad \text{(Equation 2.1)}$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \qquad \text{(Equation 2.2)}$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \qquad \text{(Equation 2.3)}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad \text{(Equation 2.4)}$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \qquad \text{(Equation 2.5)}$$

2.2.1 Synthesis of Iron Nanoparticles

Borohydride reduction of an aqueous iron salt is the most commonly used method to produce nZVI in research labs (Li et al, 2006; Zhang and Elliot, 2006). This is a very simple method, which can be carried out in aqueous phase at room temperature without the need for highly specialized instruments. Moreover, this method requires only two common reagents, i.e. iron precursor and sodium borohydride ($NaBH_4$). Many studies have utilized aqueous solutions of ferric chloride ($FeCl_3.6H_2O$) and ferrous sulphate ($FeSO_4.7H_2O$) as precursors to iron nanoparticles (Lien and Zhang, 2001; Zhang et al, 2003; Li et al, 2006). For instance, Lien and Zhang (2001) synthesized nZVI by adding 1:1 volume ratio of 0.25M $NaBH_4$ into 0.045M $FeCl_3.6H_2O$ (Equation 2.6).

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2 \quad \text{(Equation 2.6)}$$

The excess amount of borohydride accelerates the synthesis reaction as well as ensures uniform growth of nanoiron (Zhang et al, 2003). Although ferric chloride hexahydrate is often used as the iron precursor, ferrous sulphate has been proposed as an alternative due to the potential health and safety concerns associated with handling the highly hygroscopic and acidic ferric chloride salt. Zhang and Elliot (2006) prepared nZVI from 0.28M $FeSO_4.7H_2O$ by reducing it with 0.5M of $NaBH_4$ solution (equation 2.7)

$$2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 + H_2BO_3^- + 4H^+ + 2H_2 \quad \text{(Equation 2.7)}$$

Less borohydride is required to reduce ferrous sulphate (stoichiometric excess of 3.6) than the ferric chloride (stoichiometric excess of 7.4) (Zhang and Elliot 2006; He and Zhao, 2007). Moreover, the use of sulphate allows for an easier monitoring of chloride production during dechlorination reactions of chlorinated organic compound (Zhang and Elliot 2006, He et al, 2007).

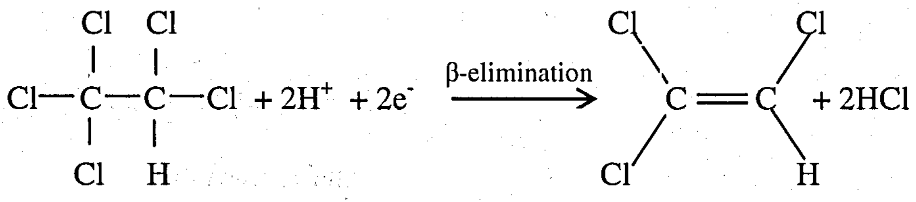
2.2.2 Reactivity of Nano Iron with Chlorinated Compounds

The contaminants that can be treated with nZVI particles include chlorinated ethylenes, methanes, ethanes, nitroaromatics, polychlorinated biphenyls, chlorophenols, heavy metals and inorganic anions (Zhang et al, 1998; Liu et al, 2005a; Liu et al, 2005b; Song and Carraway, 2008). The dechlorination of halogenated compounds by nZVI involves several steps: mass transport of the contaminant from the solution to the surface of nanoparticles, the adsorption of the contaminant to the reactive surface of nanoparticles, reactions at the surface, desorption of products from the surface and finally mass transport of products to the solution (Matheson and Tratnyek, 1994; Lien and Zhang, 2007). The slowest reaction step requires the highest activation energy and controls the kinetics of a reaction (Lien and Zhang, 2007).

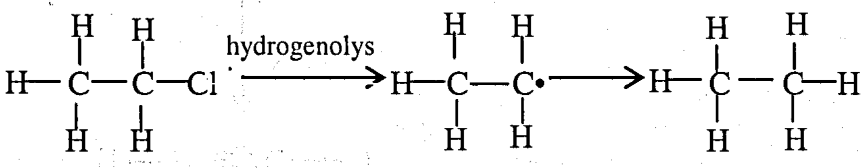
When Fe^0 is oxidized to Fe^{2+} (equation 2.8), it donates two electrons and these can be used in a variety of reactions to transform contaminants. The addition of two electrons from the reduction of nZVI to a chlorinated ethylene may result in the release of chloride ion with the concurrent formation of a new C-H bond (equation 2.9) (Bylaska et al, 2008). These reactions can follow two different pathways: β-elimination (equation 2.10) and hydrogenolysis (equation 2.11). It has been proposed, based on mechanistic studies, that the electron transfer to the surface adsorbed molecule is the rate-limiting step (Schrick et al, 2002; Bylaska et al, 2008).

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$ (Equation 2.8)

$$C_2H_XCl_{4-X} + 2e^- + H^+ \rightarrow C_2H_{X+1}Cl_{3-X} + Cl^-$$ (Equation 2.9)



(Equation 2.10)



$$H_3C{-}CH_2{-}Cl \xrightarrow{\text{hydrogenolys}} H_3C{-}CH_2{\bullet} \longrightarrow H_3C{-}CH_3$$

(Equation 2.11)

Fig 2.2 shows the possible reaction pathways for trichloroethylene (TCE) dechlorination by Fe^0.

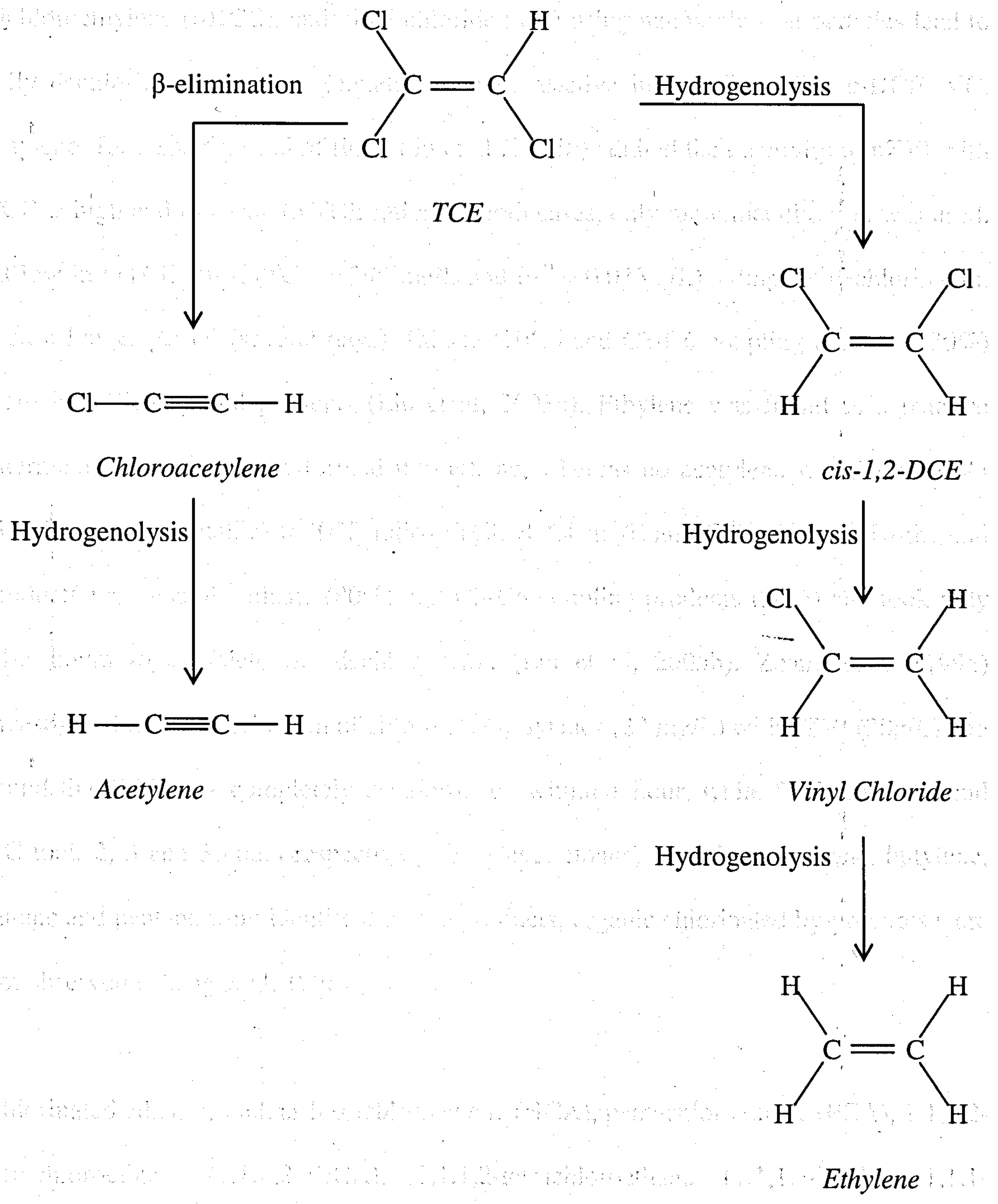


Fig: 2.2 Pathways of TCE dechlorination with Fe^0

Laboratory research has showed that the transformation of chlorinated ethylenes, such as-tetrachloroethylene (PCE), trichloroethylene (TCE), cis- dichloroethylene (c-DCE), trans-dichloroethylene (t-DCE), and vinyl chloride (VC) using nanoscale iron particles lead to fully dechlorinated products (e.g.ethane) with reactive intermediates like c-DCE, VC, ethylene for a short period of time. Liu et al (2005b) studied the reactivity of nZVI with TCE at high and low iron to TCE ratios. In both cases, only monometallic iron was used. At low iron/TCE ratios (TCE = 290 mg/L and Fe^0 = 0.035 g/L), complete dechlorination took a longer period (several days). Ethane (70%) and C3-C6 coupling products (30%) were identified as end products (Liu et al, 2005b). Ethylene was found as a reactive intermediate that later transformed into ethane, whereas no acetylene was detected. At high iron (monometallic) to TCE ratios (TCE = 4.4 mg/L and Fe^0 = 0.194 g/L) the end products were mainly ethane (80%) and C3-C6 coupling products (20%) and took only ~1.5 hours to complete the dechlorination (Liu et al, 2005b). Zhang et al (1998) investigated the dechlorination of chlorinated ethylenes (20 mg/L) with nZVI (20g/L) and found that TCE was completely dechlorinated within 1 hour, while PCE, cis-DCE and VC took 2, 3 and 3 hours respectively. Ethylene, ethane, propylene, propane, butylene, butane and pentane were identified as end products; organic chlorinated by-products were not observed (Zhang et al, 1998).

Chlorinated ethanes, such as hexachloroethane (HCA), pentachloroethane (PCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) 1,1,1-trichloroethane (1,1,1-TCA) and 1,1-dichloroethane (1,1-DCA) along with chlorinated ethylenes are another major group of groundwater contaminants with low reduction potentials (~ -0.68 to + 0.15 V) (Song and Carraway, 2005). Their structural stability makes them persistent in the environment. The reactions of chlorinated ethanes with nZVI particles form many chlorinated by-products and generally the reactivity rate is slower than those of chlorinated ethylenes (Lien and Zhang, 2005). The degree of chlorination of the chlorinated ethane controls their reactivity with nZVI particles (Lien and Zhang, 2005). When there are more than four chlorine atoms the reaction rates are high whereas, lesser chlorinated ethanes with chlorine number less than two show little reactivity (Lien and Zhang, 2005). Reactions of chlorinated ethanes with conventional iron powders produce mainly chlorinated by-products and no ethane (Lien and Zhang, 2001). According to Song and Carraway (2005), HCA was one of the most reactive chlorinated ethanes and when it reacted with 0.08g/L nZVI, it formed PCE at the end of 1.4 hours. Song and Carraway (2005) also showed that 1,1,1,2-TeCA transformed into 1,1-DCE and then ethane after an 80 hours reaction with 0.08 g/L of nanoiron. In case of 1,1,2-TCA the same amount of nZVI resulted in a much slower rate but also formed ethane at the end of 110 hours (Song and Carraway, 2005).

During Fe^0 corrosion in aqueous system, H_2 is generated through water reduction (equation 2.1). The dissociative chemisorption of this H_2 generates a new activated reductant, atomic hydrogen, on the nanoparticle surface in the presence of a catalyst, which is responsible for bimetallic reactivity (Schrick et al, 2002). In a bimetallic nZVI system, Fe^0 acts as the electron donor and the catalyst functions as hydrogen dissociator (Song and Carraway, 2008). This hydrogen initiates rapid dehalogenation of the contaminant forming benign hydrocarbons and inorganic chlorides (Fig 2.3). However, in the absence of a catalyst, hydrogen cannot contribute directly to the dechlorination; rather the presence of an excess amount of hydrogen on the metal surface may inhibit the iron corrosion (Matheson and Tratnyek, 1994). The large amount of hydrogen gas produced as minute gas bubbles might perform as barriers inhibiting the contact of iron particles and target pollutants (Wang et al, 2009). Therefore, the catalytic effects of a second metal through a direct hydrogen reduction (Schrick et al, 2002) and a galvanic corrosion leading to the increased corrosion rates (Zhang et al, 1998) are the main reasons behind the enhanced reactivity of bimetallic nZVI particles. The use of catalysts with nZVI reduces the activation energy required for hydrogen dissociation over the catalyst surface (Lien and Zhang, 2007). The lower activation energy for bimetallic nZVI particles indicates the dechlorination reaction to be catalytic, resulting in an increase in the dechlorination rate and decreasing the production of toxic intermediates such as dichloroethylenes and vinyl chloride (Song and Carraway, 2008; Yan et al, 2010).

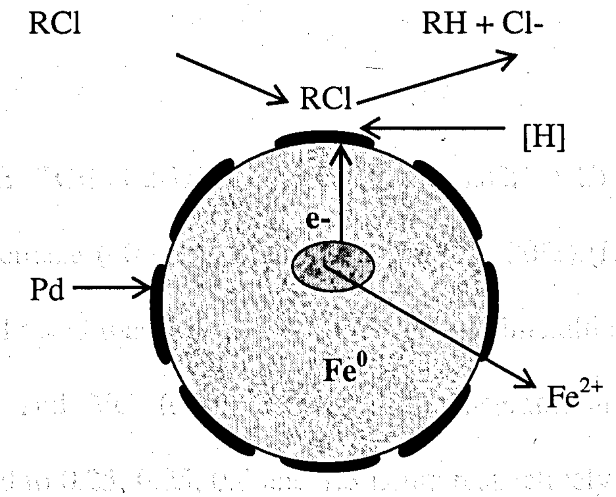


Fig. 2.3 Schematic of reactivity of Pd/Fe nanoparticles with chlorinated solvents
(Ref: Zhang et al,1998)

Noble metals, such as- Pd, Pt, Ru, or Ni have been found to serve as catalyst for dechlorination using nZVI particles (Zhang et al, 1998; Liu et al, 2004). The differences in the surface atomic structure and electronic properties of Pd, Pt, Ru and Ni give them different catalytic properties when used as part of bimetallic nZVI particles (Zhang et al, 1998). Pd/Fe shows the highest activity among bimetallic particle formulations (e.g Pd/Fe, Ru/Fe, Pt/Fe) used for dechlorination of TCE as it has low activation barrier for hydrogen dissociation (2 kcal/mol) on Pd surface (Lien and Zhang, 2007). It has been found that metals such as Pd or Pt have low cathodic hydrogen overpotentials. On the other hand metals like Fe^0 have high hydrogen overpotential (Lien and Zhang, 2007). The much lower cathodic hydrogen overpotential of Pd compared to that of Fe^0 causes easy catalyzation of hydrogen dissociation on Pd surface with a slow activation barrier. (Zhou et al, 2010). In general, activation energies for Pd/Fe bimetallic nanoparticles and bare nZVI particles for dechlorination reactions are 31.1 and 44.9 kJ/mol respectively (Lien and Zhang, 2007).

Chlorinated ethylenes (PCE, TCE, 1,2-DCE, cis- and trans- DCE, VC) are completely reduced by Pd/Fe forming ethane (60 ~ 90%) and ethylene (3 ~ 20%) (Lien and Zhang, 2001). Zhang et al (1998) showed that the reaction times using bimetallic Pd/Fe (20 g/L) for PCE, TCE, cis-DCE and VC (each with initial concentration of 20 mg/L) dechlorination were reduced to 0.25, 0.25, 0.8 and 1.5 hours respectively (i.e., about 100 times faster than that with monometallic nZVI). In the presence of Pd, the reduction of chlorinated ethanes also tends to be more complete leading to ethane formation. With 5g/L of bimetallic Pd/Fe, ethane was detected as the major end product (~87%) when

HCA was the reactant (Lien and Zhang, 2005). On the other hand, 1,1,1-TCA with 5g/L of Pd/Fe formed ethane (~60%) just after 7 hours.

Table 2.1 gives a summary of the studies discussed above regarding the dechlorination of chlorinated ethylenes and ethanes with nZVI particles.

Table 2.1: Summary of dechlorination reaction of chlorinated ethylenes and ethanes with nZVI

Research Group	Parent compound (mg/L)	nZVI concentration (g/L)	Type of Catalyst	Degradation time	Degradation Products Observed
Liu et al, 2005b	TCE=290	0.035	none	Several days	Ethane=70%, C3-C6 coupling products=30%
Liu et al, 2005b	TCE=4.4	0.194	none	1.5 hours	Ethane=80%, C3-C6 coupling products=20%
Zhang et al, 1998	TCE=20	20	none	1 hour	Ethene, ethane, propene, propane, butene, butane and pentane
Song and Carraway, 2005	HCA = 24	0.08	none	1.4 hours	PCE
Song and Carraway, 2005	PCA = 22	0.08	none	1.3 hours	PCE, TCE
Song and Carraway, 2005	1,1,1,2-TeCA = 16	0.08	none	80 hours	1,1-DCE, ethane
Song and Carraway, 2005	1,1,2-TCA=12	0.08	none	110 hours	Ethane
Zhang et al, 1998	TCE=20	20	Pd	0.25 hour	Ethene, ethane, propene, propane, butene, butane and pentane
Lien and Zhang, 2001	TCE=20	5	Pd	1.25 hour	Ethane =87%, Ethylene= 5.8~7.1%
Lien and Zhang, 2001	PCE=20	5	Pd	1.5 hour	Ethane =89%
Lien and Zhang, 2001	HCA = 30	5	Pd	2 hours	Ethane=87%, ethene = 6%, PCE= 7.5%
Lien and Zhang, 2001	1,1,1-TCA=30	5	Pd	7 hours	Ethane =60%

Therefore, it can be concluded that environmentally benign and highly efficient nZVI particles show excellent performance in the remediation of chlorinated ethylenes and ethanes. Monometallic nZVI particles, when reacted with TCE, form primarily ethane with lesser amount of even numbered saturated hydrocarbons like butane and hexane and inorganic chlorides. In case of HCA, PCA, 1,1,1,2-TeCA, less chlorinated byproducts and ethane formed at the end of the reaction. On the other hand, the utilisation of bimetallic nZVI particles such as Pd/Fe ensures a complete reduction at a faster rate forming mainly ethane as end products; however a smaller amount of chlorinated byproducts may be evolved during reaction which disappears instantly.

2.2.3 Stabilization of Iron Nanoparticles

In an aqueous system, direct inter-particle interactions such as Van der Waals forces and magnetic interactions cause nanoiron particles to form larger flocs and thus induce agglomeration, which in turn decreases chemical reactivity of nZVI particles (He and Zhao, 2007; Sakulchaicharoen et al, 2010). Supporting nanoparticles with selected stabilizers can diminish agglomeration, decrease particle size and thus result in a substantial gain of net reactivity by either electrostatic repulsion or steric hindrance (Schrick et al, 2002; He and Zhao, 2005; He and Zhao, 2007; Sakulchaicharoen et al, 2010). Schrick et al (2002) used carbon nanoparticles and poly acrylic acid (PAA) as supports for nZVI particles. Saleh et al (2007) utilized triblock copolymer (PMAA-PMMA-PSS) and the surfactant sodium dodecylbenzene sulfonate (SDBS) for modifying commercial nZVI to dechlorinate DNAPLs. Starch-stabilized bimetallic nanoparticles were prepared for degradation of chlorinated hydrocarbons in water by He and Zhao

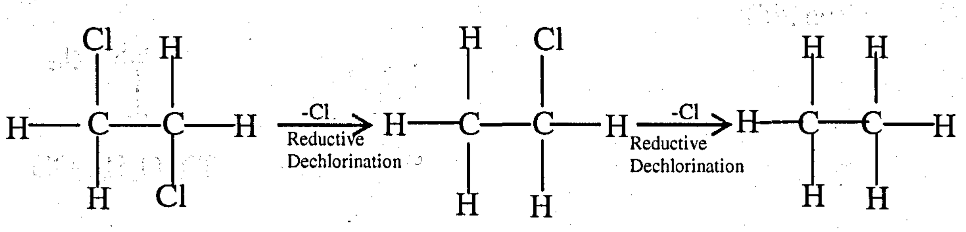
(2005). In a different study, He and Zhao (2007) successfully used carboxymethyl cellulose (CMC), a water soluble, low-cost and environmentally friendly polyelectrolyte for the same purpose. The starched nanoparticles in the study of He and Zhao (2005) displayed much less agglomeration and greater dechlorination than bare nZVI; however a stronger interaction and higher dechlorination rate was observed when CMC is used instead of starch with nZVI particles. (He and Zhao, 2007). CMC molecules adsorb onto the surface of the nanoparticles forming a thin negatively charged layer that suppresses agglomeration and exhibits higher reactivity compared to nonstabilized nanoparticles (He and Zhao, 2007). Sakulchaicharoen et al (2010) found that bimetallic Pd/Fe (Fe=0.1 g/L, Pd=0.1 wt%) encapsulated with 0.2% (w/w) CMC700K completely degraded TCE (nZVI/TCE=2 wt ratio) within 6 hours whereas Pd/Fe without CMC was able to dechlorinate only 37% of TCE at the end of 24 hours. He and Zhao (2007) showed that 0.2% (w/w) CMC-stabilized Pd/Fe transformed 50 mg/L of TCE (nZVI/TCE=1.17) into ethane and Cl- within 40 minutes. On the other hand, in the same study non-stabilized Pd/Fe took 2 hours for about 40% TCE dechlorination (He and Zhao, 2007). Thus compared to non-stabilized nZVI partcles, supported nZVI particles display faster reactivity, which enhances their efficacy for groundwater remediation.

2.3 DEGRADATION OF 1,2-DCA

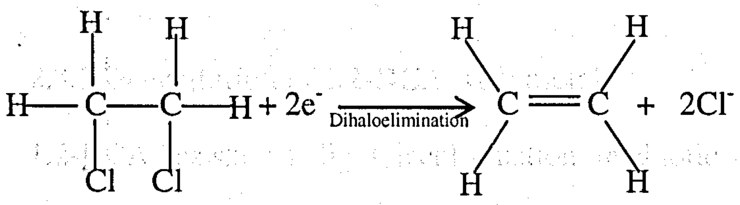
The degradation of 1,2-dichloroethane (1,2-DCA) or ethylene dichloride (EDC) is of particular interest in this study because unlike other halogenated alkanes, 1,2-DCA shows no response to nZVI treatment. 1,2-DCA is a chlorinated hydrocarbon, highly flammable and colorless liquid with a chloroform like odor. It is used in chemical manufacturing as an intermediate in the synthesis of polyvinyl chloride and as a solvent in pharmaceutical products synthesis (Klecka et al, 1998; Marzorati et al, 2005). The health risks associated with 1,2-DCA are linked to acute and long-term toxic effects affecting human liver, kidneys, neurological, cardiovascular, and immune systems. Chloroacetaldehyde, produced in vivo due to oxidative conversion of 1,2-DCA, has established carcinogen effects. (De Wildeman and Verstraete, 2003). The drinking water standard of 1,2-DCA in Canada is 0.005 mg/L (Health Canada). Because of its relatively high water solubility (8,700 mg/L), high density (1.253 g/cc), its potential for migration in soil and high resistance to reduction reactions, the residence time of 1,2-DCA in the environment can range from months to decades depending on environmental conditions (e.g. oxidation-reduction potential, pH, dissolved oxygen, temperature, conductivity etc.) (Marzorati et al, 2005). For these reasons, the development and implementation of reliable and effective remediation strategies for 1,2-DCA is a matter of great importance.

2.3.1 Degradation Pathways of 1,2-DCA

In the subsurface, under both aerobic and anaerobic conditions, specific microorganisms are able to transform 1,2-DCA into non-toxic end products (Zaan et al, 2009; De Wildeman and Verstraete 2003; Dyer et al, 2000; Klecka et al, 1998). Fig 2.4 describes dechlorination reactions of 1,2-DCA following different pathways depending on the prevailing reductive-oxidative conditions of an aquifer. Under aerobic conditions, through the oxidation process, 1,2-DCA is completely mineralized into CO_2, H_2O and Cl^- forming 2-chloroethanol and 2-chloroacetate as intermediates but these are not easily detectable in the field (the left hand pathway of Fig 2.4) (Zaan et al, 2009; Nobre et al, 2004; Klecka et al, 1998). Under anaerobic conditions, 1,2-DCA may also be oxidized under denitrifying conditions, with nitrate as the electron acceptor, forming CO_2, H_2O and Cl^- (the middle pathway in Fig 2.4) (Dyer et al, 2000; Nobre et al, 2004). Anaerobic degradation can take place through both biotic and abiotic processes (the right hand pathways of Fig 2.4). Reductions such as reductive dechlorination (equation 2.12) and dihaloelimination (equation 2.13) are involved in biotic process whereas hydrolysis (equation 2.14) takes place under abiotic conditions. Vinyl chloride, formed as an intermediate during the abiotic process of hydrolysis under alkaline condition, needs to undergo anaerobic oxidation to form CO_2 because of its low oxidation state (Dyer et al, 2000). Although anaerobic biological remediation can lead to successful dechlorination of 1,2-DCA, it is a very slow process and may take years to decades to complete the dechlorination reaction in the sub-surface environment.



(Equation 2.12)



(Equation 2.13)

$$R\text{-}X + OH^- \xrightarrow{\text{Hydrolysis}} R\text{-}OH + X^-$$ (Equation 2.14)

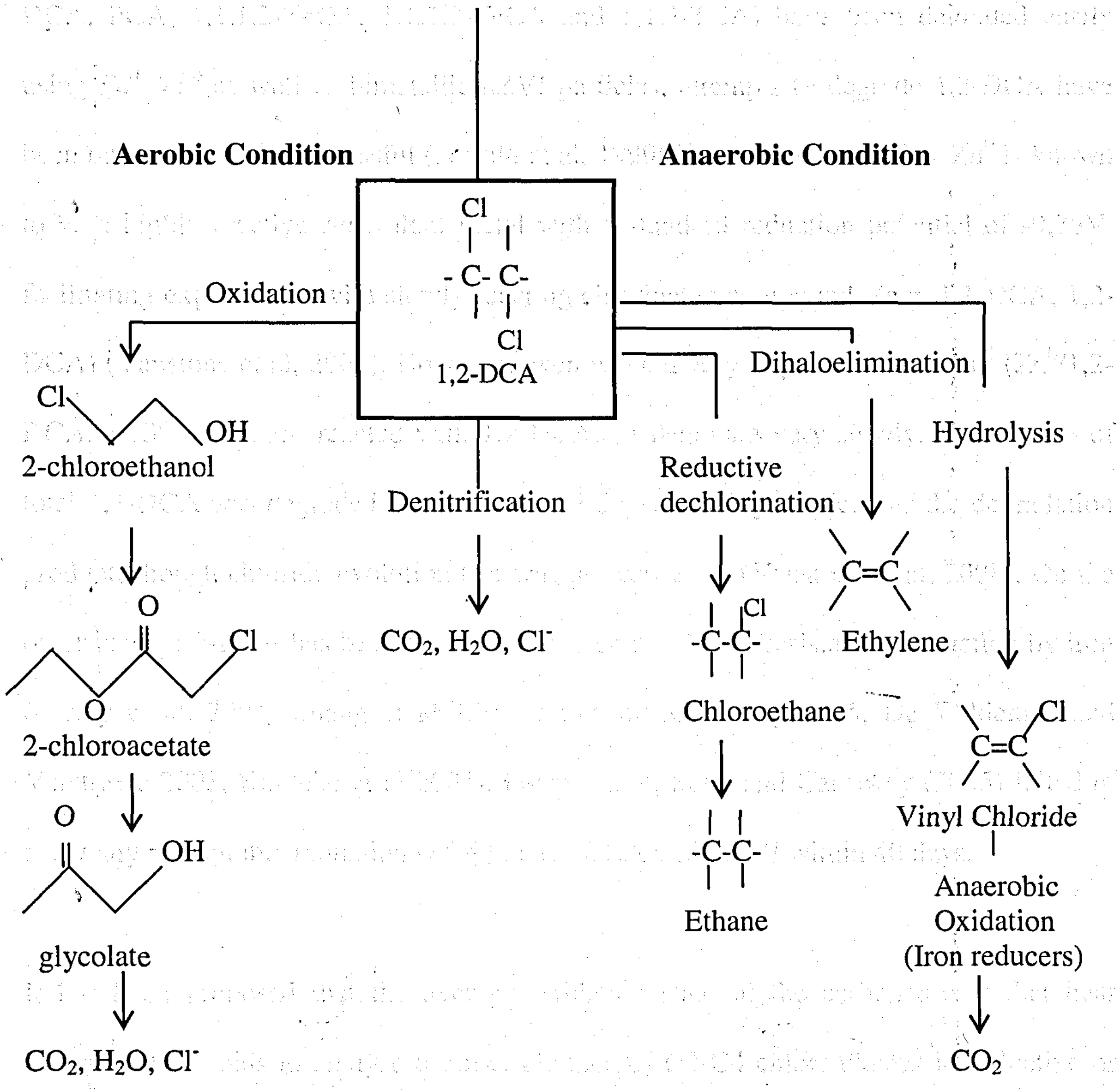


Fig-2.4- 1,2-DCA Transformation Pathways under Different Conditions (Nobre et al, 2004)

2.3.2 Degradation of 1,2-DCA with metals

1,2-DCA has shown slight dechlorination in abiotic systems by metals due to its extreme recalcitrance to reduction whereas other halogenated alkanes were successfully remediated through this method (Ferrey et al 2004; Zhang et al 1998; Song and Carraway 2005; De Wildeman and Verstraete 2003). While a variety of chlorinated ethanes (e.g., HCA, PCA, 1,1,1,2-TeCA, 1,1,2,2-TeCA and 1,1,2-TCA) have been degraded easily using Fe^0, Zn^0 as well as bimetallic nZVI particles, attempts to degrade 1,2-DCA have been only marginally successful (Arnold et al, 1999; Vanstone et al, 2008). Zn^0 is known to be a highly reactive zerovalent metal with a standard reduction potential of -0.76V, facilitating experiments with slowly reacting chlorinated compounds (e.g. 1,1-DCA, 1,2-DCA) (Vanstone et al, 2008). However, even when a very large amount of Zn^0 (Zn^0/1,2-DCA = 8000 wt ratio) reacted with 1,2-DCA, it degraded very slowly. About 30% of total 1,2-DCA was degraded at the end of 12 days, forming ethylene as the degradation product; though chloride evolution test was not carried at (Vanstone et al, 2008). On the other hand, 1,2-DCA has been found so far to be absolutely resistant to reduction by iron (Ferrey et al. 2004; Zhang et al 1998; Song and Carraway 2005; De Wildeman and Verstraete 2003, Kopinke et al 2004). For instance, Song and Carraway (2005) failed to show any measurable reduction (<5%) of 1,2-DCA with nZVI within 40 days.

It has been proposed that the average oxidation state of the carbon atoms that bear chlorine atoms aids to analyse the recalcitrance of C2-C4 chloroalkanes in reductive or oxidative environments (De Wildeman and Verstraete, 2003). The lower the oxidation state of the carbon atoms, the less susceptible they are to reduction (De Wildeman and Verstraete, 2003).

Table 2.2 presents the nominal oxidation states for several chlorinated hydrocarbons and their dechlorinated products.

Table 2.2- Redox Table (Ref: De Wildeman and Verstraete, 2003)

	+2	+1	0	-1	-2
Ethylenes	PCE →	TCE →	cis-1,2-DCE →	VC →	Ethylene
Ethanes			1,1,2-TCA→	1,2-DCA→	Ethylene

Table 2.2 reflects a zone, moving to the right from oxidation state 0, where reductive dechlorination is uncommon. For instance, carbon atoms associated with PCE have an oxidation state of +2 that makes reduction very easy but oxidation difficult. On the other hand, cis-1,2-DCE and VC with oxidation state of 0 and -1 respectively show comparatively slower reduction than PCE (De Wildeman and Verstraete, 2003). Although VC, with an oxidation state of -1, is susceptible to slow reduction, 1,2-DCA despite having the same oxidation number (-1) exhibits stability to reductive dechlorination (De Wildeman and Verstraete, 2003). Almost no degradation in the reductive conditions has been discussed for lower chlorinated alkanes containing 2-4 chlorine atoms (De Wildeman and Verstraete, 2003). The role of halogenated compounds as electron acceptors in anaerobic environments has also been rationalized by the Gibb's free energy (ΔG^0) of reactions. Table 2.3 reflects the half reaction Gibb's free energies for reductive dechlorination. Here PCE, having a ΔG^0 -55.4 kJ/electron, reduces more easily than TCE (ΔG^0 -53.1 to -50.9 kJ/electron) and 1,2-DCA is placed at the bottom of the table with $\Delta G^0 = -36.2$ kJ/electron acting as the weakest electron acceptor that supports the data provided in Table 2.2. Although 1,1-DCA being just above 1,2-DCA in table 2.3 with a ΔG^0 value of -38.3 is transformed at a very slow rate by reacting with

nZVI producing ethane as end product (Song and Carraway, 2005), 1,2-DCA has so far failed to breakdown by reacting with nZVI.

Table 2.3: Half Reactions Gibb's Free Energies of Reductive Dechlorinations. The ΔG^0 electron values are calculated at standard conditions partial pressures 1 atm, pH=7.0 and $[Cl]^-$=1mM. (Ref: Dolfing and Mueller)

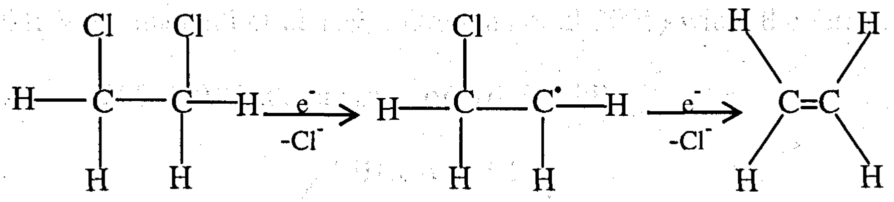
Electron Acceptor	Half-reaction of reductive transformation			ΔG^0 (kJ/electron)	E^0 (mV)
Pd^{2+}	$Pd^{2+} + 2e^-$	→	Pd^0	-88.3	915
PCE	$C_2Cl_4 + H^+ + 2e^-$	→	$C_2HCl_3 + Cl^-$	-55.4	574
1,1,1-TCA	$CCl_3\text{-}CH_3 + H^+ + 2e^-$	→	$CHCl_2\text{-}CH_3 + Cl^-$	-54.1	561
TCE	$C_2HCl_3 + H^+ + 2e^-$	→	$C_2H_2Cl_2 + Cl^-$	-53.1 to -50.9	550 to 527
1,1,2-TCA	$CHCl_2\text{-}CH_2Cl + H^+ + 2e^-$	→	$C_2H_4Cl_2 + Cl^-$	-51.9 to -49.8	538 to 516
VC	$C_2H_3Cl + H^+ + 2e^-$	→	$C_2H_4 + Cl^-$	-43.4	450
1,2-DCE	$C_2H_2Cl_2 + H^+ + 2e^-$	→	$C_2H_3Cl + Cl^-$	-40.6 to -38.3	420 to 397
1,1-DCA	$C_2H_4Cl_2 + H^+ + 2e^-$	→	$C_2H_5Cl + Cl^-$	-38.3	397
1,2-DCA	$CH_2Cl\text{-}CH_2Cl + H^+ + 2e^-$	→	$C_2H_5Cl + Cl^-$	-36.2	375
Fe^{2+}	$Fe^{2+} + 2e^-$	→	Fe^0	+42.5	-440
Zn^{2+}	$Zn^{2+} + 2e^-$	→	Zn^0	+73.6	-763

Moreover, the dechlorination reactivity of chlorinated hydrocarbons is expected to be affected by the bond strength of the carbon-chlorine bond, the electron affinity of the carbon chlorine bond and the stability of the carbon-radical species resulting from an initial electron transfer pathway (Larson and Weber, 1994). Table 2.4 illustrates the dependence of reactivity on structures of chlorinated ethanes where the order of reactivity of HCA, 1,1,2,2-TeCA and 1,2-DCA is linked to differences in the dissociation energy of the C-Cl bond. (Larson and Weber)

Table 2.4 Relative Rates for the Vicinal Dechlorination of Chlorinated Ethanes in Reducing Sediment-Water Slurry (Larson and Weber, 1994)

Compound	k^{obs} (min^{-1})	$t_{1/2}$	Bond dissociation energy (C-Cl; kcal/mol)	Electron Affinity of Associated chlorine(kcal/mol)
Hexachloroethane	1.9×10^{-2}	36 min	72	83
1,1,2,2-Tetrachloroethane	7.3×10^{-5}	6.6 d	69.8	77.5
1,2-Dichloroethane	$<1.4 \times 10^{-5}$	735 d	< 47	70.5

Under the experimental conditions of the study by Larson and Weber, alkenes were formed at the end of reactions through the pathway of vicinal dechlorination (equation 2.15).



(Equation 2.15)

Vicinal Dechlorination

2.3.3 Degradation of 1,2-DCA with hydrogen and a catalyst

Although metal-based reduction has been found to be marginally successful in 1,2 DCA chemical dechlorination, catalytic hydrodechlorination (a dechlorination reaction in the presence of H_2 gas and a catalyst where chlorinated organic compounds are dechlorinated into benign compounds) has been reported to be successful in this respect (Vadlamannati et al 1999; Choi and Lee, 2000; Kovalchuk et al 2004; Orellana et al 2005). Here, the dechlorination reaction occurs between an organic molecule containing a C-Cl bond and gaseous H_2 in the presence of a highly selective metal catalyst, leading to the formation of HCl and a new C-H bond (Orellana et al 2005). It has been found that, for the process to be successful, the metal must be able to catalyze the dissociation of hydrogen (Kovalchuk et al 2004). According to Vadlamannati et al (1999), the catalyst participates in a catalytic cycle where the chlorinated molecules cover the metal surface. The reduction of highly reactive hydrogen adatoms remove the chlorine atoms and eventually form ethane (Vadlamannati et al, 1999). Group VIII-B metals (e.g. platinum, palladium, rhodium etc.) satisfy this condition and have shown good performance in the hydrodechlorination of 1,2-DCA forming ethane as end product (Fig 2.4) (Kovalchuk et al 2004; Vadlamannati et al 1999; Orellana et al 2005) when the temperature lies within the range of 200-250°C at a pressure of 101.325 kPa.

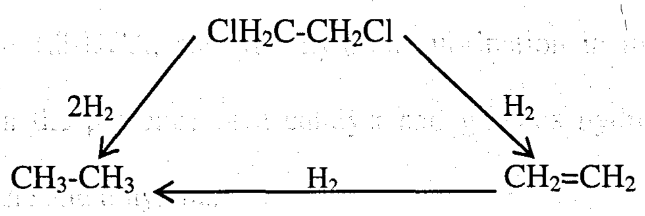


Fig 2.5: Reaction Scheme for Catalytic Hydrodechlorination of 1,2-DCA (Ref: Kovalchuk et al, 2004)

Monochlorinated aliphatic hydrocarbons are also susceptible to catalytic hydrodechlorination; for example, methyl chloride dechlorination catalyzed by silica supported Ru, Rh, Pd, Pt, Ag lead to methane and hydrochloric acid (HCl) in the presence of H_2 (equation 2.16) (Fung and Sinfelt, 1987). Although Pd, Pt, Rh, Ni, Ru, Cu can effectively dechlorinate 1,2-DCA to ethane, the best performance of catalysts in terms of conversion of 1,2-DCA (~30%) has been found with Pd (Table 2.5).

$$CH_3Cl + H_2 \rightarrow CH_4 + HCl \qquad \text{(Equation 2.16)}$$

Table 2.5: Summary of Catalytic Hydrodechlorination of 1,2-DCA

Research Group	Temp (°C)	Catalyst	Conversion	Final Product
Heinrichs et al (1997)	350	Pd/SiO_2	30%	90% Ethane
Vadlamannati et al (1999)	200	Pt/C	4%	92% Ethane, 2% Monochloroethane
Vadlamannati et al (1999)	200	Cu/C	0.6%	100% Ethylene
Srebowata et al (2007)	230-250	Ni/SiO_2	4%	70% Ethylene, 30% Ethane
Srebowata et al (2007)	230-250	Ru/SiO_2	2%	25% Ethylene, 55% Ethane

Therefore, it can be found that although the reductive treatment with nZVI particles failed to dechlorinate 1,2-DCA, catalytic hydrodechlorination in the laboratory at very high temperature, in the presence of a catalyst and gaseous hydrogen could transform 1,2-DCA into ethane and ethylene.

2.3.4 Modified Approach to Degrade 1,2-DCA with nZVI, Catalyst and Hydrogen

So far, the beneficial application of zero-valent iron nanoparticles in aqueous phase for remediation of chlorinated hydrocarbons has been discoursed. However, 1,2-DCA has been found to be an exception in this respect due to its recalcitrance to reduction. On the other hand, gas-phase catalytic hydrodechlorination at an elevated temperature using an adequate catalyst could dechlorinate this compound. Nonetheless, the requirement of high temperature and gaseous H_2 makes this approach impractical for field remediation. Therefore, the study of an alternate methodology for in-situ 1,2-DCA degradation in contaminated aquifers is a worthwhile task. Since the main concept of hydrodechlorination to remediate 1,2-DCA lies in replacing the chlorine atoms by hydrogen, liquid phase reduction using an alternate source of hydrogen presents an interesting alternative to gas phase reduction of 1,2-DCA. This type of reduction has been favourably applied for dechloritation of polychlorinated biphenyles, chlorobenzenes and chlorotoluenes (Ukisu et al, 1997; 1998). In this case, relatively mild conditions with reaction temperatures rarely exceeding 100°C have been proved adequate for the dechlorination to take place. Moreover, instead of H_2 gas, various sources of hydrogen, like formic acid and formates, phosphinic acid and phosphinates, phosphorous acids and phosphates, alcohols, hydrazine or borohydrides, can be used (Ukisu et al 1998, Urbano and Marinas, 2001). The use of hydrogen donors has potential advantages on hydrogen transfer reduction compared with catalytic reduction with molecular H_2. The H_2 released from the hydrogen donors is transformed into atomic hydrogen (H^*) onto the catalyst surface through catalyzed decomposition of H_2 (Zhou and Lim, 2010). This H^* reacts with chlorinated compounds, releases Cl- and forms hydrocarbons (Fig. 2.6) (Urbano et al, 2001). According to Urbano et al. (2001), the hydrogen transfer mechanism may take place in various ways: the H_2 may serve as a proton, atom or hydride during its transfer from donor depending on the reagents and conditions.

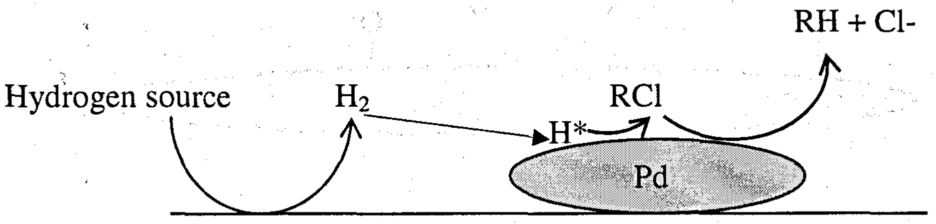


Fig: 2.6 Schematic of Proposed Hydrogen Transfer Mechanism on Pd (Ref: Zhou and Lim, 2010)

When formic acid is used as the H_2 donor and Pd is used as catalyst to dechlorinate RCl, Kopinke et al (2004) proposed that, in the presence of Pd, RCl utilises directly the hydride hydrogen from the chemisorbed formate and breaks into RH and Cl^- (Fig 2.7a). In fact, under alkaline conditions, it is found that the relatively slow hydride mechanism dominates (Fig 2.7a), while at lower pH values the fast radical mechanism through H atoms is favoured under acidic or neutral conditions (Fig 2.7b) (Kopinke et al, 2004)

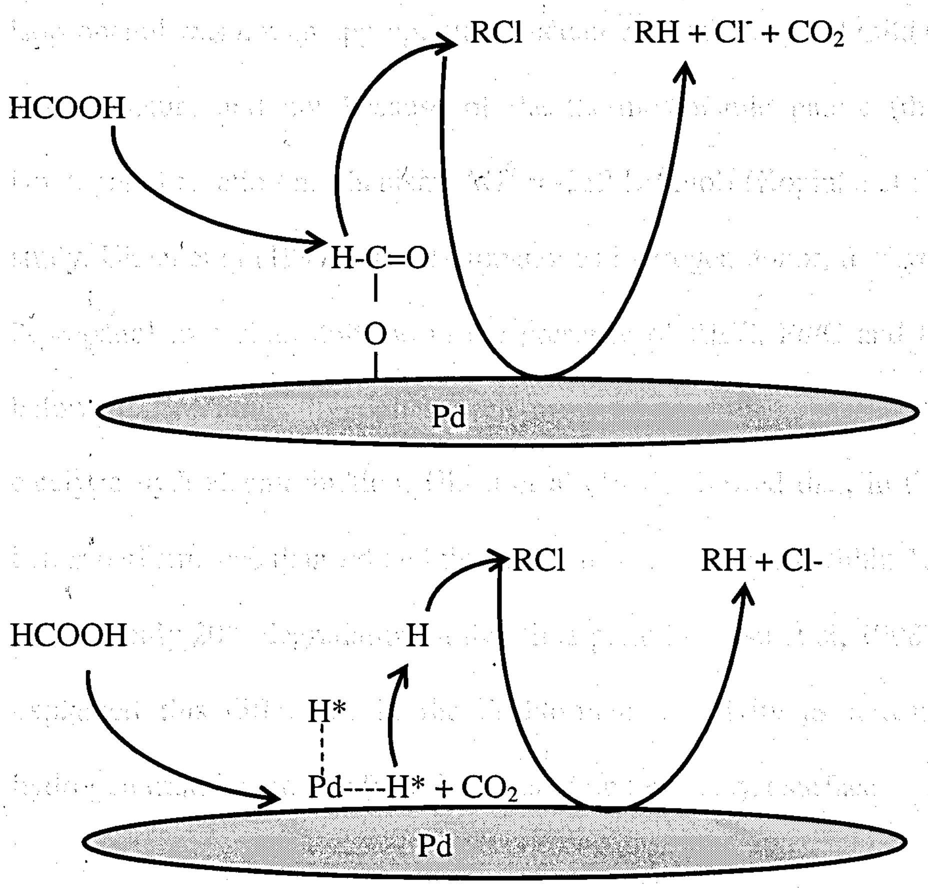


Fig 2.7: Possible mechanism of Pd-catalyzed hydroechlorination in the presence of formic acid a) hydride mechanism b) radical mechanism (Kopinke et al, 2004)

Literature reports indicate the combination of HCOOH, used as a H_2 donor, with Pd, is a powerful reductant. Under acidic or neutral conditions, formic acid was found to be as reactive as H_2. Kopinke et al (2004) observed that at 23°C and a pH = 3.5, 0.05mM chlorobenzene was completely dechlorinated using 5.5mM HCOOH and 250 mg/L Pd/Al_2O_3, forming benzene and chloride at the end of 20 hours. When isopropanol was used as hydrogen source, only 15% of chlorobenzene was converted to benzene after 2 weeks. The activity of the catalyst was tested and found to be reactive even after 2 weeks. Therefore, the partial dechlorination might be because the combination of Pd and isopropanol was not an appropriate reductant under the applied mild conditions due to its kinetic nature and not because of the thermodynamic nature (the driving force for isopropanol reaction mechanism, ΔG^0 = -212 kJ/ mol) (Kopinke et al, 2004). In another study, Ukisu et al (1997) used 2-propanol as hydrogen donor, for hydrogen transfer from 2-propanol to p-chlorotoluene in the presence of Rh/C, Pd/C and Pt/C at temperatures below 82°C. Although Pd has been proven to show the best catalytic properties in catalytic hydrodechlorination, Ukisu et al (1997) showed that, in this case, Rh exhibits better performance than Pd and the reaction was completed within 180 minutes while Pd showed only 20% degradation in that time period (Ukisu et al, 1998). Ukisu et al (1998) explained this difference in the dechlorination activity as a result of efficiency of hydrogen transfer process from 2-propanol on the catalyst surface.

Although nZVI itself performs as a source of hydrogen in aqueous phase for reduction of chlorinated solvents, it was completely unsuccessful to dechlorinate 1,2-DCA. Being encouraged by the idea of liquid phase reduction, along with nZVI, a suitable hydrogen donor and catalyst have been used in this research work to create a reducing environment that could degrade 1,2-DCA to a certain extent. The choice of hydrogen donor and catalysts were selected by analyzing the literature. Details of this selection to formulate different experimental conditions for 1,2-DCA has been resolved in the next chapter.

2.4 SUMMARY

Nanoscale zero valent iron particles have been proposed as a preferred option for remediation of chlorinated solvents, such as chlorinated ethylenes and ethanes. The high surface area, nanoscale dimensions and high density of reactive sites on the surface enable nZVI particles to degrade contaminants at a faster and more complete manner than micro or macroscale iron systems. In aqueous environments, Fe^0 is oxidized and this causes reduction of H_2O into H_2. Addition of noble metals to nZVI particles enhances the reactivity, the noble metals serving as catalysts. In a bimetallic nZVI system, the catalyst performs as the dissociator of H_2; absorbing and dissociating it into atomic H. This highly reactive form of hydrogen then attacks the adsorbed contaminants on the iron surface, replacing chlorine leading to the formation of benign products. However, in the absence of a catalyst, H_2 cannot contribute directly to the dechlorination. Moreover, the presence of a catalyst on the iron surface preserves the Fe^0 core from being oxidized and thus maintains its reactivity for dechlorination. Both mono and bimetallic nZVI particles showed excellent performance in remediating chlorinated compounds like PCE, TCE, cis-DCE and VC. The final products were mainly saturated hydrocarbons. Although a number of chlorinated ethanes responded to the treatment with nZVI particles, 1,2-DCA was an exception because its chemical-physical properties did not allow it to respond positively towards the treatment involving nZVI. However, catalytic hydrodechlorination could successfully remediate this compound. The main strategy of this study is to create a nZVI based formulation combing the concept of catalytic hydrodechlorination and liquid-phase reduction that will provide a positive methodology to dechlorinate 1,2-DCA successfully.

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3.0 DEGRADATION OF 1,2-DCA WITH NZVI PARTICLES

3.1 INTRODUCTION

Chlorinated Organic Compounds (COCs) are difficult to remediate directly under most natural or abiotic conditions and are persistent in the environment for decades to centuries, causing widespread contamination in both groundwater and soil. The application of nanoscale zero-valent iron particles (nZVI) for abiotic remediation of chlorinated aliphatics, aromatics and polychlorinated biphenyls is a promising technology (Zhang et al, 1998; He and Zhao, 2005; Li et al, 2006; Wang et al 2008; Sakulchaichareon et al, 2010). Nanoscale zero-valent iron particles-are very effective electron donors possessing a standard reduction potential (E_0) of - 0.44 V. In an aqueous solution, Fe^0 is oxidized to Fe^{2+} and forms H_2 by reduction of H_2O (equations 3.1 and 3.2). When iron particles are doped with a catalytic metal (e.g., Pd, Pt, Ni or Ag), the catalyst adsorbs the H_2 and dissociates it into atomic H (equation 3.3) which then attacks the adsorbed chlorinated contaminant (RCl in equation 3.4) on the iron surface, leading to dehalogenation of the organic substrate (equation 3.4).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad \text{(Equation 3.1)}$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \qquad \text{(Equation 3.2)}$$

$$H_2 \xrightarrow{\text{catalyst}} 2H\bullet \qquad \text{(Equation 3.3)}$$

$$Fe + H_2O + H\bullet + RCl \longrightarrow RH + HCl + FeO_x \qquad \text{(Equation 3.4)}$$

Many COCs of concern (e.g., tetrachloroethylene PCE, trichloroethylene TCE, cis-dichloroethylene cis-DCE) are rapidly and completely dechlorinated without the formation of toxic by-products (e.g., vinyl chloride) using nZVI doped with a catalytic metal known as bimetallic nZVI systems (He and Zhao, 2005; Lien and Zhang, 2001). Both mono and bimetallic nZVI particles exhibited a good performance in degradation of chlorinated ethanes like hexachloroethane (HCA), pentachloroethane (PCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) and 1,1-dichloroethane (1,1-DCA) forming ethane at the end of the reaction (Lien and Zhang, 2005; Song and Carraway, 2005).

Although chlorinated ethanes like HCA, PCA, 1,1,2,2-TeCA and 1,1-DCA showed response to nZVI dechlorination, 1,2-dichloroethane (1,2-DCA) has been resistant to degradation using nZVI technology (Ferrey et al. 2004; Zhang et al 1998; Song and Carraway 2005; De Wildeman and Verstraete 2003, Kopinke et al 2004). For instance, Song and Carraway (2005) found no measurable reduction of 1,2-DCA (conversion below 5%) even after 40 days of reaction (nZVI/1,2-DCA=83 wt ratio). The limited reactivity of nZVI to 1,2-DCA has been ascribed to factors such as bond strength of the carbon-chlorine bond, the low electron affinity of the carbon-chlorine bond and the low stability of the carbon-radical species resulting from the initial electron transfer step required for dechlorination (Larson and Weber, 1994). Generally, the higher the oxidation state of the carbon atom, the more responsive it is to reduction and the more resistant to oxidation (De Wildeman and Verstraete, 2003). 1,2-DCA with an oxidation state of -1 exhibits a low tendency to reduction under conventional conditions.

As discussed earlier, in the nZVI system the source of H_2 is water. Hydrogen generation occurs through Fe^0 corrosion and this hydrogen is used during the transformation of the chlorinated compounds into benign products. Therefore, introducing a more efficient H_2 source in the dechlorination system could potentially enable a more effective dechlorination process. Previous studies have shown that a H_2 source coupled with an active hydrogenation catalyst (such as, Pd, Rh, Ni or Pt) can reduce reticent organic halides such as- chlorotoluene, chlorobenzene, and polychlorinated biphenyls. (Johnstone and Wilby, 1985, Ukisu et al 1998; Kopinke et al 2004). The adsorption of hydrogen released from the hydrogen donors onto the catalyst surface influences the dechlorination rate (Urbano et al, 2001). Formic acid has been found as an effective hydrogen source and a combination of formic acid and Pd acts as a powerful reductant to dechlorinate compounds like chlorobenzene (Kopinke et al, 2004). Alcohols have been proposed as hydrogen sources as well. In this case, the alcohol acts both as a hydrogen source and solvent for the dechlorination reaction. However, in this case, the addition of a base (e.g. NaOH, KOH, NH_4OH) is necessary to neutralize the HCl formed because HCl can deactivate the catalysts. (Urbano and Marinas, 2001; Ukisu et al, 1998). The use of alcohols as hydrogen donors coupled with a hydrogenation catalysts such Rh, Pd and Pt has been proved successful in the dechlorination of contaminants like p-chlorotoluene (Ukisu et al 1998). Nonetheless, the literature lacks reports on the use of these systems for the dechlorination of 1,2 DCA.

The studies discussed in Chapter 2 and briefly discussed in this section indicate that, while thermodynamically feasible, the right conditions for dechlorination of 1,2 DCA are yet to be found. Based on results observed on the dechlorination of other organic species, it can be hypothesized that a combination of liquid-phase reduction using hydrogen donors, a catalyst and nZVI should be able to initiate the degradation of 1,2-DCA under the right experimental conditions. In our study formic acid and isopropanol (IPA) were selected as hydrogen donors while Rh and Pt along with Pd were used as catalysts. The selection of these specific systems were based on reports indicating that both Rh and Rh-Pt catalysts showed significant performance in dechlorinating chlorotoluene in the presence of 2-propanol and NaOH (Ukisu et al, 1998) whereas HCOOH catalyzed by Pd was as reactive as gaseous H_2 to completely degrade chlorobenzene (Kopinke et al, 2004). The objectives of this study are i) to find the nZVI-based formulation to dechlorinate 1,2-DCA under aqueous conditions similar to those in the field. ii) to optimize the experimental conditions for this process and iii) to investigate the degradation pathways under which 1,2-DCA dechlorination takes place.

3.2 MATERIALS AND METHODS

3.2.1 Chemicals

The following chemicals were used for experiments as received: 1,2-DCA(>99%, A.C.S. Reagent, Sigma-Aldrich), TCE (99+%, extra pure, stabilized, ACROS Organics), n-hexane (>95% GC, Fluka Analytical), formic acid (98%, GR ACS, EMD Chemicals Inc), isopropyl alcohol (for GC, HPLC, Residue Analysis, Spectophotometry; EMD Chemicals Inc), $FeSO_4.7H_2O$ (99+%, A.C.S. Reagent, Sigma-Aldrich), $NaBH_4$ (98+%, ACROS), K_2PdCl_6 (99%, ACROS Organics), Pd-acetate (99.98%, trimer, Pd min 47%, Alfa Aesar), Rh-acetate (dimmer, 99.99%; Alfa Aesar), $PtBr_2$ (99.9%, Pt min 54.5%; Alfa Aesar), sodium carboxymethyl cellulose (90K, Sigma-Aldrich), sodium chloride (EMD Chemicals Inc), Scotty Analyse Gases, N_2 (ultra high purity, PRAXAIR), Gas Mix (5% H_2 balance Ar, PRAXAIR), He (PRAXAIR), Compressed air (PRAXAIR), 5% CH_4 balance Ar (PRAXAIR).

3.2.2 Synthesis of non-stabilized nZVI Particles

The non-stabilized nZVI particles were synthesized using $NaBH_4$ to reduce an aqueous solution of $FeSO_4.7H_2O$ following the protocol of Schrick et al (2002). The synthesis procedure was carried out in an anaerobic chamber to avoid Fe oxidation. In order to remove dissolved O_2, deionized (DI) water used for the experiments was purged with purified N_2 for at least 2 hours before synthesis. $FeSO_4.7H_2O$ was added to DI water to achieve 0.161M iron. The reaction mixture was homogenized using a magnetic stirrer operating at 600 rpm. After complete dissolution of the iron salt, an equal volume of 0.322M aqueous solution of $NaBH_4$ was added drop wise (1drop/ sec) to the iron solution to reduce ferrous iron to its zero-valent form (Equation 3.5):

$$2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 + H_2BO_3^- + 4H^+ + 2H_2 \qquad \text{(Equation 3.5)}$$

Upon addition of the $NaBH_4$ solution, the clear yellowish solution rapidly changed to a dark black suspension, indicating the formation of Fe nanoparticles. After complete addition of $NaBH_4$, the solution was mixed for about 30 minutes until H_2 gas evolution ceased. The resulting nZVI particles were thoroughly rinsed with DI water (100 mL/g).

In order to prepare Pd/Fe bimetallic nanoparticles, an aqueous slurry of Fe nanoparticles was equilibrated with an 3.38 x 10^{-6} M ethanolic solution of $[Pd(C_2H_3O_2)_2]_3$. This mixture was stirred for 30 minutes. This resulted in the reduction and subsequent deposition of Pd on the iron surface (equation 3.6):

$$Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+} \qquad \text{(Equation 3.6)}$$

The palladium-doped nanoiron particles were then washed with DI water, collected in 120 mL reaction vials and capped with Teflon Mininert Valves.

Transmission Electron Microscopy (TEM) images give information about the shape, size and size distribution of particles. A very dilute solution of Pd/Fe nZVI particles was prepared in acetone or IPA in order to take their TEM images. This solution was then dispersed for 20 ~ 30 minutes. On a copper lacey carbon grid, a few drops of nZVI solution was deposited, stored in the fume hood until the acetone or IPA is completely evaporated from the grid and then it was analyzed by the TEM. TEM analysis was performed using a FEI Titan 80-300 Cryo-in situ Transmission Electron Microscopes. Fig 3.1 shows the TEM image of Pd/Fe bimetallic particles.

Pd/Fe bimetallic NPs

Fig 3.1 TEM image of Pd/Fe bimetallic nZVI particles with scale bar 100 nm.
(Fig Courtesy: Nataphan Sakulchaicharoen)

For the preparation of Rh/Fe bimetallic particles, Rh-acetate ($C_8H_{16}O_8Rh_2$) dissolved in DI water (4.82 x 10^{-4} M) was added to the aqueous slurry of Fe particles and then equilibrated for 30 minutes. In some experiments, a mixture of catalyst precursors (Rh-Pt and Pd-Rh-Pt) was used following a co impregnation protocol. $PtBr_2$ served as the precursor of Pt. However, since this compound is insoluble in pure water, it was first dissolved in a 1M NaBr solution (through comlexation by Br^- ions) and then mixed with the aqueous solution of Rh-acetate (Rh-Pt/Fe) and/ or Pd-Rh-acetate (Pd-Rh-Pt/Fe). This mixture was then added to slurry of Fe nanoparticles and then collected following the same procedure described above for the Pd-Fe material.

3.2.3 Synthesis of CMC-stabilized nZVI Particles

The synthesis procedure was carried in an anaerobic chamber. CMC was added to the solution mixture before the reduction step with borohydride. Before synthesis, both DI water and 3% CMC (90K) stock aqueous solution were purged with purified N_2 for at least 2 hours to remove dissolved O_2.

A volume of 50mL of an aqueous solution of $FeSO_4.7H_2O$ (0.161M) prepared in DI water was added to 125 mL of 3% aqueous solution of CMC to give a final concentration of 1.5% of CMC. This mixture was stirred continuously with a mixer for about 15 minutes to complete the formation of the Fe-CMC complex where the carboxylic groups of CMC, after being almost fully disassociated, interacted with the Fe^{2+} cations. After this period, 50mL of an aqueous $NaBH_4$ solution (0.322M) was added drop wise (1drop/ sec) to the CMC-Fe^{2+} solution. After addition of the total volume $NaBH_4$, the mixture was allowed to homogenize for about 30 more minutes and then 25 mL of 2.35 x 10^{-3} M of K_2PdCl_6 dissolved in a 0.005M NaCl solution was added to the CMC-nZVI solution in order to prepare bimetallic nanoparticles. Pd was deposited on the nZVI surface according to equation 3.7:

$$PdCl_6^{2-} + 2Fe^0 \rightarrow Pd^0 + 2Fe^{2+} + 6Cl^- \qquad \text{(Equation 3.7)}$$

The synthesized iron particles were collected in a 120 mL reaction vial and were immediately capped with Teflon Mininert Valves. Fig 3.2 shows the TEM image of CMC (90K) stabilized Pd/Fe nZVI particles.

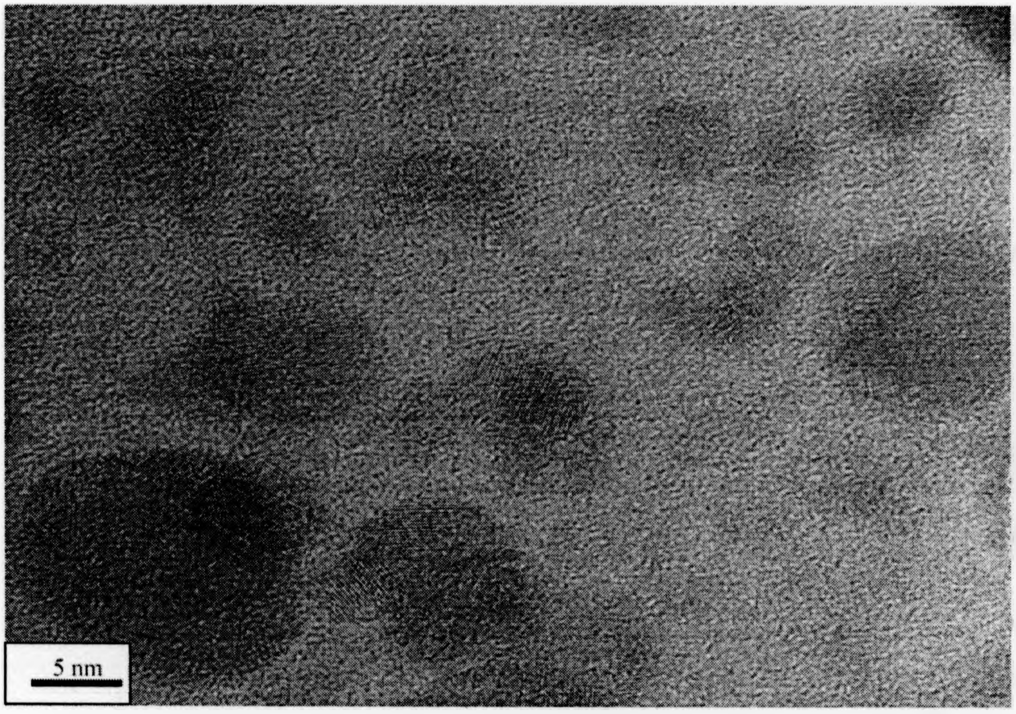

Fig 3.2 TEM image of CMC (90K) stabilized Pd/Fe bimetallic nZVI particles with scale bar 5 nm (Fig Courtesy: Nataphan Sakulchaicharoen)

3.3 BATCH EXPERIMENTS

Batch experiments were carried out in 120 mL amber bottles to test the reactivity of the laboratory synthesized nanosized zero-valent iron particles for the dechlorination of 1,2-DCA and TCE. The purpose of using amber bottles was to restrict any kind of photodegradation of the chlorinated solvents. Along with the reaction vials, blank experiments were conducted without metal particles. Stock solutions of both 1,2-DCA and TCE were prepared in isopropanol and appropriate volumes of the stock solutions were spiked through gas-tight syringes in both vials to achieve the desired concentration of the chlorinated solvents. In those experiments requiring formic acid, an appropriate amount of this chemical was added to the vials before 1,2-DCA spiking. About 25~50% of inert headspace was maintained in the vials to allow for good homogenization of the reaction mixture. The vials were shaken either by wrist action shaker at room temperature or in a temperature controlled orbital shaker at 165 rpm.

Table 3.1 indicates the different experimental conditions for 1,2-DCA and TCE dechlorination testing.

Table 3.1: Experimental Conditions for 1,2-DCA and TCE Dechlorination

Exp #.	Chlorinated Compound (mg/L)	Fe^0 conc (g/L)	Catalyst (wt % of Fe^0)	Temp (°C)	H_2 donor / Stabilizer added	Degradation after 7 days
1.	TCE=100	1.5	none	25	none	25% after 6 days
2.	TCE= 100	1.5	Pd=0.1%	25	none	100% after 3 hours
3.	1,2-DCA= 50	1.5	Pd=0.5%	25	none	none
4.	1,2-DCA= 5	20	Pd=0.2%	25	none	7%
5.	1,2-DCA= 10	20	Pd=0.2%	25	none	8%
6.	1,2-DCA= 5	2.5	Pd=0.2%	25	HCOOH= 250 mg/L	7%
7.	1,2-DCA= 10	5	Pd=0.2%	35	HCOOH= 500 mg/L	11%
8.	1,2-DCA= 10	10	Rh=0.5%	35	IPA and NaOH	none
9.	1,2-DCA= 10	10	Rh=0.2%, Pt = 0.1%	35	IPA and NaOH	none
10.	1,2-DCA= 10	10	Rh=0.7%, Pt= 0.35%	35	IPA and NaOH	none
11.	1,2-DCA= 10	10	Rh=1.42% Pt= 1.42%	35	IPA and NaOH	none
12.	1,2-DCA= 10	10	Rh=0.2% Pd=0.2% Pt= 0.1%	35	HCOOH= 500mg/L	12%
13.	1,2-DCA= 10 TCE= 10 (after 7 days)	5	Pd=0.5%	25	HCOOH= 500 mg/L CMC=1.5%	9%
14.	TCE=10	5	Pd=0.5%	25	HCOOH= 500 mg/L CMC=1.5%	not detected
15.	1,2-DCA= 10	5	Pd=0.5%	45	HCOOH= 500 mg/L CMC=1.5%	17%
16.	1,2-DCA= 10	10	Pd=0.2%	35	HCOOH= 500mg/L	12%

3.4 ANALYTICAL METHODS

3.4.1 Solvent Extraction Analysis

The concentrations of 1,2-DCA and TCE were analyzed using the Solvent Extraction method. n-Hexane was used as the extracting solvent. At selected time intervals, 0.25~1 mL of an aqueous aliquot was collected from both the reaction and blank vials and transferred to a 2-mL GC vial containing 1 mL of n-Hexane. This GC vial was shaken for about 10 seconds and then kept undisturbed for about 2 hours, to allow for equilibration. After this time, the organic phase was removed for GC analysis. A 1 μL of extract was withdrawn by the autosampler for GC analysis.

Sampling

The sample was analyzed for the determination of the concentration of 1,2-DCA and TCE using an Agilent 7890 Gas Chromatograph equipped with a DB-624 capillary column (75m x 0.45 mm x 2.55 μm) and an Electron Capture Detector (ECD). The temperature program used for the analysis was: 35°C for 12 min, then 5°C / min to 60°C held for 1 min; 17°C/ min to 200°C held for 5 min. A sample volume of 1 μL was injected in split less mode. Standard calibration curves for 1,2-DCA and TCE were used to calculate the aqueous concentration of the solvents in the reaction mixture. The standards were prepared using isopropanol and DI water and were analyzed using the same method as the samples. The retention time of 1,2-DCA and TCE found were about 15.77 min and 18.21 min respectively for this temperature program. Along with 1,2-DCA and TCE, 1,2-DCE was also quantified during the analysis for identification of the formation of chlorinated intermediates during the dechlorination reaction.

Standard

3.4.2 Headspace Analysis

Static headspace analysis was done to detect the hydrocarbons produced during dechlorination reactions on an Agilent 7890 GC equipped with a 7693 Auto sampler, a Mass detector (5975C MSD) and Flame Ionization Detector (FID). A GS-Gas Pro Column (3.0m x 320 µm) was used for this analysis. The temperature program used under this program was 35°C for 5 min, then 10°C / min to 220°C held for 7 min. Sample injection was carried out using both manual injection and auto-sampling. For the case of manual injection, a 250µL gas-tight syringe was used to take the gaseous sample from the headspace of the reaction and blank vial. For the case of auto sampling, two different methods were used. In the first case, 1 mL of aqueous sample withdrawn from the reaction mixture was put into a 2mL GC vial. This sample was heated at 50°C for 1 min and stirred at a speed of 1000 rpm before a 250µL headspace sample injection into the GC. The second case involved 2 mL of liquid sampling from the reaction mixture into a 10 mL autosampler GC glass vial. This was followed by heating the vial at 85°C for 28 min and stirring at 1500 rpm followed by injection of a 2.50 mL headspace sample to the GC. The hydrocarbons were identified based on their mass spectra. Quantification was carried out by performing a calibration using a gaseous mixture of ethane, propane, butane, pentane, hexane, ethylene, propylene, 1-butylene, 2-butylene, pentylene and 1-hexylene of known concentration in nitrogen.

3.4.3 Chloride Analysis

The production of chloride from the dechlorination reaction of 1,2-DCA and TCE was monitored for selected experiments. For this purpose, the aqueous phase left in the 2 mL

GC vial after n-Hexane extraction was used. The evolution of chloride was monitored using a Waters 717 plus Autosampler High Performance Liquid Chromatograph (HPLC) equipped with a conductivity detector and an IC pak^{TM} anion column (4.6m x 50 mm). An isocratic program was used. The eluant used was a mixture of 12% acetonitrile in deionized water and the flow rate was set to 1.2 mL/min at a pressure of 595 psi. The injection volume was 100 μL. The calibration for chloride evolution was done using different standards of NaCl solution (0.01, 0.05, 0.5, 1 and 5 mM).

3.5 RESULTS AND DISCUSSION

3.5.1 The Formulation for 1,2-DCA Dechlorination

Before attempting 1,2-DCA dechlorination, a number of experiments were carried out to confirm the general appropriateness of the nZVI synthesis procedure for dechlorination of chlorinated hydrocarbons and to compare results to those reported in the literature. TCE was selected as the representative contaminant since it is well known that TCE can be readily reduced by nZVI (Zhang et al, 1998; Kim and Carraway, 2002; Schrick et al, 2002; Liu et al, 2005; Lien and Zhang, 2007). In these initial experiments, TCE was dechlorinated with both mono and bimetallic nZVI. In the case of monometallic nZVI (TCE = 100 mg/L, nZVI/TCE = 15 wt. ratio, Exp # 1, Table 3.1), about 25% of TCE was degraded at the end of 6 days (results not shown) whereas with bimetallic nZVI (TCE = 100 mg/L, nZVI/TCE = 15 wt. ratio, Pd=0.1 wt%, Exp # 2, Table 3.1) TCE was completely dechlorinated in one hour (Fig. 3.3). Observed degradation products were mainly ethane with a significant amount of ethylene. This is in agreement with the results obtained by Lien and Zhang (2001). They used a higher ratio of nZVI/TCE (250) with

0.05wt% Pd and obtained ~50% TCE degradation at the end of 12 minutes while, in this study, (nZVI/TCE=15, Pd=0.1wt%) it took ~30 minutes to achieve the same % of degradation. This difference in rate of reaction is mainly due to the different nZVI/TCE ratio. A small amount of 1-butylene and 2-butylene also appeared as coupling products as the reaction proceeded further in this study; these products have been previously observed by others (Liu et al 2005). Unfortunately, due to analytical error only 32% of carbon mass balance was recovered in the experiment. The total recovery of chloride ions was 86.5% of the total expected chloride based on the disappearance of TCE (Fig 3.4). Though some TCE could be lost due to volatilization it is more likely that chloride is adsorbed onto the nZVI surface (Barnes et al, 2010).

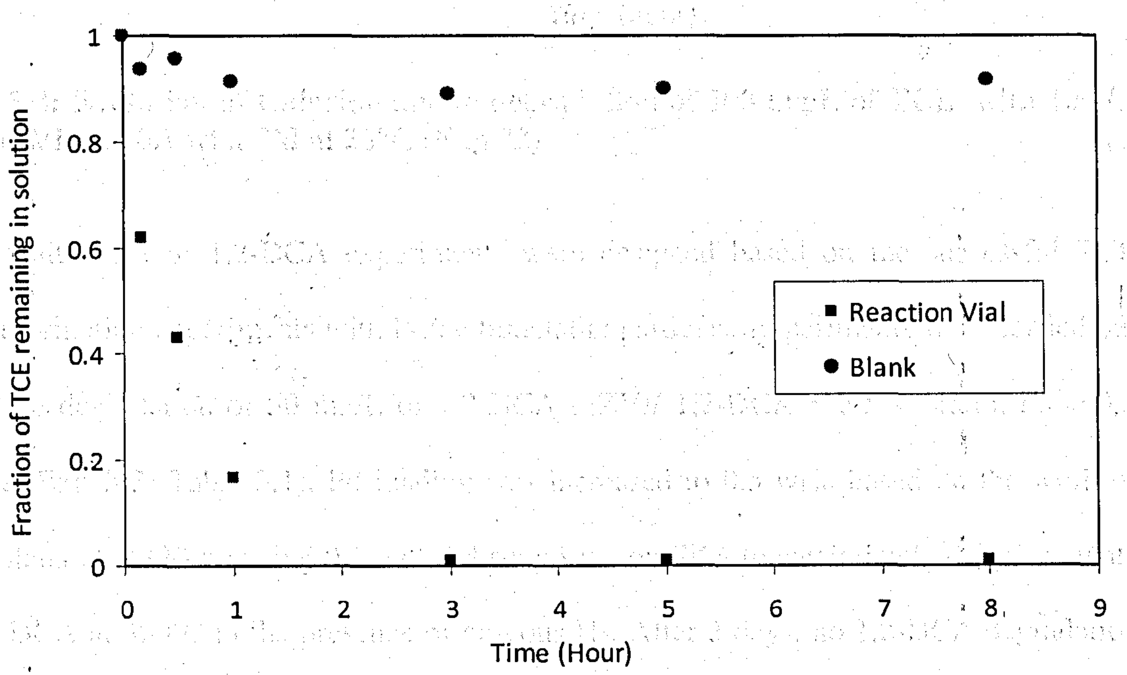

Fig 3.3: Degradation of 100 mg/L of TCE with 1.5g/L of nZVI and 0.1 wt% Pd at 25°C (Exp #2)

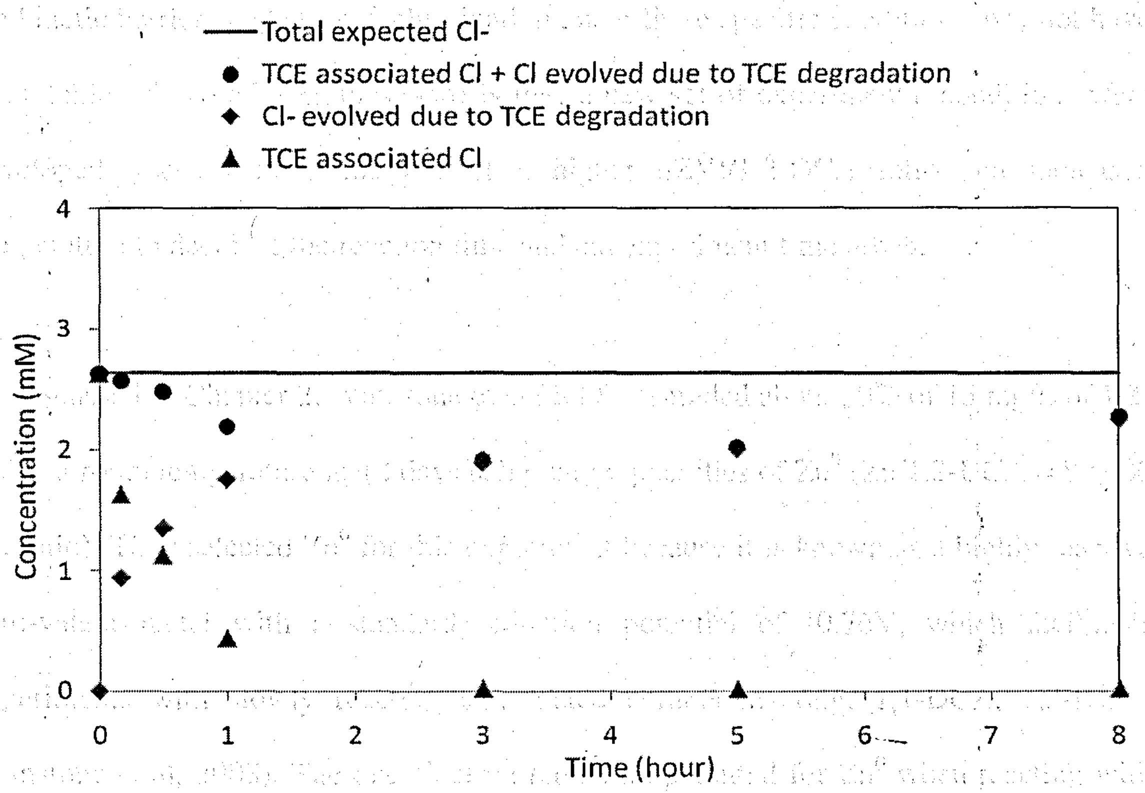

Fig 3.4: Evolution of Chloride due to degradation of 100 mg/L of TCE with 1.5g/L of nZVI and 0.1 wt% Pd at 25°C (Exp #2)

The initial set of 1,2-DCA experiments were designed based on the successful TCE dechlorination experiments with Pd/Fe bimetallic particles. Experiments were carried out for the degradation of 50 mg/L of 1,2-DCA (nZVI/ 1,2-DCA = 30 wt. ratio, Pd = 0.5 wt%, Exp # 3, Table 3.1). Pd loading was increased to 0.5 wt% based on the work of Orellana et al (2005) using 0.5 wt% Pd supported on SiO_2 to catalytically dehydrogenate 1,2-DCA at 300°C in the presence of gaseous H_2. After 3 days, no 1,2-DCA degradation was observed in this experiment. This unsuccessful result might be due to a lower nZVI/1,2-DCA ratio, compared to Lien and Zhang (2005) (where, nZVI/1,2-DCA = 250 wt. ratio, though this high ratio was unable to degrade 1,2-DCA). It should also be noted that the temperature used here was much lower than Orellana et al (2005) used. As such the kinetic barrier needed for dechlorination under these specific conditions may not have been achieved. To address these two issues, a new set of experimental conditions were developed; these include the use of a higher nZVI/1,2-DCA ratio and increased temperature to decrease the reaction time and cut experiment time down.

As discussed in Chapter 2, Vanstone et al (2008) degraded about 30% of 15 mg/L of 1,2-DCA at room temperature in 12 days using large quantities of Zn^0 (Zn/1,2-DCA = 80,000 wt. ratio). They selected Zn^0 for this experiment because it is known as a highly reactive zero-valent metal with a standard reduction potential of -0.76V, which facilitates experiments with slowly reacting chlorinated compounds (e.g. 1,1-DCA, 1,2-DCA) (Vanstone et al, 2008). The one electron reduction potential for Zn^0 when reacting with 1,2-DCA is -0.558V at {Cl-} =1mM in the presence of all other species at unit activity (Arnold et al, 1999). However, Zn^0 becomes easily oxidized in the sub-surface affecting its dechlorination capacity (Wang et al, 2010). Moreover, the use of Zn^0 in the field is limited as it releases Zn^{2+}, a harmful metal ion (Vanstone et al, 2008). On the other hand, the application of nZVI to dechlorinate COCs is a preferred option due to its high efficiency and environmentally benign nature; though the reduction potential for the reaction between 1,2-DCA and nZVI was not quantified because of its resistance to nZVI reactivity. Furthermore, Pd doped nZVI corrodes at a lower rate than Zn^0 (Wang et al, 2010). The use of Pd together with Fe^0 reduces the activation energy for dechlorination. For instance, for dechlorination of PCE with nZVI, the activation energy is 44.9 kJ/mol whereas, the use of Pd/Fe reduces the activation energy to 31.1 kJ/mol (Lien and Zhang, 2007). Therefore, instead of Zn^0, in this study Pd/Fe bimetallic nZVI has been selected.

Since Vanstone's results indicate that a very large excess of reductant is required to carry 1,2-DCA dechlorination, a set of experiments were designed using a high concentration of highly active bimetallic Pd/Fe particles (1,2-DCA= 5 mg/L, Fe^0/1,2-DCA = 4000 wt ratio, Pd = 0.2 wt%, Exp #4, Table 3.1), The result of this experiment is shown in Fig 3.5.

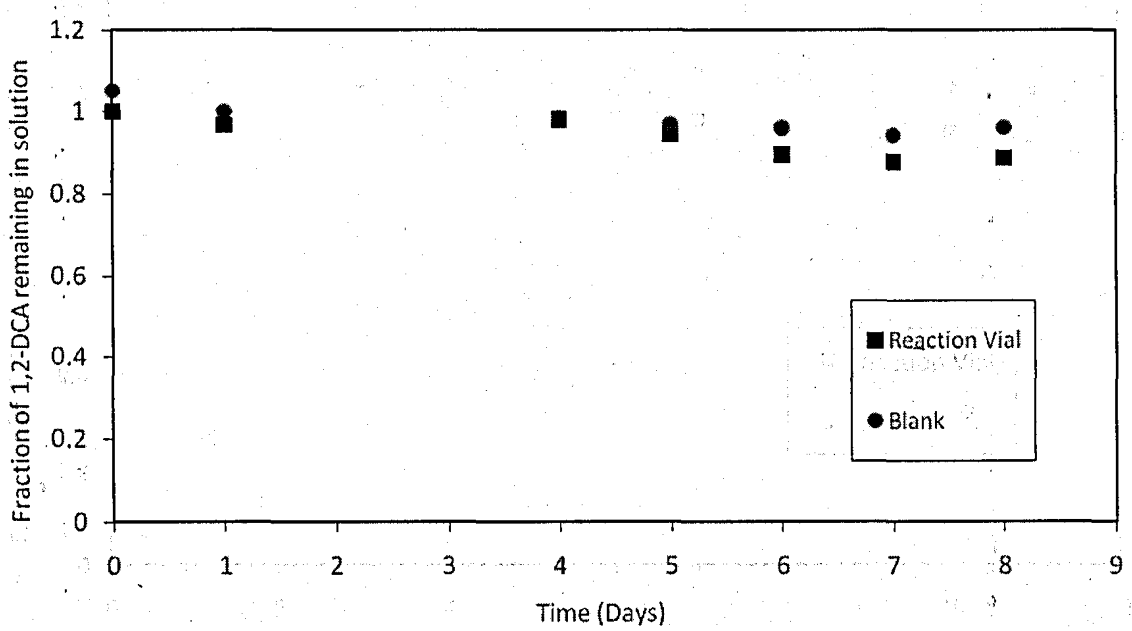

Fig 3.5: Degradation of 5 mg/L of 1,2-DCA with 20g/L of nZVI and 0.2 wt% Pd at 25°C (Exp # 4)

Comparison of 1,2-DCA in the reaction and blank vials suggests disappearance of 7% of the 1,2-DCA after 7 days; however no chloride was detected in the reaction vials. The amount of chloride that would have been evolved due to 7% of 1,2-DCA dechlorination is 0.125 mg/L; which is lower than the detection limit of the chloride analysis method used (0.5 mg/L). Hydrocarbons were not measured in this experiment. To confirm whether degradation was indeed taking place a second experiment under similar conditions was carried out; however, in this case, the 1,2-DCA concentration was doubled (1,2-DCA = 10 mg/L, Fe^0/1,2-DCA= 2000 wt ratio, Pd = 0.2 wt% Exp #5, Table 3.1). Here, 8% of the initial 1,2-DCA disappeared after 7 days (Fig 3.6) and ethane and propane were detected in the reaction vial as degradation products. This indicates that 1,2-DCA degradation was taking place, though at a relatively slow pace.

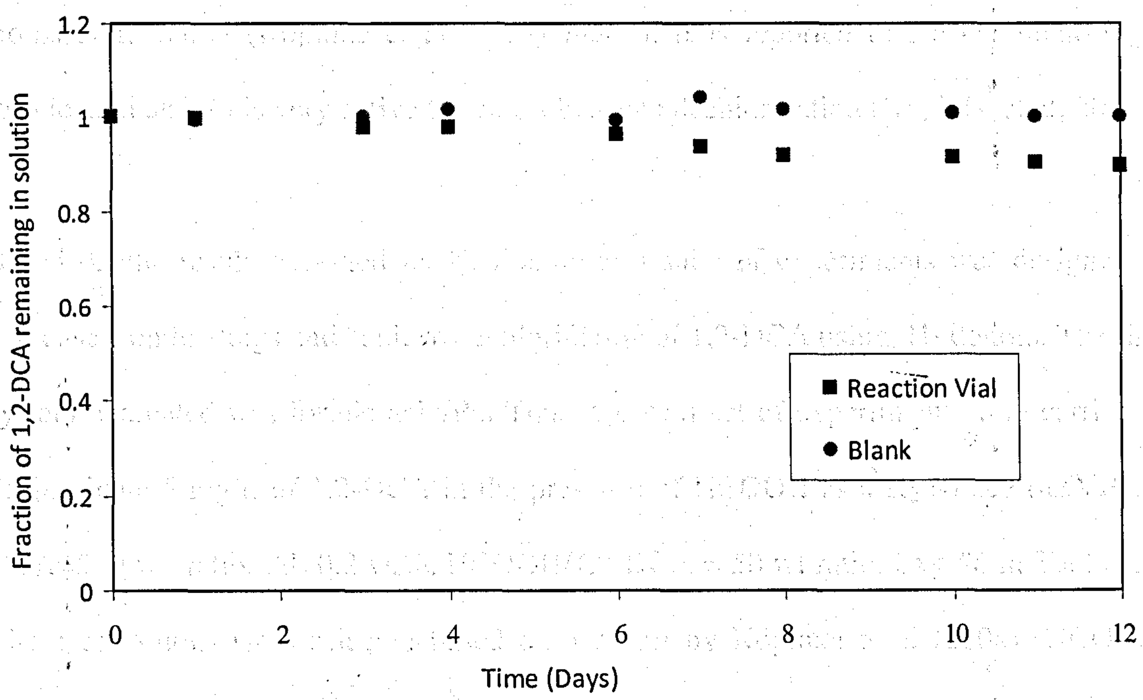

Fig 3.6: Degradation of 10 mg/L of 1,2-DCA with 20g/L of nZVI and 0.2 wt% Pd at 25°C (Exp # 5)

These results indicate that 1,2-DCA degradation can be achieved using Pd doped nZVI particles at relatively high loadings (e.g., nZVI/1,2-DCA= 2000 wt. ratio, nZVI= 20g/L), which is rather high compared to typical field applications that can go as high as 10 g/L. Given this, alternate nanometal formulations that include the addition of different hydrogen donors and catalysts were explored to lower nZVI loadings while increasing dechlorination rates.

3.5.2 Formic Acid as H_2 Source

Previous reports indicate that formic acid (HCOOH) is an efficient H_2 donor under acidic and neutral conditions (Kopinke et al, 2004). When formic acid is used together with Pd for dechlorination it has been observed that the relatively slow hydride mechanism dominates while under acidic or neutral conditions the fast radical mechanism through H atoms is favoured (Kopinke et al, 2004) Indeed, it is reported that a combination of formic acid and Pd is very active for chlorobenzene dechlorination (Kopinke et al, 2004).

Based on the results reported in the literature, a suite of experiments was designed to decrease iron loadings and achieve dechlorination of 1,2-DCA using H_2 donors. The first system evaluated was formic acid/Pd. Thus, the next set of experiments were carried to dechlorinate 5 mg/L of 1,2-DCA in the presence of HCOOH as a H_2 source (nZVI/1,2-DCA=500 wt. ratio, Pd=0.2 wt%, HCOOH/1,2-DCA = 50 wt ratio, Exp #6 in Table 3.1) These conditions were selected based on a report by Kopinke et al (2004) (HCOOH/ Chlorobenzene = 45 wt ratio, Pd/Al_2O_3= 0.5 wt.%, 23°C). Our results using this formulation (Fig 3.7) show that at the end of 7 days, around 7% dechlorination of 1,2-DCA was achieved in the presence of HCOOH. This is similar to the results obtained in Exp #5 which required large ratios of nZVI/1,2-DCA (2000 wt. ratio) and definitely offers a better and more economic methodology. The presence of ethane and propane in the headspace analysis of reaction vial confirmed the degradation as no hydrocarbons were detected in the blank vials. A chloride analysis was unsuccessful because of interference by formate ions.

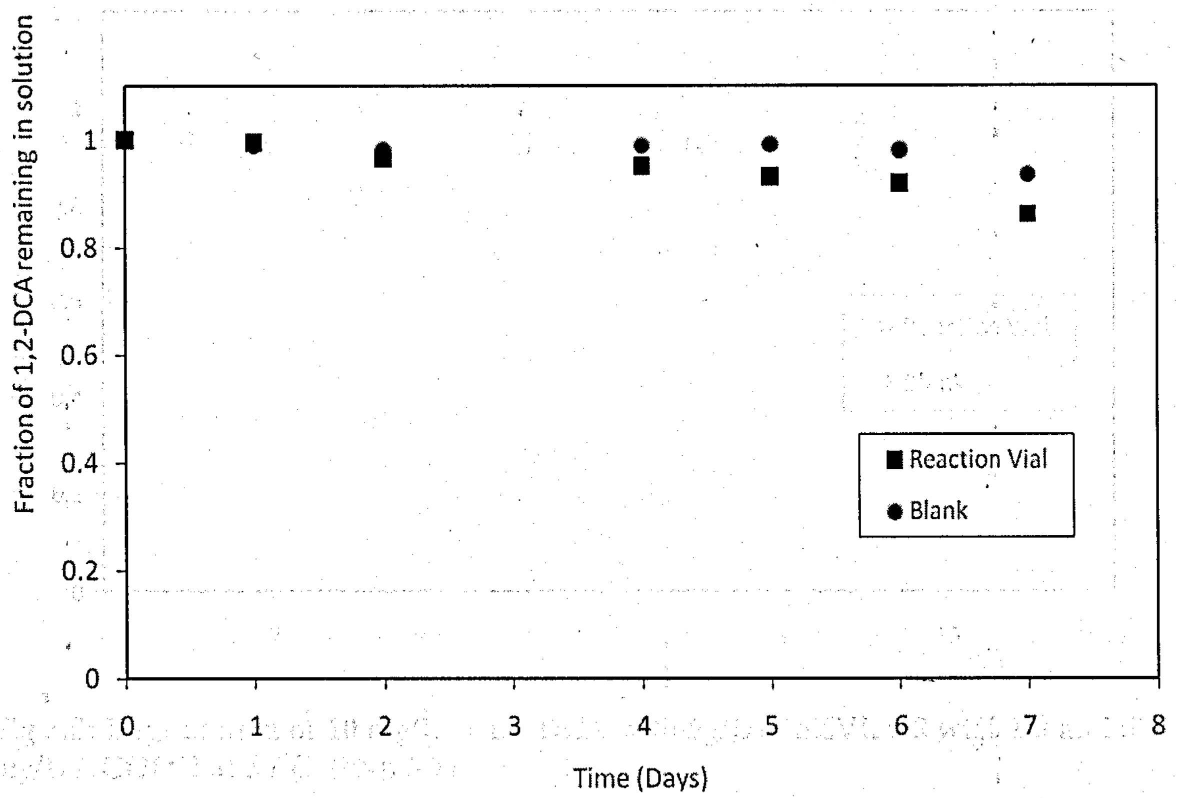

Fig 3.7: Degradation of 5 mg/L of 1,2-DCA with 2.5g/L of nZVI, 0.2 wt% Pd and 250 mg/L HCOOH at 25°C (Exp # 6)

To get a faster rate of dechlorination, the reaction temperature was increased to 35°C. (1,2-DCA=10 mg/L, nZVI/1,2-DCA=500 wt ratio, Pd=0.2 wt%, HCOOH/1,2-DCA=50 wt ratio, Exp #7 in Table 3.1 and Fig 3.8). At the end of 7 days, 11% degradation was observed (compared to 7% observed when running the same experiment at 25°C).

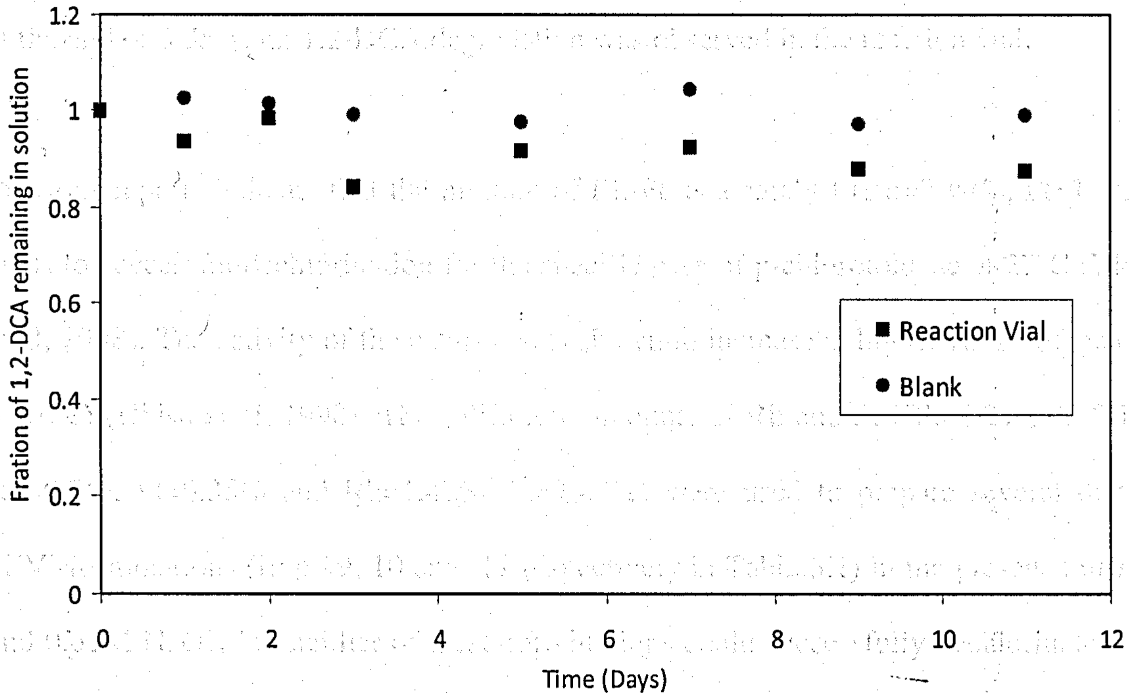

Fig 3.8: Degradation of 10 mg/L of 1,2-DCA with 5g/L of nZVI, 0.2 wt% Pd and 500 mg/L HCOOH at 35°C (Exp # 7)

3.5.3 Optimization of Experimental Conditions

The experiments done so far showed that when HCOOH was used as a hydrogen source and Pd as a catalyst with nZVI at a temperature of 35°C, it was possible to degrade 1,2-DCA up to 11% at the end of 7 days. The next objective was to optimize the experimental conditions to get even better results. For that purpose, instead of HCOOH, isopropanol was selected as hydrogen source. This selection was based on a study done by Ukisu et al (1997) where 2-propanol was used as a hydrogen donor in the presence of NaOH and Rh as catalysts to dechlorinate chlorobenzene. This system displayed the ability to fully degrade chlorobenzene within 3 hours. Based on this specific results we attempted to use Rh-doped Fe nanoparticles for 1,2-DCA degradation (1,2-DCA=10 mg/L, nZVI/1,2-DCA= 1000 wt ratio, Rh=0.5 wt%, reaction medium isopropanol (IPA), NaOH/Cl^-=3 molar ratio, Exp # 8 in Table 3.1). The reaction temperature was kept at 35°C. However, at the end of 5 days, no 1,2-DCA degradation was observed in the reaction vial.

Previous reports indicate that the mixture of Rh-Pt as a catalyst (Rh=2 wt%, Pt=1 wt%) leads to successful dechlorination for the specific case of p-chlorotoluene at 27°C (Ukisu et al, 1998). The activity of the catalyst was shown to increase at higher Rh loadings (1 – 3 wt.%) (Ukisu et al, 1998). Thus, different amounts of Rh and Pt (Rh=0.2%, Pt=0.1%; Rh=0.7%, Pt=0.35% and Rh=1.42%, Pt=1.42%) were used to prepare several doped-nZVI formulations (Exp #9, 10 and 11 respectively in Table 3.1) in the presence of IPA and 0.61M NaOH but neither of these formulations could successfully dechlorinate 1,2-DCA (Appendix A). Ukisu et al (1998) have proposed that dechlorination activity is intimately linked to H_2 transfer and adsorption efficiencies. Therefore it can be proposed that the activation of H_2 by Rh and Pt might not be as efficient as that of Pd, leading to poor results in 1,2-DCA dechlorination.

Another nZVI formulation containing 0.2 wt% Pd, 0.2 wt% Rh and 0.1 wt% Pt was tested as well. In this particular case HCOOH was used as hydrogen donor for the catalytic hydrodechlorination of 10 mg/L of 1,2-DCA at 35°C (nZVI/1,2-DCA= 1000 wt ratio, Exp #12 in Table 3.1) instead of IPA. This particular formulation yielded 12% degradation of 1,2 DCA at the end of 7 days (Fig 3.9). This result is very similar to Exp # 7 suggesting that dechlorination takes places due to the presence of HCOOH and Pd rather than due to the use of Pt and Rh in this formulation. To confirm this, Exp#16 (nZVI/1,2-DCA= 1000 wt ratio, 0.2 wt% Pd, HCOOH= 500 mg/L, Table 3.1) was done and 12% degradation was found after 7 days supporting the result of Exp # 12 (Appendix A).

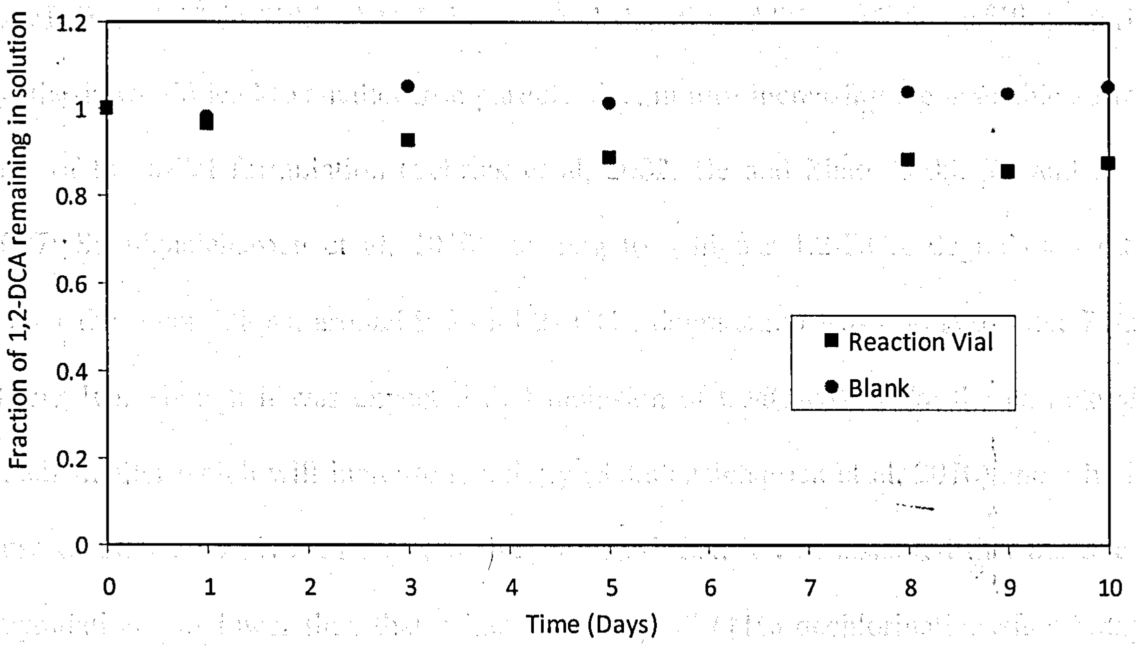

Fig 3.9: Degradation of 10 mg/L of 1,2-DCA with 10g/L of nZVI, 0.2 wt% Pd, 0.2 wt% Rh, 0.1 wt% Pt in 500 mg/L HCOOH at 35°C (Exp # 12)

Thus, up to this point, our results indicate that the most active formulation is nZVI/1,2-DCA=500 wt. ratio, Pd=0.2 wt% and HCOOH/1,2-DCA=50 wt ratio (Exp# 7, Table 3.1). Our next step was to improve the observed reaction rates through stabilization of the iron nanoparticles. It is well known that nZVI particles have tendency to form larger flocs and induce agglomeration which in turn, decreases reactivity. Several stabilizers have been used with nZVI to diminish agglomeration, decrease particle size and therefore increase reactivity (Ponder et al, 2001; He and Zhao, 2005; Saleh et al, 2007; He and Zhao, 2007). Among different stabilizers, carboxymethyl cellulose (CMC) has been proved to be the most effective (He and Zhao, 2007). As a result, the next set of experiments for this project was conducted using CMC stabilized Pd/Fe bimetallic particles in the presence of HCOOH along with increasing the Pd content to 0.5%.(1,2-DCA=10 mg/L, nZVI/1,2-DCA=500 wt ratio, Pd=0.5 wt% HCOOH/1,2-DCA=50 wt ratio, CMC (90K) 1.5 wt% of nZVI, Exp # 13 in Table 3.1) It is expected that the addition of the stabilizer during synthesis would lead to smaller iron particle size, in turn increasing the available surface area of the nZVI formulation (Schrick et al, 2002; He and Zhao, 2005; He and Zhao, 2007; Sakulchaicharoen et al, 2010), leading to a higher 1,2-DCA degradation rates. Under these conditions, around 9% of 1,2- DCA degradation was observed after 7 days (Fig 3.10). Though it was expected that inclusion of CMC will make the particle size much smaller which will increase reactivity (Sakulchaicharoen et al, 2010) and a higher dose of Pd would give a faster reactivity of 1,2-DCA, it was observed that the rate of degradation was lower than that achieved in Exp #7 (11% dechlorination after 7 days) where no CMC was added. The failure of CMC to increase reactivity can be rationalized using the explanation by Phenrat et al (2009) who proposed that when stabilizers are adsorbed on nZVI surfaces, reactivity is decreased primarily due to blocking of the iron active sites. On the other hand, according to Wang et al (2009) though an increase in Pd loading increases the rate of dechlorination, this is true only at loadings below 0.2% Pd weight. A further increase in Pd content might hinder Fe^0 corrosion and thus hydrogen formation by covering the active reactive sites of nZVI particles (Wang et al, 2009). Unfortunately no experiments were done without CMC and with Pd=0.2% at 45°C keeping all other experimental conditions same to confirm the role of temperature on increase in reactivity.

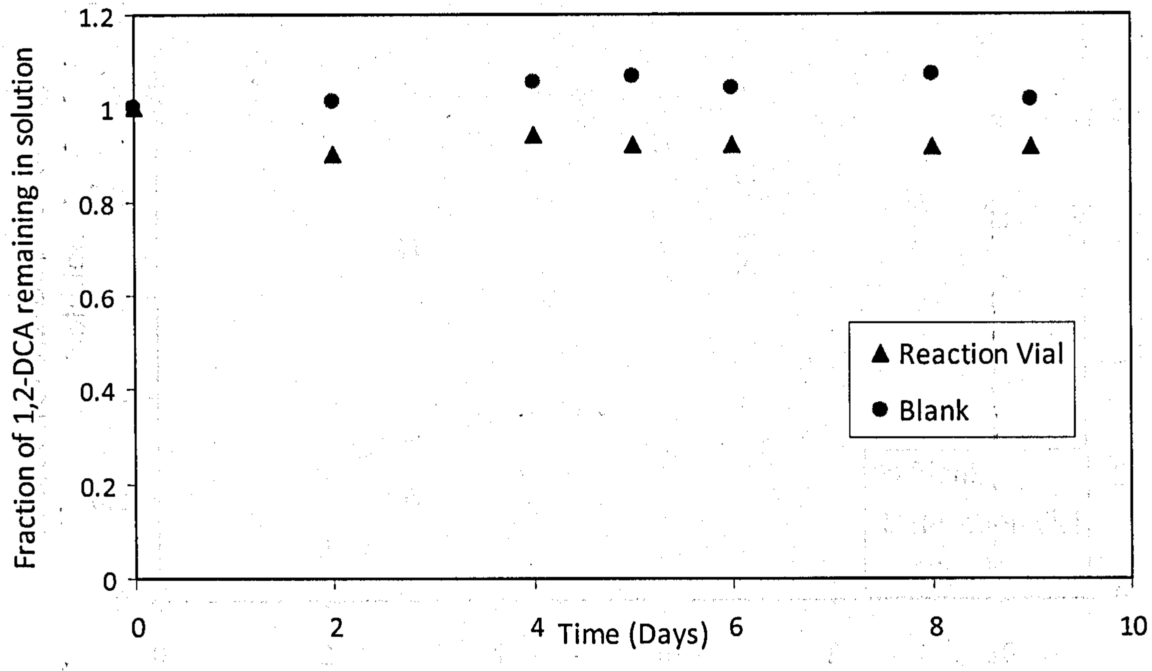

Fig 3.10: Degradation of 10 mg/L of 1,2-DCA with 1.5% CMC stabilized 5g/L of nZVI, 0.5 wt% Pd, in 500 mg/L HCOOH at 25°C (Exp # 13)

The next set of experiments was carried out at 45°C, while keeping all other experimental conditions unchanged (Exp #15, Table 3.1), to check if increase in temperature could improve the rate of degradation.

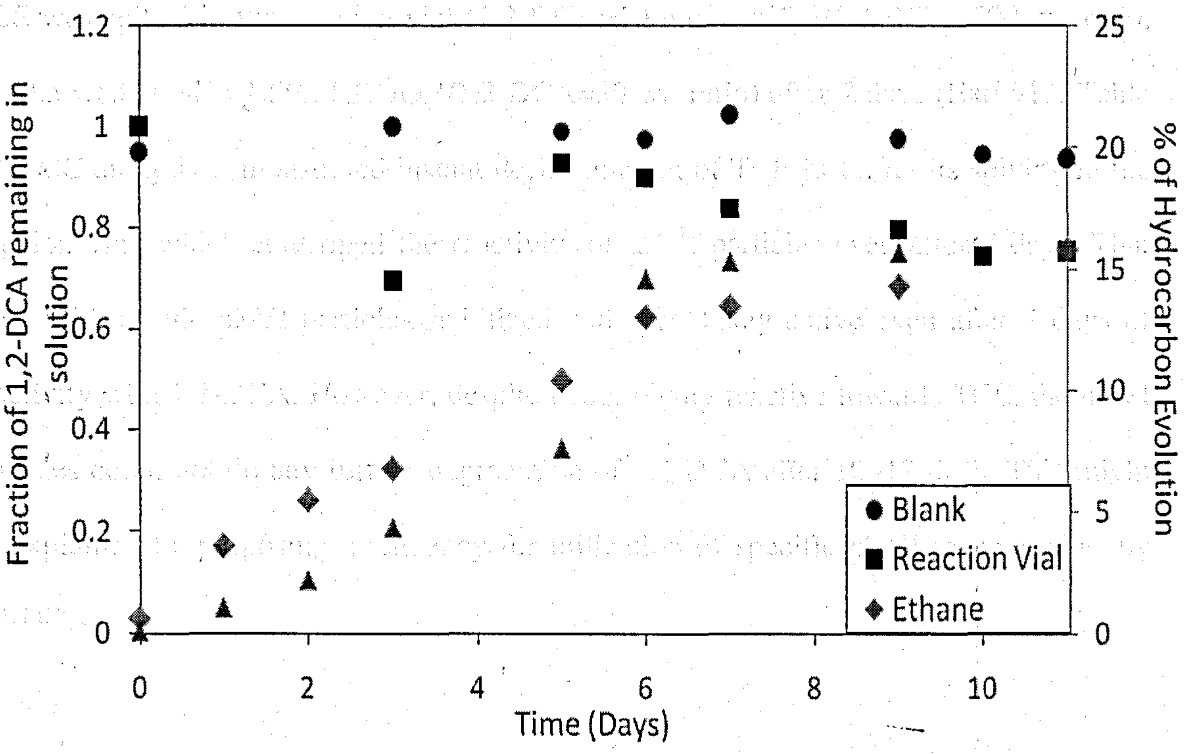

Fig 3.11: Degradation of 10 mg/L of 1,2-DCA with 1.5% CMC stabilized 5g/L of nZVI, 0.5 wt% Pd, in 500 mg/L HCOOH at 45°C (Exp # 15)

Fig 3.11 shows the results of this experiment. 17% of 1,2-DCA degradation was observed at the end of 7 days. A replicate of this experiment was done at the same time which also gave 17% degradation (Appendix F). To the best of our knowledge, this is the first time in which significant degradation of 1,2-DCA using nZVI has been achieved. The dechlorination reaction lead to the formation of ethane and propane as degradation products from the very first day of reaction; the amount of these gases increased as dechlorination progressed (Fig: 3.11). However, no vinyl chloride was present in the reaction vial.

Since the experiments continued up to 10~12 days, it was necessary to check the reactivity of nanoscale iron particles towards the end. For that purpose, about 10 mg/L of

TCE was spiked in the reaction vial (1,2-DCA=10 mg/L, nZVI/1,2-DCA=500 wt. ratio, Pd=0.5 wt%, CMC=1.5%, HCOOH/1,2-DCA=50 wt. ratio) after 7 days (Exp #13, Table 3.1). GC analysis demonstrated instant dechlorination of TCE just after its spiking in the reaction vial, which confirmed the reactivity of nZVI particles even after 7 days. That means, bimetallic nZVI particles stabilized with CMC stay active even after 7 days of reactivity with 1,2-DCA. However, despite being highly reactive towards TCE, the nZVI particles could not do any further degradation of 1,2-DCA after 10~12 days. This might be explained by proposing a tendency for utilization of specific nZVI reactive sites by 1,2-DCA.

3.5.4 Degradation pathways during the dechlorination of 1,2-DCA

According to our results it can be concluded that the combination of nZVI, Pd as catalyst, HCOOH as hydrogen source, CMC as stabilizer at a temperature of 45°C (1,2-DCA=10 mg/L, nZVI/1,2-DCA=500 wt. ratio, Pd=0.5 wt%, CMC=1.5%, HCOOH/1,2-DCA=50 wt. ratio Exp #15, Table 3.1) produced the best performance of all experiments done to dechlorinate 1,2-DCA. The dechlorination of 1,2-DCA evolved about 44% of ethane and 56% of propane (Fig:3.11). After 7 days, a very small amount of ethylene, propylene, butane and butylene were also observed as coupling products. The observed formation of ethane is consistent with previous reports where it has been demonstrated that the use of Pd with nZVI as a catalyst for dechlorination of C2 halocarbons yields ethane (Lien and Zhang, 2005) Moreover, catalytic hydrodechlorination of 1,2-DCA also forms ethane as an end product when only Pd is used as catalyst (Kovalchuk et al, 2004; Orellana et al, 2005). Arnold et al (1999) have proposed a scheme for the dechlorination of vicinal (a term used to describe the location of two identical atoms which are bonded to adjacent carbon atoms) chloroethanes and chlorinated ethylenes with Zn^0. According to their hypothesis, reductive β-elimination is the only pathway through which species containing the requisite α, β pair of chlorine atoms react with Zn^0. Therefore, the pathway of 1,2-DCA degradation on highly reactive Zn^0 is reductive β-elimination (vicinal elimination) involving net transfer of two electrons to the organohalides and the net loss of two nucleophiles (Cl^-) from neighbouring atoms (Fig 3.12).

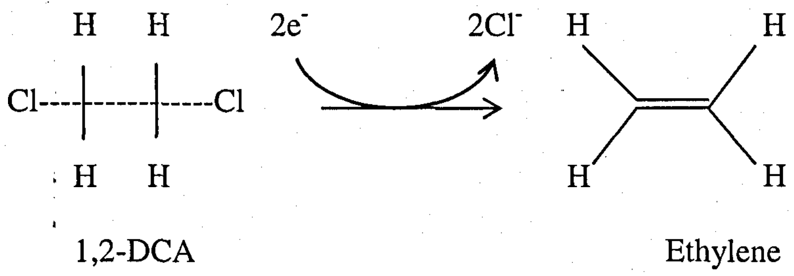

Fig 3.12: Dechlorination of 1,2-DCA (Ref: Vanstone et al, 2008).

However, ethylene was not observed during the first 6~7 days in our experiment. This can be explained based on the fact that Arnold et al (1999) used Zn^0 without any catalyst, while in our case Pd, a very powerful hydrogenation catalyst was used. It is plausible to hypothesize that though ethylene was formed through β-elimination, it was immediately hydrogenated by the Pd catalyst. However, the pathway for the formation of propane has not been explained in the literature. In case of one molecule of ethane production, 2 hydrogen replaces 2 chloride ions from one molecule of 1,2-DCA. Whereas, it might be proposed that, when the degradation product is propane, 4 hydrogen replaces 4 chloride ions from 3 molecules of 1,2-DCA and forms 2 molecules of propane. Since both ethane and propane are evolved from the very first day of degradation, it plausible to assume that propane is not coming from ethane.

Figure 3.13 shows a proposed reaction scheme that can be used to rationalize the observed results we obtained for dechlorination of 1,2-DCA with Pd/Fe in the presence of HCOOH:

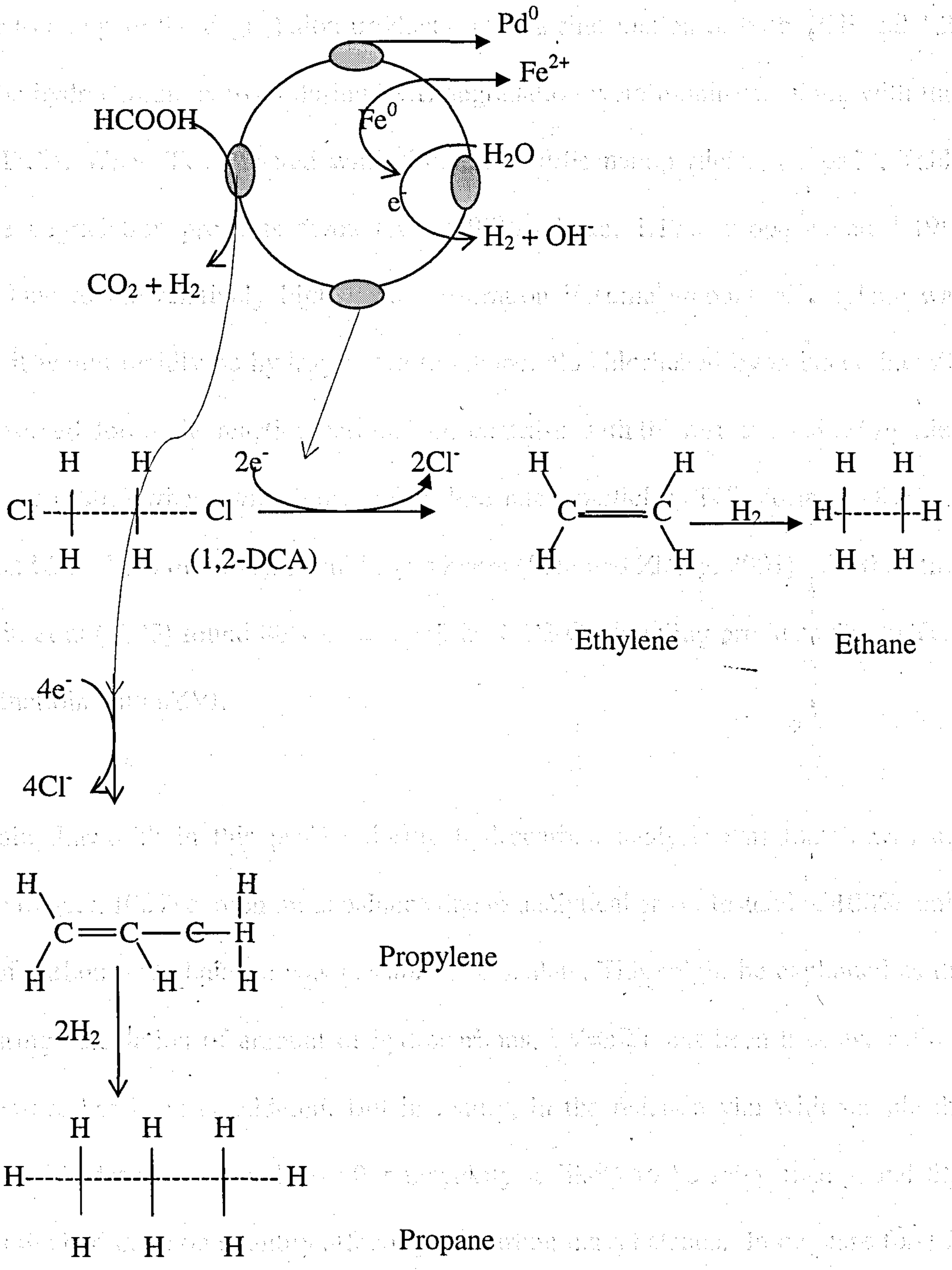

Fig. 3.13: Proposed 1,2-DCA transformation pathway while reacting with bimetallic Pd/Fe and HCOOH.

In order to compare the degradation products from dechlorination of both TCE and 1,2-DCA, the hydrocarbon evolved during TCE degradation were monitored along with that for 1,2-DCA. When TCE reacted with bimetallic Pd/Fe nanoparticles, (Exp#14, Table 3.1), the degradation products formed were 97% ethane, 1.17% propane and 1.19% butane. Due to the relatively high Pd concentration if some amount of ethylene was formed, it would rapidly be hydrogenated to ethane. No chlorinated byproducts like VC were observed during the reaction period. This contrasts with the results obtained by Lien and Zhang (2001) where with bimetallic Pd/Fe nanooparticles, TCE formed ~87% of ethane and 5.8~7.1% of ethylene within two hours (Lien and Zhang, 2001). On the other hand, Liu et al (2005) found 80% ethane and 20% C3-C6 coupling products due to TCE dechlorinatioin with nZVI.

One main drawback in this project during hydrocarbon analysis was that it was not possible to get a 100% carbon mass balance due to analytical error. Instead of 100%, only ~33% of carbon mass balance was possible to calculate. This might be explained as the fact, during calculation of amount of hydrocarbons, PV=nRT has been used were P= 1 atm pressure has been considered. But in reality, in the reaction vial with sample the pressure of hydrocarbons evolved after reactivity is likely to be more than 1 and that changes the hydrocarbon quantity affecting the carbon mass balance. In our case for 1,2-DCA dechlorination ethane comprised ~44% of the observed degradation products whereas for TCE, ethane was the main product covering (97% of total the hydrocarbons generated at the end of reaction). On the other hand, for the case of 1,2-DCA degradation propane was the main end product (~56%). However, only 1.17% of TCE converted to propane.

3.6 SUMMARY AND CONCLUSIONS

The lower C-Cl bond dissociation energy (<47 Kcal/mole) of 1,2-DCA makes its dechlorination difficult in reductive environments. Nonetheless the thermodynamic free energy dechlorination value (-36.2 KJ/electrons) indicates that 1,2-DCA dechlorination is thermodynamically possible. Though different researchers report the inability of nZVI particles to dechlorinate 1,2 DCA, by exploring and adopting proper experimental conditions, 1,2-DCA can successfully be dechlorinated using nZVI formulations.

A very high concentration of nZVI (20g/L) catalyzed by 0.2 wt% Pd degraded 1,2-DCA by ~8% after 7 days of time. But this amount of nZVI is very high for field application. Therefore, to find a more convenient methodology, the combination of a hydrogen donor, nZVI and a catalyst was used. The use of formic acid as hydrogen donor with a lower concentration of nZVI (5g/L) and 0.2% Pd at 35°C was mildly successful in degrading 1,2-DCA (11% after 7 days). The reactivity was even higher (~18% after 7 days), when both the temperature and the Pd content were increased to 45°C and 0.5 wt% respectively and nZVI was stabilized using 1.5% CMC. It can be postulated that 1,2-DCA is breaking following dihaloelimination into ethylene and propylene; but due to the utilization of a high concentration of Pd, the ethylene and propylene get instantly hydrogenated into ethane and propane. Both ethane and propane evolve from the very first day of reaction and increase progressively.

In this study, the present nZVI based dechlorination methodology offers a 1,2-DCA degradation of about 17%. Therefore the future step of this study should be to improve the rate of degradation by modifying the current experimental approach. Through an improvement in the experimental conditions such using different hydrogen donors (e.g. formates instead of formic acid), maintaining a lower pH during the reaction period as well as raising the temperature might develop a better dechlorination methodology.

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4.0 SUMMARY AND RECOMMENDATIONS

4.1 SUMMARY AND CONCLUSIONS

Through a combination of nZVI, a hydrogen source, a hydrogenation catalyst, and a nZVI suspension stabilizer a suitable reductive environment to dechlorinate 1,2-DCA has been created. This particular approach can be applied in the field relatively easily since it requires neither high temperature nor gaseous hydrogen, unlike catalytic hydrodechlorination. In addition reaction times are fast meaning it will not take decades to centuries to breakdown 1,2-DCA, as required for subsurface microorganisms.

The results from this study indicate that:

- nZVI by itself cannot initiate 1,2 DCA dechlorination, even at unusually high Fe^0/1,2 DCA ratios. The presence of a hydrogenation catalyst is required in order to provide highly active hydrogen species able to carry out 1,2 DCA degradation.

- A hydrogen donor and a noble metal catalyst is required to decrease the amount of nZVI required to degrade 1,2-DCA. This is because, in the nZVI system, hydrogen generation occurs through Fe^0 corrosion that is used during the transformation of the chlorinated compounds into benign products. Introducing an efficient H_2 source along with an active hydrogenation catalyst can substitute a part of the hydrogen required from nZVI and reduce reticent organic halides through reaction with the active form of hydrogen adsorbed in the catalyst. This will need less excess iron making the process more economical.

- As demonstrated in this work when compared to the other catalysts (e.g., Rh and Pt) Pd is the most effective, removing chlorines from 1,2-DCA thus yielding ethane. Rh and Pt were unable to catalyze 1,2-DCA degradation despite the presence of another hydrogen source (i.e., isopropanol). This might be due to the inadequate activation of hydrogen by Rh and Pt for 1,2-DCA dechlorination.

- The degradation pathway observed for 1,2-DCA followed a β-elimination mechanism followed by a very rapid hydrogenation of the unsaturated products formed (e.g. ethylene and propylene) leading to the formation of ethane and propane.

4.2 RECOMMENDATIONS

This work found an appreciable amount of 1,2-DCA dechlorination using nanoscale zero-valent iron particles, which was, to date, almost impossible. After 7 days ~17% of the 1,2-DCA was dechlorinated and little additional was degraded up to 12 days. Under the existing experimental conditions this was the highest observed conversion. However, it can be proposed that by optimizing the experimental conditions, 1,2-DCA conversion can be increased even more. For that purpose, a number of steps can be taken for future work.

- Since hydrogen donor plays a vital role in the dechlorination of 1,2-DCA, a more appropriate hydrogen source could be examined. Some reports indicate that formate salts are superior to formic acid as hydrogen donors (Rajagopal and Spatola (1995). Therefore, a next step in improving 1,2 DCA dechlorination efficiency is to carry out the experiments using formate salts instead of formic acid (e.g., Cs and K).

- Since the rate of chemical reaction increases with an increase in temperature, the next step of the experiments in the lab can be carried over at higher reaction temperatures. This will help in reducing the duration of the experiments when evaluating different nZVI formulations.

- Another important factor controlling the reactivity is the pH. At low pH, Fe^0 corrosion is faster leading to the production of more hydrogen through reduction of water which can potentially increase the dechlorination rates. Therefore, if the pH can be controlled throughout the duration of the reactivity, that might help to improve the dechlorination rate.

APPENDIX A

Comparison of reactivity between 1,2-DCA and different catalysts

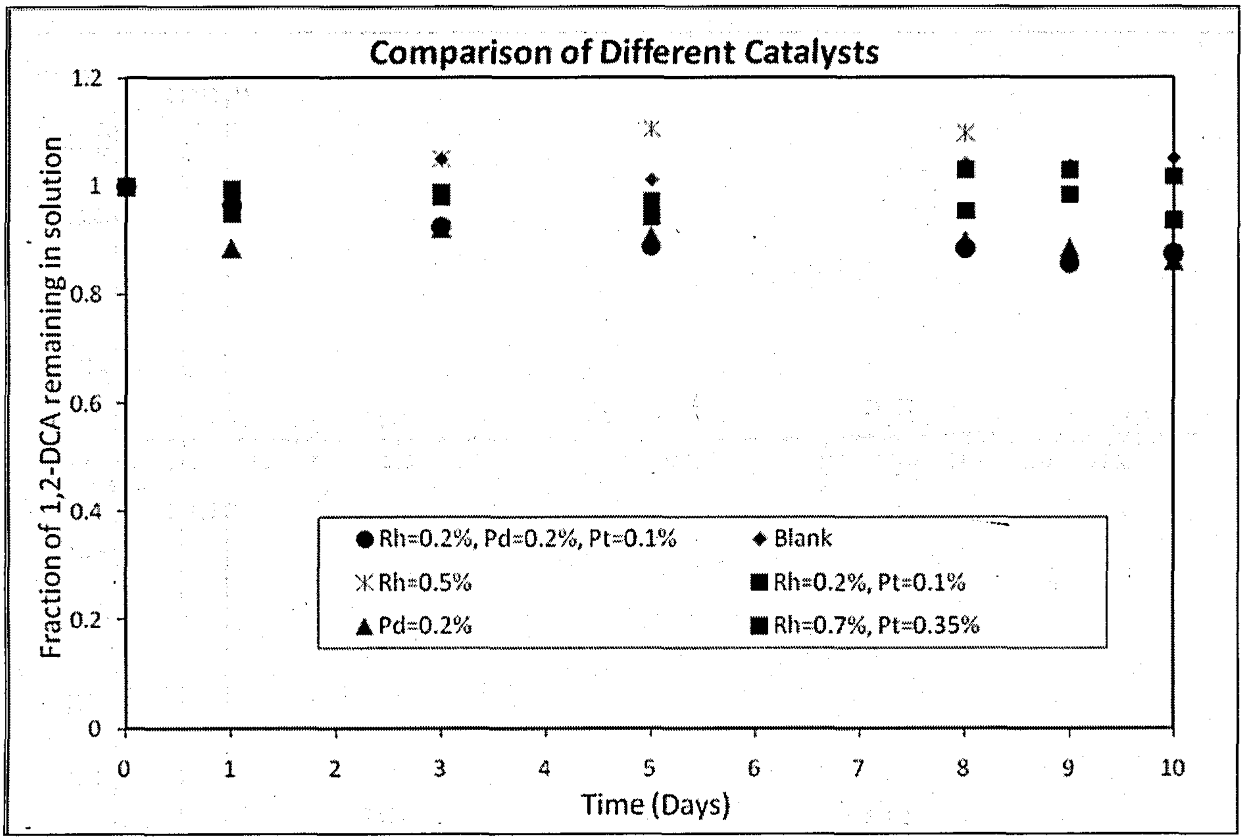

Figure A: Comparison of reactivity of different catalysts when nZVI=10 mg/L, 1,2-DCA=10 mg/L, temp=35°C i) Rh=0.5% 1% ii) Rh=0.2%, Pt=0.1%, iii) Rh=0.7%, Pt=0.35%, iv) Rh=0.2%, Pd=0.2%, Pt=0.1% v) blank

APPENDIX B

Chromatogram from GC/MS during dechlorination of 1,2-DCA

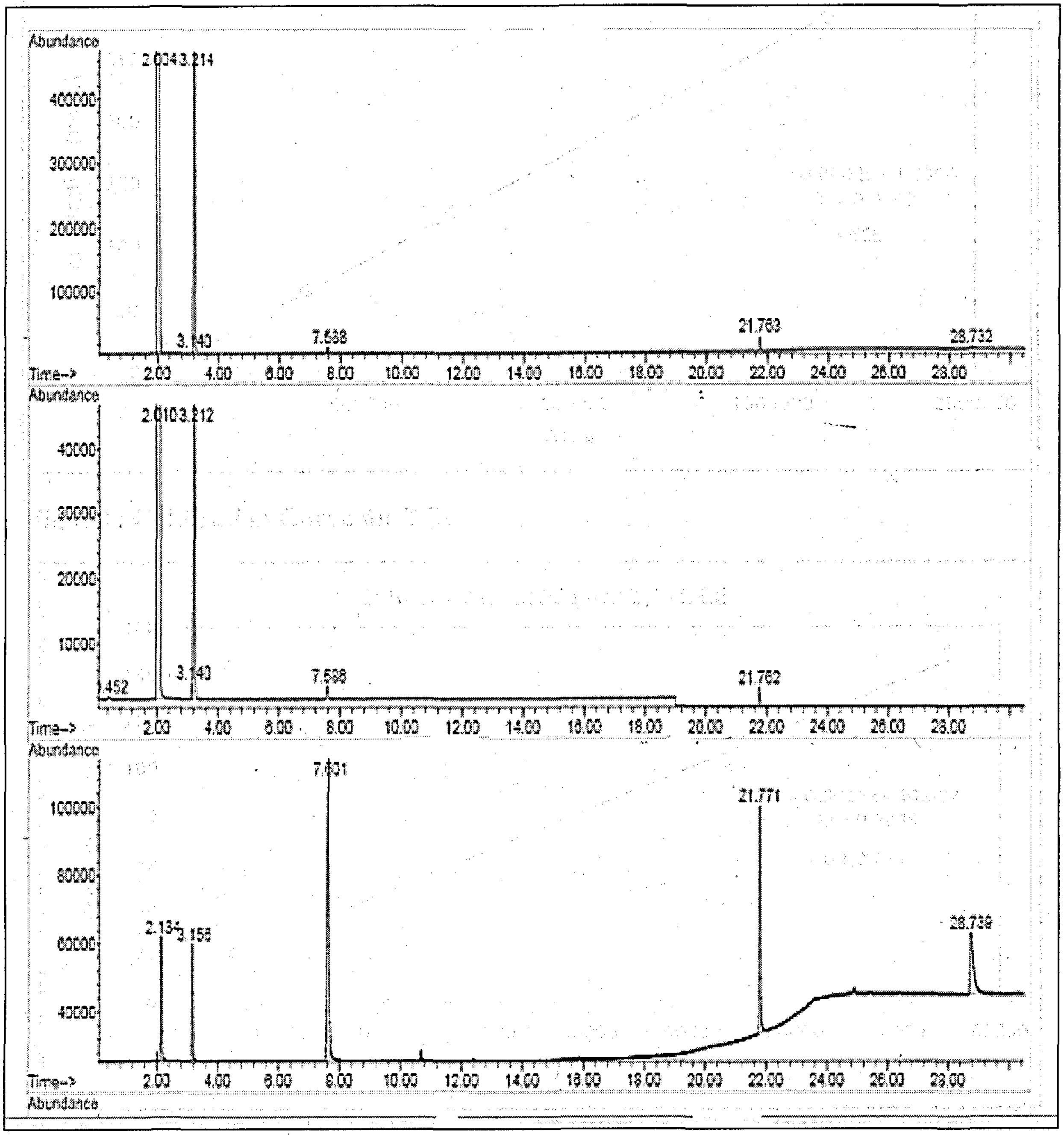

Fig B: Chromatogram for degradation products of 1,2-DCA:- retention time for i) ethane = 3.15 min ii) propane = 7.6 min, iii) 1,2-DCA

APPENDIX C

Calibration Curves for TCE and 1,2-DCE

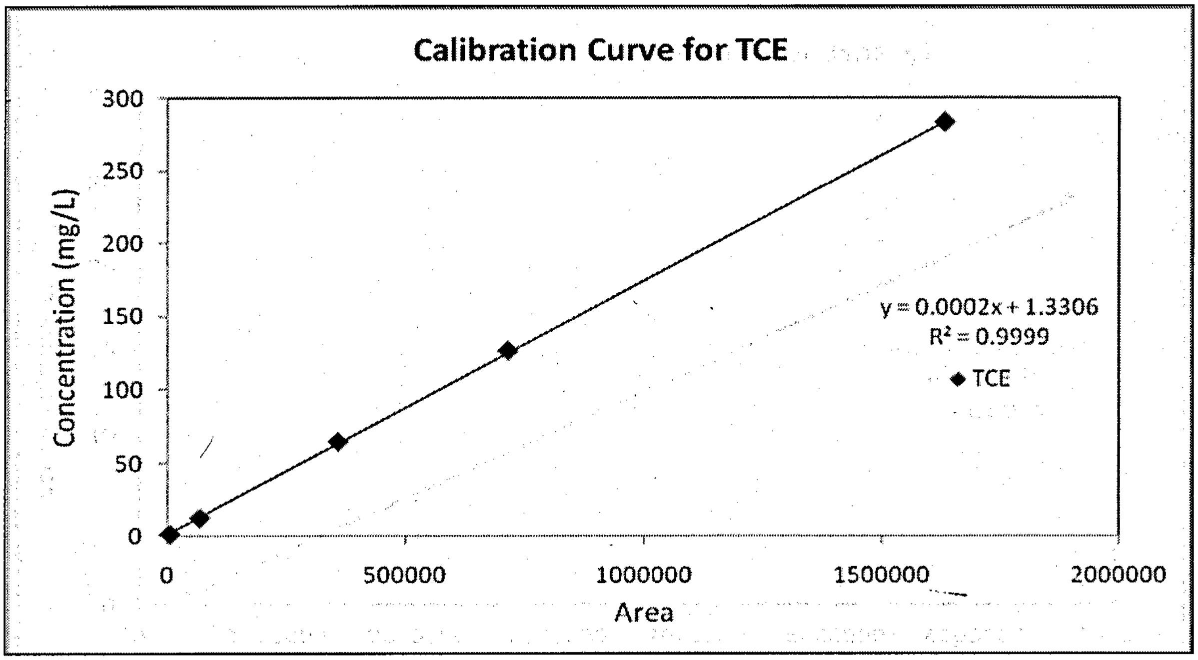

Fig C-1: Calibration Curve for TCE

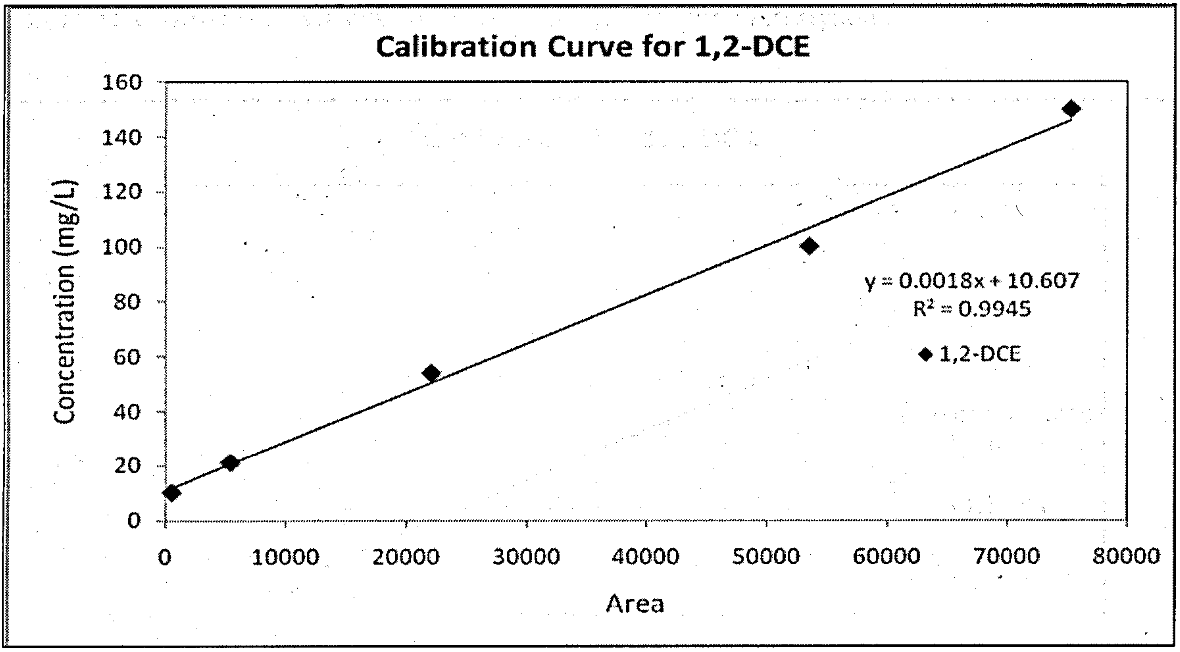

Fig C-2: Calibration Curve for 1,2-DCE

APPENDIX D

Calibration Curves for 1,2-DCA

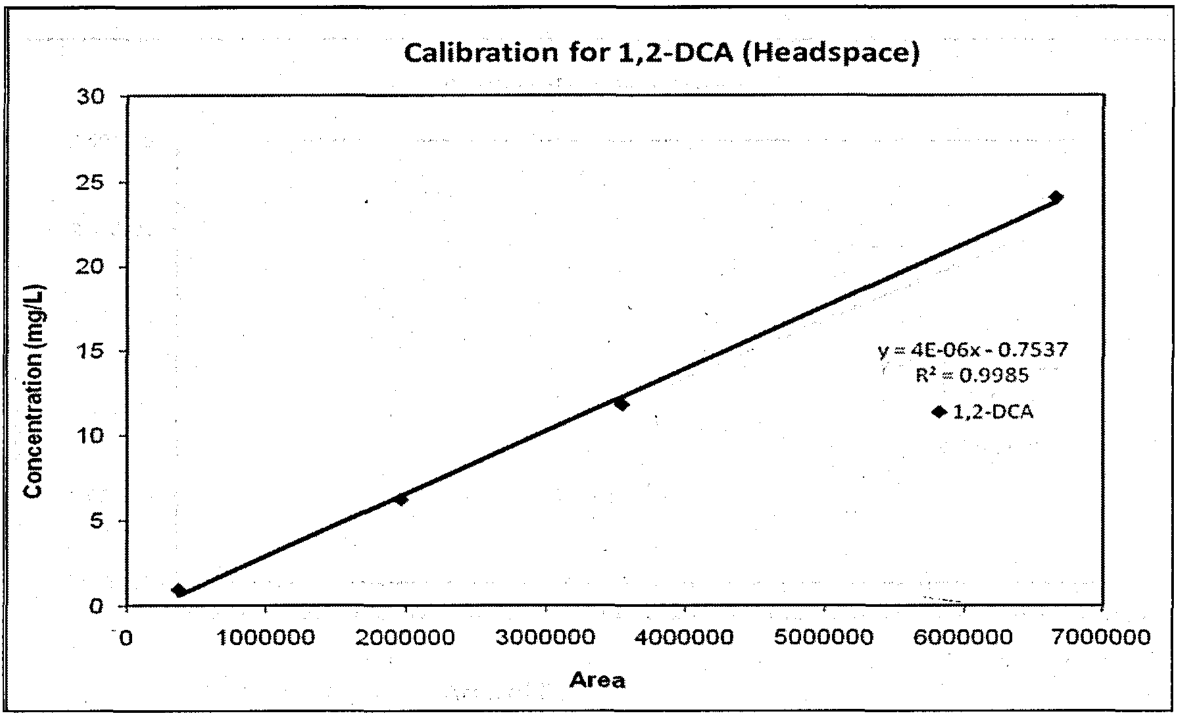

Fig D-1: Calibration Curve for 1,2-DCA (Headspace Analysis)

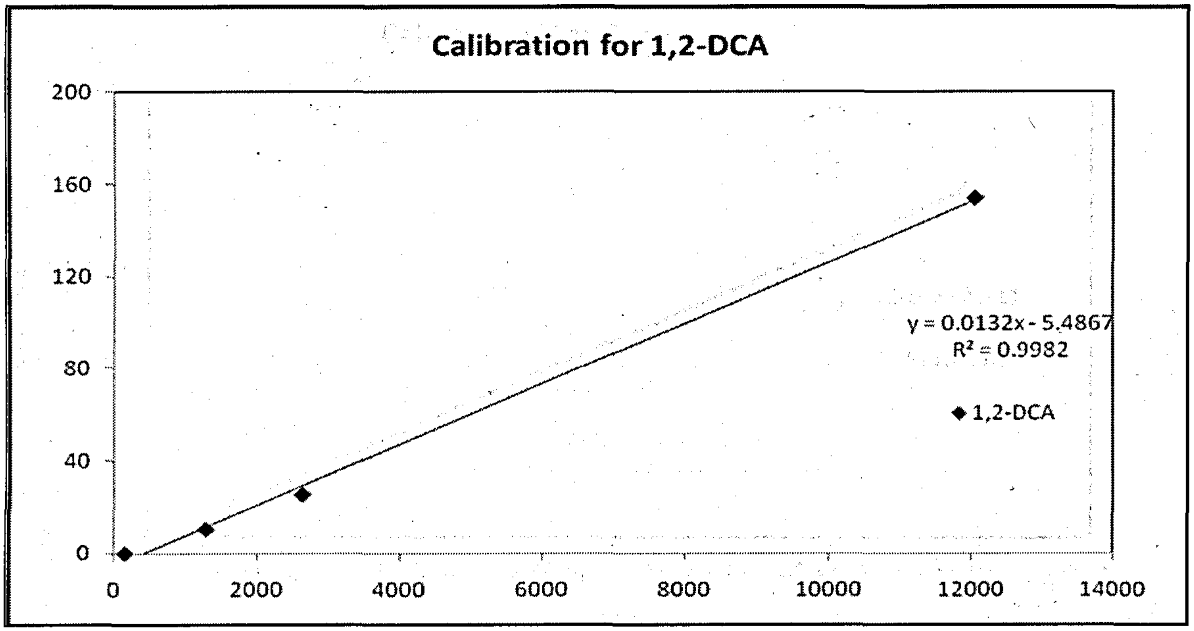

Fig D-2: Calibration Curve for 1,2-DCA (Liquid Analysis)

APPENDIX E

Calibration Curves for Hydrocarbons

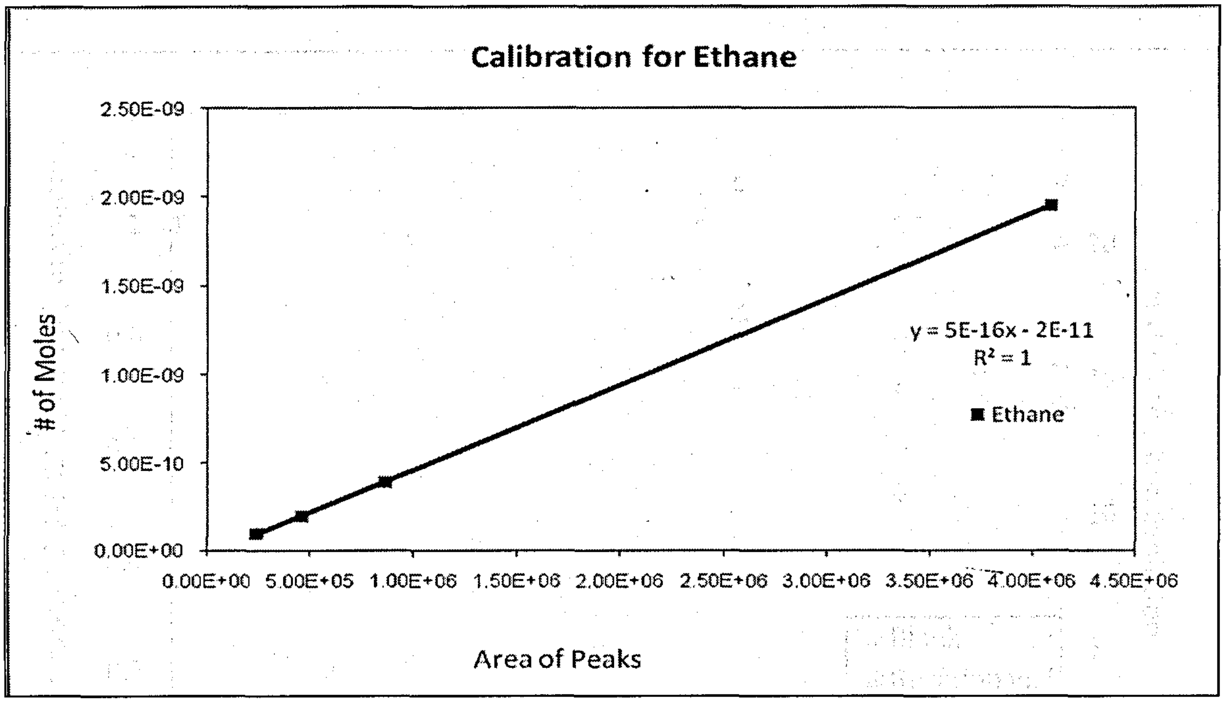

Fig E-1: Calibration Curve for Ethane (Headspace Analysis)

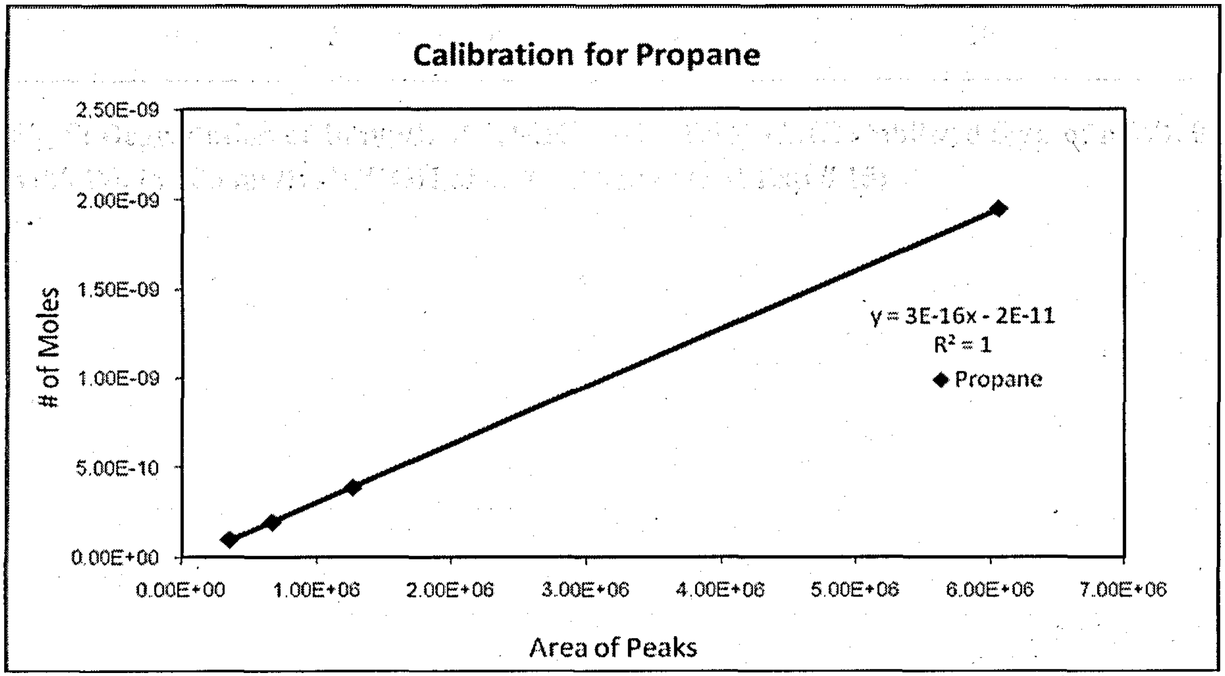

Fig E-2: Calibration Curve for Propane (Headspace Analysis)

APPENDIX G

Comparison of Experiment # 8 and 11

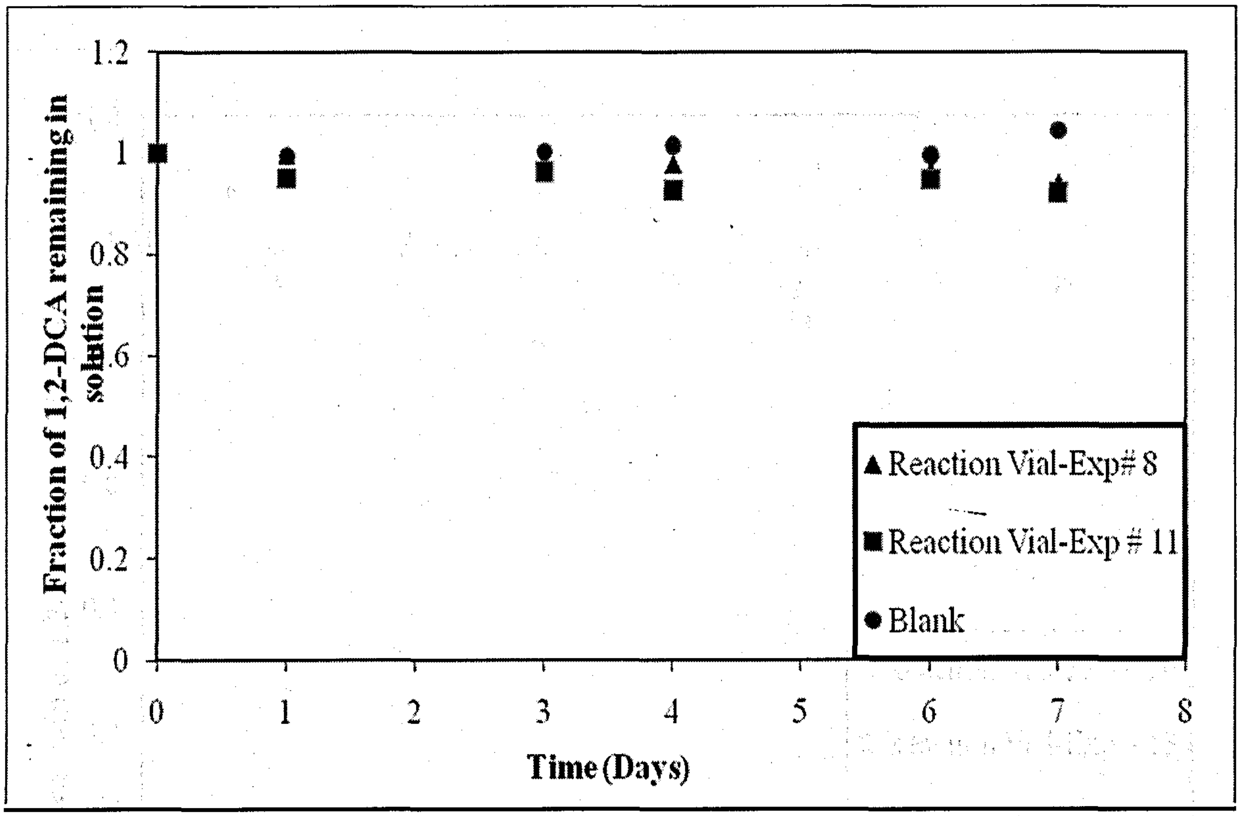

Fig G: Degradation of 10 mg/L of 1,2-DCA with 20g/L of nZVI, 0.2 wt% Pd, at 25°C (Results of Exp # 8 & 11)

APPENDIX H

Comparison of Experiment # 10 and 13

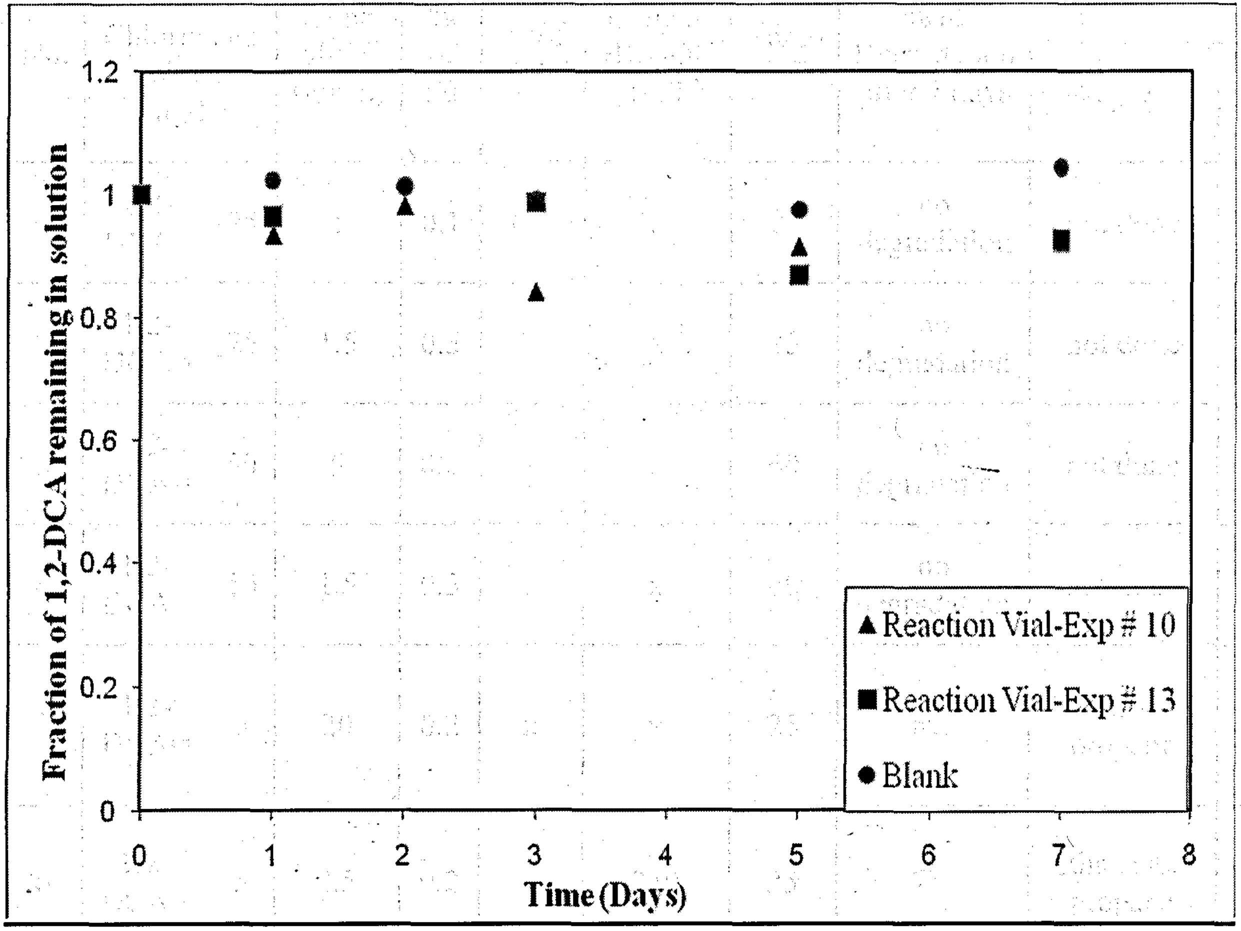

Fig H: Degradation of 10 mg/L of 1,2-DCA with 5g/L of nZVI, 0.2 wt% Pd at 25°C (Results of Exp # 10 & 13)

APPENDIX I-1

Table I-1: Experiments with 1,2-DCA

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe^0 (gm/L)	% of Pd	% of CMC	Conc of HCOOH (mg/L)	Temp (°C)	% of Degradation after 7 days	Degradation Products	
								C-H	Cl-
1	1,2-DCA= 25	1	0.1	0.8	x	25	no degradation	not done	not done
2	1,2-DCA= 25	1.5	0.5	0.8	x	25	no degradation	not done	not done
3	1,2-DCA= 50	5	0.2	x	x	60	no degradation	not done	0%
4	1,2-DCA= 50	1.5	0.5	x	x	60	no degradation	not done	0%
5	1,2-DCA= 5	20	0.2	x	x	25	8%	Ethane and propane	below detection limit
6	1,2-DCA= 5	2.5	0.2	x	250	25	7%	Ethane and propane	below detection limit
7	1,2-DCA= 5	20	0.2	x	x	25	6%	not done	not done
8	1,2-DCA= 10	20	0.2	x	x	25	8%	Ethane and propane	not done

APPENDIX I-2

Table I-2: Experiments with 1,2-DCA (contd)

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe^0 (gm/L)	% of Pd	% of CMC	Conc of HCOOH (mg/L)	Temp (^{o}C)	% of Degradation after 7 days	Degradation Products	
								C-H	Cl-
9	1,2-DCA= 10	5	0.2	x	500	25	9%	not done	not done
10	1,2-DCA= 10	5	0.2	x	500	25	8%	not done	8 times more
11	1,2-DCA= 10	20	0.2	x	x	25	8%	Ethane and propane	2.6 times more
12	1,2-DCA= 10	10	0.2	x	500	35	12%	Ethane and propane	60%
13	1,2-DCA= 10	5	0.2	x	500	25	8%	Ethane and propane	not done
14	1,2-DCA= 10	20	0.2	x	x	25	17% decrease after 25 days	Ethane and propane	not done
15	TCE = 10	5	0.5	x	500	25	100%	not done	not done
	1,2-DCA= 5						9%		

APPENDIX I-3

Table I-3: Experiments with 1,2-DCA (contd)

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe^0 (gm/L)	% of Pd	% of CMC	Conc of HCOOH (mg/L)	Temp (°C)	% of Degradation	Degradation Products	
								C-H	Cl-
1	1,2-DCA= 10	5	0.5	1.5	500	25	12%	40% ethane, 60% propane	not done
2	1,2-DCA= 10	5	0.5	1.5	500	45	17%	44% ethane, 56% propane	not done
3	1,2-DCA= 10	5	0.5	1.5	500	45	15%	49% ethane, 51% propane	not done

APPENDIX I-4

Table I-4: Experiments with 1,2-DCA (contd)

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe^0 (gm/L)	% of Pd	% of Pt	% of Rh	Temp (°C)	% of Degradation	Degradation Products	
								C-H	Cl-
1	1,2-DCA= 5	5	x	x	0.5	35	no degradation	not done	not done
2	1,2-DCA= 10	10	x	0.1	0.2	35	no degradation	not done	not done
3	1,2-DCA= 10	10	x	1.42	1.42	35	no degradation	not done	not done
4	1,2-DCA= 10	10	x	0.35	0.7	35	no degradation	not done	not done
5	1,2-DCA= 10	10	0.2	0.1	0.2	35	12%	Ethane and Propane	not done

APPENDIX J-1

Table J-1: Experiments with TCE

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe^0 (gm/L)	% of Pd	% of CMC	HCOOH (mg/L)	% of Degradation	Degradation Products	
							C-H	Cl-
1	TCE = 700	10	x	x	x	32%	not done	not done
2	TCE = 700	10	x	x	x	26%	not done	33% of expected Cl-
3	TCE = 100	1.5	x	x	x	61%	not done	not done
4	TCE = 100	1.5	x	x	x	37%	Ethane and Ethene	not done
5	TCE = 100	1.5	x	x	x	31%	Ethane and Ethene	11% of expected Cl-
6	TCE = 4.4	1.9	x	x	x	31%	not done	not done
7	TCE = 100	1.5	0.1	x	x	100%	not done	not done
8	TCE = 100	1.5	0.1	x	x	100%	not done	50% of expected Cl-
9	TCE = 100	1.5	0.1	x	x	100%	not done	not done
10	TCE = 10	5	0.2	x	500	100%	not done	not done
11	TCE = 100	1.5	0.1	x	x	100%	not done	not done
12	TCE = 100	5	0.2	x	500	100%	not done	not done

APPENDIX J-2

Table J-2: Experiments with TCE (contd)

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe^0 (gm/L)	% of Pd	% of CMC	HCOOH (mg/L)	% of Degradation	Degradation Products	
							C-H	Cl-
13	TCE = 100	1.5	0.1	x	x	100%	Ethane, Ethene, 1-Butene, 2-Butene	117% of expected Cl-
14	TCE = 100	1.5	0.1	x	x	100%	Ethane, Ethene, 1-Butene, 2-Butene	118% of expected Cl-
15	TCE = 100	1.5	0.1	x	x	100%	Ethane, Ethene, 1-Butene, 2-Butene	98% of expected Cl-
16	TCE = 100	1.5	0.1	x	x	100%	Ethane, Ethene, 1-Butene, 2-Butene	84% of expected Cl-
17	TCE = 100	1.5	0.1	x	x	100%	Ethane, Ethene, 1-Butene, 2-Butene	126% of expected Cl-
18	TCE = 100	1.5	0.1	x	x	100%	Ethane, Ethene, 1-Butene, 2-Butene	not done

APPENDIX J-3

Table J-3: Experiments with TCE (contd)

No.	Conc of Chlorinated Solvent (mg/L)	Conc of Fe0 (gm/L)	% of Pd	% of CMC	HCOOH (mg/L)	% of Degradation	Degradation Products	
							C-H	Cl-
19	TCE = 100	5	0.2	x	500	100%	Total = 31.26% (Ethane = 31.11%, Propane = 0.073% Butane = 0.307)	not done
20	TCE= 10	5	0.5	1.5	500	100%	Total = 31.26% (Ethane = 31.11%, Propane = 0.073% Butane = 0.307%)	not done
21	TCE= 10	5	0.5	1.5	500	100%	Total = 30.44% (Ethane = 30.33%, Propane = 0.089% Butane = 0.023%)	not done
22	TCE= 10	5	0.5	1.5	500	100%	Total = 25.34% (Ethane = 24.26%, Propane = 0.199% Butane = 1.073%)	not done
23	TCE= 10	5	0.5	1.5	500	100%	Total = 34.79% (Ethane = 34.41%, Propane = 0.144% Butane = 0.232%)	not done
24	TCE= 10	5	0.5	1.5	500	100%	Total = 54.81% (Ethane = 54.37%, Propane = 0.403% Butane = 0.44%)	not done
25	TCE= 10	5	0.5	1.5	500	100%	Total = 31.197% (Ethane = 31.06%, Propane = 1.512% Butane = 0.136%)	not done