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Metalloporphyrin catalyzed degradation of PCE: Effects of reductants, buffers and cosolvent concentration

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METALLOPORPHYRIN CATALYZED DEGRADATION OF
PCE: EFFECTS OF REDUCTANTS, BUFFERS AND
COSOLVENT CONCENTRATION

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Science

By
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December 2007

Accepted by
Dr. Mark A. Schlautman, Committee chair
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ABSTRACT

Reductive dechlorination of chlorinated organic contaminants using metalloporphyrins as catalysts may be an effective approach to treat widespread contamination. However, most previous studies have examined water-soluble rather than insoluble metalloporphyrins despite the fact that the latter category makes up the largest fraction found in nature. Recent studies have shown that addition of different cosolvents to water can activate otherwise non-reactive metalloporphyrin catalysts and facilitate the reduction of tetrachloroethylene (PCE), presumably by the mere process of making the otherwise insoluble metalloporphyrins dissolve in solution. Therefore, solubility has been advanced as a key factor in the ability of metalloporphyrins to catalyze organic contaminant degradation.

This study was designed to test the solubility hypothesis by examining whether a higher concentration of co-solvent, in this case dimethylformamide (DMF), would result in more metalloporphyrin catalyst remaining in solution and subsequent enhancement in the degradation of PCE. The primary objective was to determine the relationship between co-solvent concentration (0-10% DMF) and the rate of PCE degradation catalyzed by water-insoluble metalloporphyrins such as Fe(III) Cl-TPP and Ni-TPP. Secondary objectives were to examine whether the metalloporphyrin catalyzed degradation of PCE was dependent on different reductants and pH buffers.

Results from this study demonstrate that although addition of DMF is, in fact, required to activate insoluble metalloporphyrin catalysts, there appears to be some threshold whereby continued addition of cosolvent begins to adversely affect the

catalyzed degradation of PCE. For Fe(III) Cl-TPP, the rate of PCE degradation increased from 0 to 2% DMF, remained relatively constant at 3% DMF, then declined at higher DMF concentrations. Similar trends were observed for Ni-TPP. Collectively, these findings suggest that solubility of metalloporphyrins is not the only governing factor in their ability to catalyze PCE degradation. A secondary finding was that Fe(III) Cl-TPP appears to be more effective than Ni-TPP for catalyzing PCE degradation, possibly because it may be forming dimers in water-DMF mixtures.

A secondary objective of this study was to compare the effects of different pH buffers and bulk electron donors on the rate of metalloporphyrin-catalyzed PCE degradation to better understand whether these experimental variables might play a potential role in the reaction. Titanium (III) citrate was found to be as effective an electron donor as dithionite. Also, little difference was observed when using bicarbonate versus TRIS buffers, as long as the concentration of buffer was high enough to keep the pH from decreasing too much during the reaction.

DEDICATION

This thesis is dedicated to my wonderful parents, brother and fiancé. Thank you for the unconditional love, support and guidance that you have given me during good times and bad. Thank you for instilling the confidence in me that I have what it takes to get through tough times. Thank you for everything. Love you all!

I would specially like to dedicate this thesis to the memory of my loving father. Dad, I hope I have done you proud.

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LIST OF ABBREVIATIONS

Abbreviations

CH	Chlorinated Hydrocarbon
CT	Carbon Tetrachloride
DMF	Dimethyl Formamide
EPA	Environmental Protection Agency
GC	Gas Chromatograph
MCL	Maximum Contaminant Level
PCE	Perchloroethylene
TCE	Trichloroethylene
DCE	Dichloroethylene
VC	Vinyl Chloride
NOM	Natural Organic Matter

CHAPTER 1

INTRODUCTION

Chlorinated hydrocarbons (CH) have found wide industrial applications as solvents, refrigerants, propellants, and synthetic intermediates for plastics and pesticides. The discharge of chlorinated solvents into the environment by industrial processes has led to extensive contamination of groundwater (Burriss et al., 1996). The persistence of chlorinated organic compounds depends on their susceptibility to biotransformation and/or abiotic degradation. Those compounds which are resistant to biodegradation persist in the environment and exhibit their toxicity over extended periods of time (Gantzer and Wackett, 1991). Such compounds are recalcitrant in nature and are found to accumulate in surface water, sediments and groundwater (Feng and Lim, 2007). To convert these chlorinated compounds to nontoxic, non-chlorinated products, various remediation technologies, both biotic and abiotic, have been developed (Dror et al., 2005).

Among chlorinated hydrocarbons, perchloroethylene (PCE), a commonly occurring contaminant in soils and aquifers and a probable human carcinogen, ranks high on the priority list of U.S Environmental Protection Agency (EPA) (Gantzer and Wackett, 1991). PCE is a colorless, nonflammable volatile liquid with an ether like odor and is soluble in alcohols and sparingly soluble in water. While lesser chlorinated ethylenes can be degraded aerobically, PCE is resistant to aerobic degradation (Gantzer and Wackett, 1991). However, PCE does undergo degradation under strictly anaerobic

conditions via sequential reductive dehalogenation to form non-toxic, non-chlorinated compounds (Gantzer and Wackett, 1991; Holliger and Schraa, 1992). Importantly, under anaerobic conditions, PCE is susceptible to both biological and abiotic degradation. However, high CH concentrations often present at contaminated sites and the presence of chromium and other contaminants can inhibit microbial activity (Mikesell and Boyd, 1990; Morris et al., 1993). Therefore, abiotic dechlorination has received considerable interest during recent years. It has been postulated that the presence of electron shuttle systems (i.e. electron transfer mediators) helps increase the rate of reduction of chlorinated organic compounds in the presence of bulk reductants. Titanium citrate and dithionite are some of the frequently used bulk electron donors as they have proven to be biologically inert (Zehnder and Wuhrmann, 1976; Nzungung et al., 2001). These bulk electron donors rapidly reduce electron transfer mediators which in turn transfer the electron to a final electron acceptor (i.e., target contaminant). The bulk electron donor regenerates the oxidized mediator, thereby starting the reaction all over again.

Recently, bacterial transition metal co-enzymes and naturally occurring metalloporphyrins have been proposed for use as electron mediators. Several porphyrin derivatives have been shown to catalyze the reductive dechlorination of CH. It has been shown that the product, rates and mechanism of reductive dechlorination are largely influenced by the core metal present in the metalloporphyrin (Dror and Schlautman, 2003). Of the several porphyrins available, only soluble porphyrins, which constitute a very small fraction of porphyrins, have been used as electron transfer mediators in these reactions. However, insoluble porphyrins can be solubilized by the addition of small

amounts of co-solvent which activates their catalytic property. This demonstrates that the solubility of a metalloporphyrin is a key factor in its ability to catalyze the reductive dechlorination of PCE and its daughter compounds (Dror and Schlautman, 2003).

Cosolvents such as low molecular weight ketones, alcohols and glycols at waste/contaminated sites can increase the aqueous phase solubility of hydrophobic compounds, decrease sorption by soils and reduce volatilization from water. Clean up of contaminated soils often involves the use of a mixture of water and water miscible co-solvents to enhance the remediation process (Li et al., 1996). Researchers have demonstrated that the addition of 5% co-solvent dissolves some otherwise insoluble porphyrins and thereby enhances the degradation rate of PCE (Dror and Schlautman, 2003). However, it is unclear whether adding co-solvent at increasing concentrations would continue to increase PCE degradation. Therefore, we have hypothesized that the addition of a co-solvent like dimethylformamide (DMF) in increasing concentrations would increase metalloporphyrin solubility and thereby augment the degradation rate of PCE.

Data from a parallel study in our research group showed that a large increase in the degradation rate of PCE was observed when the co-solvent concentration was increased from 1% to 5% DMF, but that the rate declined sharply at 10% DMF using Fe (III) Cl-TPP as the metalloporphyrin catalyst (Ramasubramanian, 2007). The research reported in this thesis will evaluate the effect of increasing DMF concentrations on the rate of PCE degradation catalyzed by the metalloporphyrins Fe (III) Cl-TPP and Ni-TPP while sampling the range of co-solvent concentration more closely. By optimizing the

amount of cosolvent added, abiotic degradation processes can be rendered more effective and cost-efficient which would then facilitate their application in the real world. This research will also compare the effect of different electron donors and buffers on the rates of PCE degradation, which will help in identifying optimal environmental conditions necessary for porphyrin-mediated degradation of PCE.

The specific aims of this project are:

1. To verify previous results regarding the effects of varying DMF concentrations on the rate of dechlorination of PCE using Fe (III) Cl-TPP while sampling the range of DMF concentration (0, 2, 3, 5, 7.5 and 10%) more closely than previous studies to better elucidate trends observed.
2. To test the effect of increasing DMF concentrations (0, 2, 5 and 10% DMF) on the rate of dechlorination of PCE using Ni-TPP as the catalyst.
3. To compare the effect of two different bulk electron donors (titanium (III) citrate and sodium dithionite) on the rate of degradation of PCE in the presence of Fe (III) Cl- TPP at fixed DMF concentration.
4. To test the effect of two different buffers (TRIS and sodium bicarbonate) on the rate of degradation of PCE in the presence of Fe (III) Cl- TPP at fixed DMF concentration

CHAPTER 2

LITERATURE REVIEW

2.1 Perchloroethylene

Perchloroethylene (PCE) is one of the most widely used industrial solvents with 550 million pounds being produced annually in the United States. Contamination resulting from such widespread use has created an urgent need for effective biological/chemical treatment (Krumholz et al., 1996). PCE is among 14 volatile organic compounds regulated under the Safe Drinking Water Act Amendment of 1986 (Freedman and Gossett, 1989). The maximum contaminant level (MCL) for PCE is set at 5 ppb (ATSDR, 1997).

PCE has been widely used for chemical intermediates, metal cleaning, vapor degreasing, dry cleaning and textile processing. It has been used as a basic raw material in the synthesis of refrigerants such as hydrofluorocarbon 134a and hydrochlorofluorocarbon 123 and 124 (Perchloroethylene White Paper, 2005). PCE efficiently dissolves fats, waxes, greases and oils without affecting the nature of fabrics and has thereby found widespread use in dry cleaning and dyeing industries. It has also been widely used to clean contaminated metal parts because of its ability to dissolve many organic compounds and some inorganic compounds (HSIA, 2005). PCE has found use as an insulating fluid in electrical transformers. It is also a component of printing inks, aerosol specialty products, adhesive formulations, paper coatings and silicones. The

total U.S. demand for the chemical was estimated to be 355 million pounds of which 36 million pounds were imported (Perchloroethylene White Paper, 2005).

2.2 Fate and transport of PCE

The fate and transport of a compound depends largely on its physical and chemical properties and on those of the environmental milieu in which it resides. Solubility, vapor pressure, Henry's law constant, and the organic carbon partition coefficient are key properties that are used to evaluate the fate and transport of organic contaminants. Pure phase PCE is classified as a Dense Non Aqueous Phase Liquid (DNAPL) because it is denser than water and has a tendency to migrate downward through the saturated zone (Glover et al., 2007). The relatively high water solubility of PCE indicates its high affinity for the aqueous phase. In addition, its relatively high Henry's law constant indicates that PCE will tend to partition to the vapor phase from either soil or aqueous phases. PCE often enters the atmosphere through volatilization from contaminated soil or surface water. PCE in the atmosphere reacts with photochemically produced hydroxyl radicals and is thereby degraded. The degradation rate however, is extremely slow for it to be of any environmental significance (Watts, 1996).

2.3 Health effects of PCE and its daughter products

Overexposure to PCE can affect the central nervous system and liver. Resulting symptoms include dizziness, confusion, headache, nausea and irritation of the eyes and mucous tissue. Exposure to concentrations greater than 1500 ppm can cause death from respiratory depression. In the case of animals, prolonged exposure to concentrations greater than 200 ppm can damage the liver and kidney (ATSDR, 1997). The International

Agency for Research on Cancer has classified PCE as a 'probable human carcinogen.' The MCL (maximum contaminant level) as established by EPA is 5 ppb and the MCLG (maximum contaminant level goal) is zero (ATSDR, 1997).

The degradation products of PCE, namely trichloroethylene (TCE), cis-dichloroethylene (cis-DCE), trans-dichloroethylene (t-DCE), 1,1-dichloroethene (1,1-DCE) and vinyl chloride (VC), are also considered to have acute health effects on both human beings and animals. Table 2.1 summarizes the health effects of PCE and its daughter compounds (ATSDR, 1997).

Table 2.1 Summary of health effects of PCE and its daughter compounds (adapted from ATSDR, 1997).

Compound	MCL	Health effects	Probable human carcinogen
PCE	5 ppb	Central nervous system depression, dizziness, confusion, headache, nausea and irritation of eyes	Yes
TCE	5 ppb	Affects central nervous system, immune system, fetus development kidneys and liver.	Yes
VC	2 ppb	Dizziness, cancer in brains and lungs	Yes- Known human carcinogen
1,1 dichloroethene	7 ppb	Central nervous system depression, liver and kidney damage	No
c-DCE	100 ppb	Nausea, vomiting and central nervous system depression	No
t-DCE	70 ppb	Nausea, vomiting and central nervous system depression	No
Acetylene	NA ^a	Dizziness and nausea	No
Dichloroacetylene	NA ^a	headaches, nausea, dizziness and mucous membrane irritation	No
Ethene	NA ^a	No acute health effects	No
Ethane	NA ^a	No acute health effects	No

^a NA: Not available

2.4 Remediation of PCE

PCE has been found to degrade both biologically and abiotically under strictly anaerobic conditions. The anaerobic biotransformation of PCE follows the sequential reductive dechlorination process which involves replacement of the chlorine atoms with hydrogen atoms. The reported end products observed are trichloroethylene (TCE), dichloroethylene (DCE), vinyl chloride (VC), ethene and ethane.

Vogel et al. (1987) have identified many other abiotic and biotic processes responsible for the degradation of halogenated aliphatic compounds such as hydrogenolysis, dihaloelimination (reductive elimination of two adjacent chlorines to form an alkene) and coupling (loss of chlorines on two separate molecules forming a C-C bond, joining the molecules). These processes involve reduction, wherein the electrons are supplied by the microbes or the chemical reductants. Dehydrohalogenation (elimination of HX to form an alkene) and hydrolysis are processes that do not involve reduction (Vogel et al., 1987). Of these reactions only hydrogenolysis and coupling apply to PCE. Table 2.2 summarizes the various abiotic and biotic processes.

Table 2.2 Abiotic and biotic processes of halogenated aliphatic compounds (Adapted from Vogel et al., 1987)

Name	Reactions
Hydrogenolysis	$RX + H^+ + 2e^- \longrightarrow RH + X^-$
Dihaloelimination	$\begin{array}{c} \quad \\ -C-C- \\ \quad \\ X \quad X \end{array} + 2e^- \longrightarrow \begin{array}{c} \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \end{array} + 2X^-$
Coupling	$2RX + 2e^- \longrightarrow R-R + 2X^-$
Dehydrohalogenation	$\begin{array}{c} \quad \\ -C-C- \\ \quad \\ X \quad H \end{array} \longrightarrow \begin{array}{c} \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \end{array} + HX$
Hydrolysis	$RX + H_2O \longrightarrow R-OH + HX$

Until recently, research was predominantly focused on degradation of chlorinated compounds using microbial processes as they were considered faster when compared to

abiotic degradation processes (Vogel et al., 1987). However, the development of zerovalent iron (ZVI) technology has fueled renewed interest in abiotic dechlorination processes. ZVI technology is one of the most commonly used techniques for the abiotic degradation of chlorinated compounds (Kriegman- King and Reinhard, 1994; Orth and Gillham, 1996; Feng and Lim, 2007). ZVI has been used as a reactive barrier to minimize migration of chlorinated compounds in the subsurface (Cantrell et al., 1995). Researchers have also studied the use of electron transfer mediators such as bacterial transition metal coenzymes, metalloporphyrins in the abiotic reductive dechlorination of chlorinated compounds (Wackett et al., 1991; Dror and Schlautman, 2003). These electron transfer mediators help catalyze the degradation of CH. Metalloporphyrins have been used as electron transfer mediators to abiotically degrade a variety of chlorinated organic compounds.

2.5 Metalloporphyrins

Porphyrins are organic tetrapyrrole macrocycles composed of four pyrrole type rings joined by methene bridges that result in a near planar macromolecular structure (Lesage et al., 1993). They are aromatic, containing 22 conjugated π electrons, of which 18 are incorporated into the delocalization pathway. The peripheral position in the porphyrin may be substituted by various side chains, thus forming a wide variety of porphyrin derivatives like chlorins, corrins and bacteriochlorins (Lesage et al., 1993). The various porphyrins that can be formed by substitution of various side chains on the peripheral position are shown in Table 2.3. The basic structure of porphine is shown in

Figure 2.5a. The addition of various functional groups R to the basic porphine structure to obtain a variety of porphyrin derivatives is as shown in Figure 2.5b.

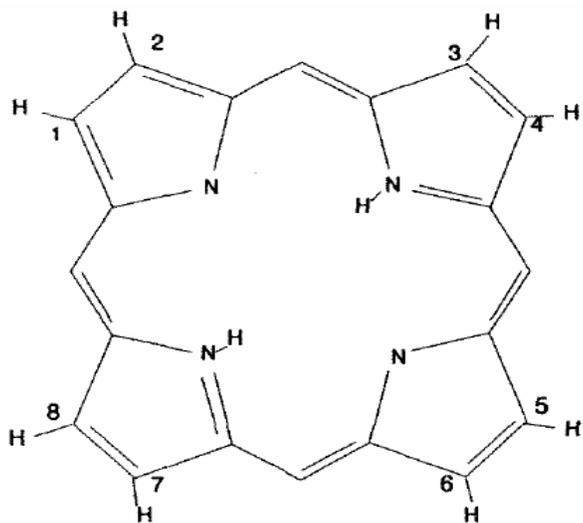
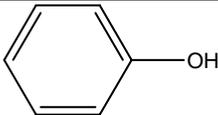
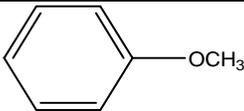
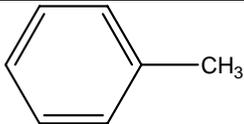
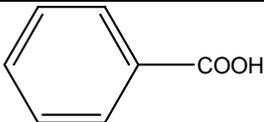
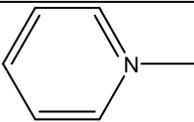


Figure 2.5.a The porphine ring (Lesage et al., 1993)

Table 2.3 Common porphyrins with various functional groups (R) (Dror and Schlautman, 2003)

Porphyrins ^a	Abbreviation	R	MW
Tetraphenyl porphine	TPP		614.75
5,10,15,20 tetrakis (4-Hydroxyphenyl 21H, 23H porphine)	TP-OHP		678.75
5,10,15,20 tetrakis (4-Methoxyphenyl 21H, 23H porphine)	T(methoxy)P		726.75
5,10,15,20 tetra <i>p</i> -tolyl 21H, 23H porphine	T(<i>p</i> -tolyl)P		662.75
4,49,40,4—(21H, 23H-porphine-5,10,15,20-tetrayl)tetrakis (benzoic acid)	T(benzoic)P		798.75
meso-tetra (1Methyl-4pyridino)porphyrin tetratosylate	TMPyP		686.75
5,10,15,20 tetra (4 Pyridyl) porphyrin	T(pyridyl)P		618.75

^a These are synthetic porphyrins .

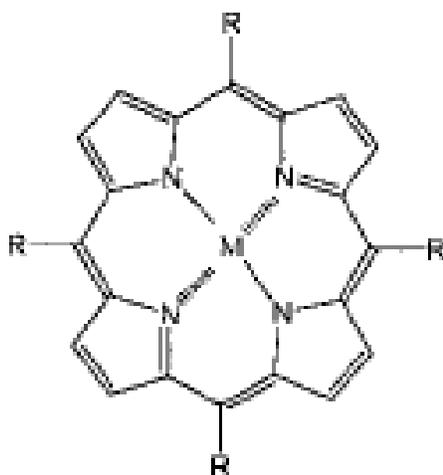


Figure 2.5.b Functional group R added to the basic porphyrin structure (Dror and Schlautman 2003)

Porphyrins occur as free bases or in the form of metal complexes. They are found in abundance in a wide variety of biogeochemical environments including living cells, soils, coal, oil shales and petroleum. Nickel and vanadium are the dominant metals complexing porphyrins in crude oil with iron, cobalt, titanium, zinc and copper observed in trace amounts (Dror and Schlautman, 2003). Geo-porphyrins represent the most abundant porphyrin type on earth. Porphyrin concentrations in sediments vary from a few ppm to thousands of ppm (Kadish et al., 2000).

One function of porphyrins and porphyrin like compounds is to bind metal atoms, which then forms active centers for major biochemical events. Protoporphyrin IX in heme (Figure 2.5c) binds iron which in hemoglobin and myoglobin helps in oxygen transportation (Milgrom et al., 1997). Chlorophylls (Figure 2.5d), found in plants and

algae, belong to a class of porphyrin derivatives and play an important role in photosynthesis.

A naturally occurring organometallic compound, Vitamin B₁₂, (Figure 2.5e) is a corrinoid that consists of a basic pyrrole ring system complexed to a metal (Co) with the structure enhanced by a few carbon bridges. Porphyrins also form a part of the cytochrome P-450 enzyme system which is present in microbes and in the livers of higher organisms. These enzymes catalyze oxidation reduction reactions which in turn result in the degradation of toxic chemicals (Lesage et al., 1993).

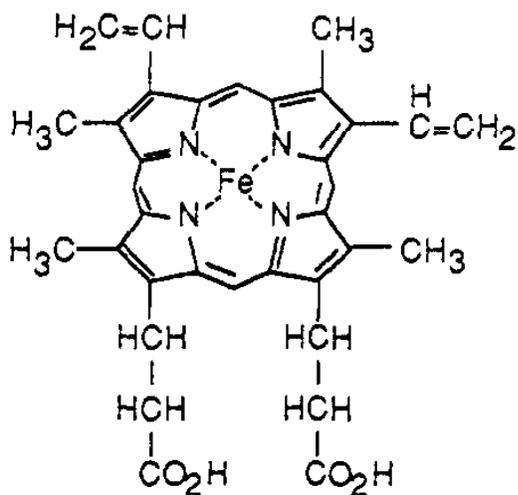


Figure 2.5.c Heme (Gantzer and Wackett, 1991).

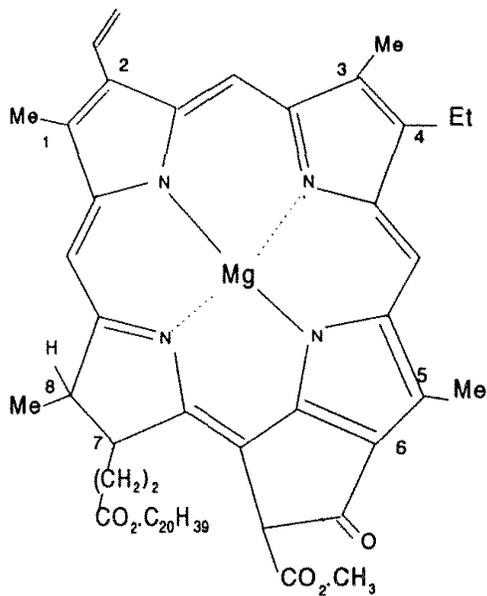


Figure 2.5.d Chlorophyll (Lesage et al., 1993).

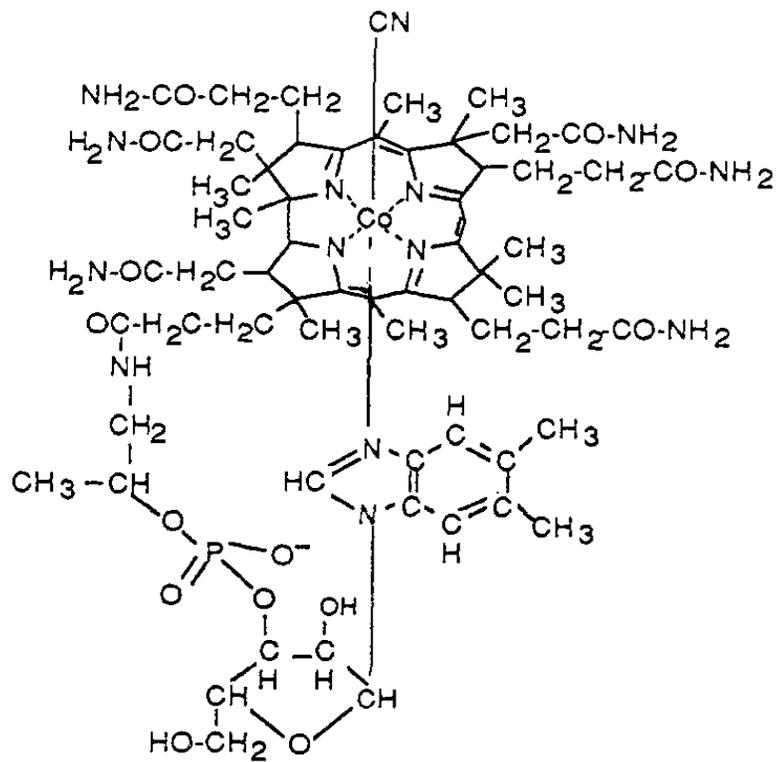


Figure 2.5.e Vitamin B₁₂ (Gantzer and Wackett, 1991).

Metalloporphyrins are porphine derivatives in which at least one of the lone pairs of electrons on the central nitrogen atoms of the porphine is shared with a metal ion acting as a Lewis acid. Metalloporphyrins have been used to treat pollutants with high oxidation states due to the following reasons (Dror and Schlautman, 2004). :

- Good redox catalysts and exhibit a large range of redox activities.
- Electrochemically active with many different core metals.
- Their high stability allows redox reactions to proceed under severe conditions which may otherwise limit alternative treatment processes.
- Naturally occurring metalloporphyrins are ubiquitous which suggests that they can be used for the *in situ* remediation of high oxidation state pollutants.

The easy accessibility of porphyrins allows biological systems to modify the redox and coordination properties of the metal ions for their own purposes (Milgrom et al., 1997).

2.6 Metalloporphyrin mediated reductive dechlorination reactions

Biological degradation of CH can be slow and requires appropriate conditions for microbial activity and growth. In some cases, high concentrations of CH present at contaminated sites are toxic to the microorganisms and/or the presence of other contaminants (e.g., Cr (VI)) may inhibit microbial activity (Mikesell and Boyd, 1990; Morris et al., 1993). Simple abiotic systems have been shown in some cases to obtain faster degradation rates when compared to biological systems. Recently, researchers have shown that abiotic reductive transformation of CH can be enhanced in the presence of

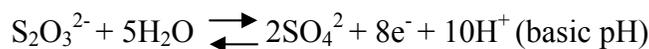
electron shuttle systems or electron transfer mediators (Larson and Weber, 1994). Abiotic electron transfer mediated reductive dechlorination systems generally do not have the drawbacks associated with bioremediation (Schanke and Wackett, 1992; Schwarzenbach et al., 1990).

Important components of a reductive dechlorination system are: bulk electron donors, pH buffers, electron transfer mediators and electron acceptors. The bulk electron donor rapidly reduces the electron transfer mediator, which in turn transfers the electron to a final electron acceptor. The oxidized mediator is then rapidly regenerated by the bulk reductant, starting the reaction all over again (Stumm and Morgan, 1996).

Commonly used bulk electron donors are sulfide, cysteine and thioglycolic acid. However, these may be toxic to microorganisms at fairly low concentrations. A strong reducing agent, Titanium (III) is not toxic to microorganisms at low concentrations. Citrate acts as a complexing agent and prevents the precipitation of Ti(III) and Ti(IV) as hydroxide. The titanium (III) citrate complex forms a blue-violet solution which turns colorless on oxidation (Zehnder and Wuhrmann, 1976). Another reducing agent, dithionite has been recommended as a potential environmentally suitable reducing agent due to the following reasons:

- Strong reductant
- Dithionite and its reaction products are non-toxic
- Dithionite treatment barriers are easier to engineer when compared to biologically created systems.

Dithionite has been observed to decompose more slowly at basic pH and faster at acidic pH (Nzengung et al., 2001). The disproportionation of dithionite to sulfate (as shown in the equations below) in a buffered system provides the necessary electrons and protons required for hydrogenolysis of chlorinated ethenes (Nzengung et al., 2001).



Buffered dechlorination systems exhibit better degradation of PCE than unbuffered systems (Nzengung et al., 2001). Some of the commonly used buffers in dechlorination systems are tris and sodium bicarbonate. TRIS one of the most frequently used pH buffers in biological studies as its buffer region falls in the neutral to slightly basic range which corresponds to natural conditions. However, there have been numerous examples where TRIS buffer inhibits reactions by interacting with metal ions through complex formation (Allen et al., 1967). Conversely, bicarbonate and especially carbonate are known to be free radical scavengers.

Laboratory studies have used biologically produced organic macrocycles complexed with transition metals to shuttle electrons from bulk reductants, thereby transforming the contaminants faster (Gantzer and Wackett, 1991). Naturally occurring electron transfer mediators like metalloporphyrins, transition metal coenzymes, quinone groups within naturally occurring organic matter and mineral bound ferrous iron species are found in many subsurface environments and contribute to the natural attenuation of some contaminants (Kriegman-King and Reinhard, 1992).

The transition metals associated with biomimetic macrocycles rely on cycling between various oxidation states to transfer electrons. For example, in the case of hematin, the reduced central metal atom Fe (II) transforms to Fe (III), yielding an electron to the final electron acceptor. The oxidized metal is converted back to Fe (II) upon accepting an electron from a bulk reductant (Baxter, 1990; Schwarzenbach et al., 1990; Gantzer and Wackett, 1991).

Quinone moieties within natural organic matter (NOM) have been used as effective electron transfer mediators in the reductive dechlorination of substituted nitrobenzene and chlorinated organic compounds (Schwarzenbach et al., 1990; Dunnivant et al., 1992). In addition, transition metal humic acid complexes have also been used as electron transfer mediators in the reductive dechlorination of TCE in which the primary degradation products observed were ethene and ethane (O'Loughlin et al., 1999).

Researchers have used Vitamin B₁₂ as a common catalyst in the degradation of chlorinated ethenes, polychlorinated biphenyls and chlorinated alkanes (Burriss et al., 1996; Assaf-Anid et al., 1991; Marks et al., 1988). The proposed pathway for PCE degradation catalyzed by Vitamin B₁₂ is as shown in Fig 2.6a. Importantly, Vitamin B₁₂ with titanium citrate has been used in a pilot scale study to evaluate its ability to treat groundwater containing CT and 1,1,2,2- tetrachloroethane (TeCA). A re-circulation well was used to deliver the chemicals and to ensure adequate mixing. CT was found to degrade completely without the accumulation of chloroform whereas the removal of TeCA ranged from 48-99.2% (Lesage et al., 2001). In addition to Vitamin B₁₂ (Co), coenzyme F₄₃₀ (Ni) and hematin (Fe) have also been found to catalyze the dechlorination

of polychlorinated ethenes and benzenes (Gantzer and Wackett, 1991). Structurally similar to Vitamin B₁₂, Tetrakis (4-carboxyphenyl) porphyrin cobalt is an example of another metalloporphyrin that has been used to catalyze the degradation of chlorinated ethenes (Fritsch and McNeill, 2005).

Core metals play an important role in enhancing the dechlorination of chlorinated organic compounds. Porphyrins without metal centers were observed to be inactive, whereas porphyrins when complexed to metals like Co, Fe, Mg, Ni, V and Mo dehalogenated chlorinated ethenes (Dror and Schlautman, 2003). Degradation of PCE did not increase in the presence of Fe-TMPyP whereas Ni and Co-TMPyP were found to enhance the degradation of PCE, each following apparently different pathways (Figure 2.6b and 2.6c). This suggests that different core metals may affect the rate and product distribution of reductive dechlorination reactions. A set of synthetic porphyrins, Co-T(benzoic)P, Co-T(pyridyl)P, CO-TP(OHP), Co-TPP and Co-T(methoxy)P were studied for reductive dechlorination of PCE and no substantial reductive dechlorination was observed which was contradictory to the results obtained for Co-TMPyP suggesting that the core metal is not the only factor involved in the reactivity of electron transfer and that the entire metalloporphyrin macrocycle should be considered as a functional system wherein, the organic macrocycle would play a key role in the dechlorination process of the contaminant (Dror and Schlautman, 2003).

Despite the large variety of porphyrins available, only soluble porphyrins (which constitute a very small fraction of porphyrins) generally have been used as catalysts in reductive dechlorination (Dror and Schlautman, 2003). Research involving the use of

insoluble metalloporphyrins has been very limited. The solubility of some porphyrins (and their metal complexes) was observed to increase with increase in pH above 11, thereby facilitating degradation of PCE. The addition of selected co-solvents was also shown to transform the non-reactive metalloporphyrins to soluble and effective catalysts thereby degrading PCE to nonchlorinated products (Dror and Schlautman, 2004). In other words, an insoluble and therefore non-reactive metalloporphyrin could be made reactive by altering the pH or by the addition of small amount of organic solvent (Dror and Schlautman, 2003). Table 2.4 summarizes commonly cited porphyrins used for reductive dechlorination of organic pollutants.

Table 2.4 Summary of commonly cited porphyrins used for reductive dechlorination of chlorinated contaminants

Electron transfer mediator	Electron acceptor	Bulk electron donor	% degraded	Author
Quinone moieties	3-chloronitrobenzene	Hydrogen sulfide	87%	Schwarzenbach et al., 1990; Dunnivant et al., 1992
Ni-Aldrich humic acid complex	TCE	Titanium citrate	100%	O'Loughlin et al., 1999
Vitamin B ₁₂	PCE and TCE	Titanium citrate	TCE- 100% PCE-100%	Burris et al., 1996
Vitamin B ₁₂	Polychlorinated biphenyl congeners and HCB	Dithiothreitol	87%	Assaf Anid et al., 1991
Vitamin B ₁₂	CTC	Dithiothreitol	NA	Chiu and Reinhard, 1995
Vitamin B ₁₂	1,2-dichloroethane	Dithiothreitol	100%	Assaf-Anid et al., 1994
Tetrakis(4carboxyphenyl)porphyrin cobalt	Polychlorinated ethenes and benzenes	Titanium citrate	PCE 89% TCE 96%	Fritsch and McNeill, 2005
Hematin and chlorophyll <i>a</i>	Lindane	Dithiothreitol	100%	Marks et al., 1999
Co -TMPyP	PCE	Titanium citrate	100%	Dror and Schlautman, 2003
Ni-TMPyP	PCE	Titanium citrate	100%	Dror and Schlautman, 2003
Ni-TPP	PCE	Titanium citrate	100%	Dror and Schlautman, 2003

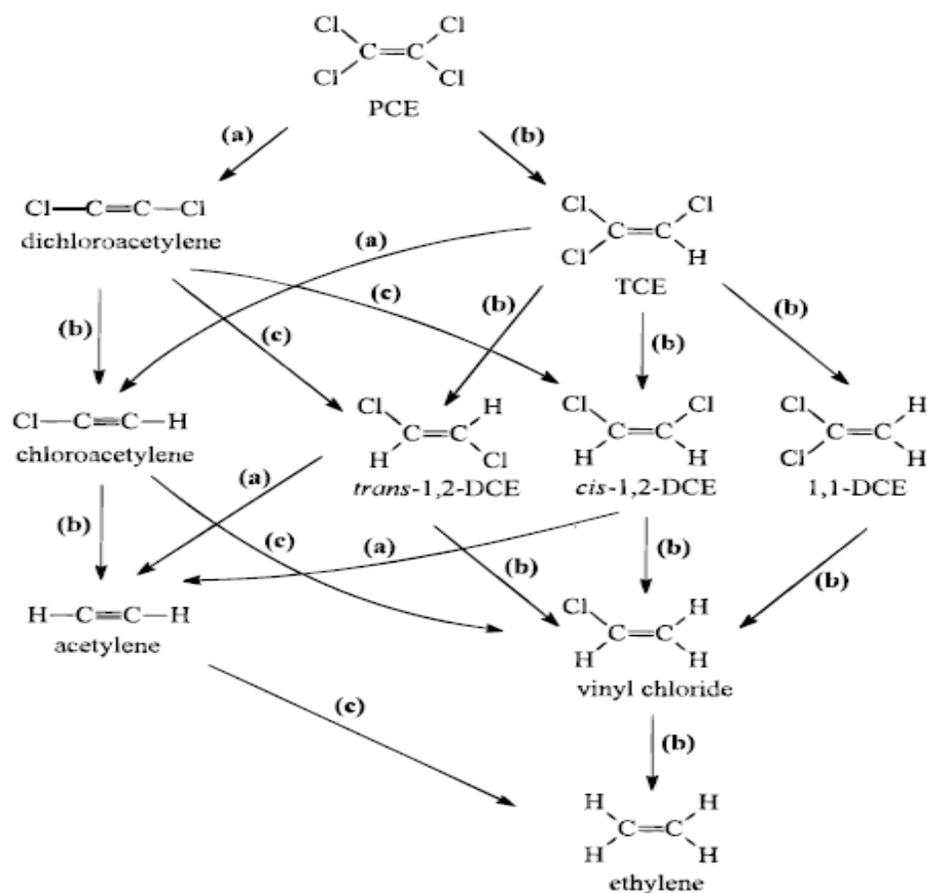


Figure 2.6.a Proposed pathways for reduction of chlorinated ethenes catalyzed by Vitamin B₁₂ with titanium citrate as the bulk reductant. Pathway (a) shows reductive β elimination, pathway (b) shows hydrogenolysis, pathway (c) shows reduction of triple bond to olefin (Burris et al., 1996).



Figure 2.6.b Proposed reaction pathway for reduction of PCE catalyzed by Co-TMPyP (Dror and Schlautman, 2003).



Figure 2.6.c Proposed reaction pathway for reduction of PCE catalyzed by Ni-TMPyP (Dror and Schlautman, 2003).

2.7 Cosolvent effect on reductive dechlorination reactions

Cosolvency, the addition of water miscible solvents to an aqueous system, is a well established method for the solubilization of insoluble drugs (Millard et al., 2002). Cosolvent is a material, which may not be an acceptable solvent on its own, but when added in small amounts to an active solvent has the ability to enhance solvent power.

Cosolvents generally contain hydrogen bond donor/ acceptor groups and small hydrocarbon regions. The hydrogen bonding groups which are hydrophilic are responsible for water miscibility whereas the hydrophobic, hydrocarbon portion reduces the overall intermolecular attraction of water by interfering with water's hydrogen bonding network (Millard et al., 2002). The cosolvent thus reduces unfavorable interactions between a hydrophobic solute and water which would otherwise prevent solubilization. In short, the addition of co-solvent makes the water environment less polar, thereby increasing solute solubility (Millard et al., 2002).

Organic solvents used by the industry have a significant impact on the solubility of hydrophobic compounds found at waste sites. The presence of co-solvents at waste sites increases solubility in aqueous phase, decreases sorption by soils and reduces volatilization from water (Li et al., 1994). They are widely used in remediation where contaminated soils are washed with a mixture of water and water miscible co-solvents (Li et al., 1996). The aqueous solubility of hydrophobic compounds is enhanced when co-solvents are present at a concentration greater than about 5-10% (Schwarzenbach et al., 2003). Commonly used cosolvents include methanol, acetonitrile, pyridine, acetone, dimethylsulfoxide, DMF, dimethylacetamide (DMA) and glycol (Kadish et al., 2000).

These completely miscible organic solvents (CMOS) affect the activity coefficient and hence the solubility and partitioning behavior of the solute. Increase in the volume fraction of CMOS results in an exponential decrease of the activity coefficient and consequent exponential increase in solubility of the organic solute (Schwarzenbach et al., 2003).

Cosolvents like acetone and DMA have been largely used in addition with surfactants like Tween 80 and sodium dodecyl sulfate to increase the solubility of a poorly soluble drug phenytoin (PHT) (Kawakami et al. 2006). Use of cosolvents has also been combined with other solubilization techniques like pH adjustment (Li et al., 1999) and addition of cyclodextrin to increase the solubility of hydrophobic organic compounds (He et al., 2003). Zhai et al. (2006) studied the cosolvent enhanced chemical oxidation of PCE by potassium permanganate. Addition of cosolvent increased solubility of DNAPL in water thereby enhancing oxidation of the DNAPL by permanganate.

Researchers observed that change in solution conditions could activate certain insoluble and non-reactive metalloporphyrins and bring about their dissolution (Dror and Schlautman, 2004). The addition of a small amount of cosolvent (5% DMF or 5% pyridine) transformed the non-reactive metalloporphyrin catalyst (Fe-TPP, Ni-TPP, VO-TPP) to soluble and effective catalysts thereby facilitating reduction of PCE. Ni-TPP was found to degrade PCE faster than Fe-TPP. The proposed pathways for PCE degradation using Ni-TPP and VO-TPP are shown in Figures 2.7a and 2.7b. The above metalloporphyrins were inactive in the absence of cosolvents. The solubility of metalloporphyrins was identified as the key factor in determining its efficacy as a catalyst

(Dror and Schlautman, 2004). Also, use of different cosolvents resulted in different degradation rates. Based on the above results, Ramasubramanian (2007) hypothesized that the addition of increasing cosolvent concentrations would increase metalloporphyrin solubility and thereby increase the degradation of PCE. The effect of increasing DMF and methanol concentrations was tested on the degradation of PCE in the presence of Fe (III) Cl- TPP catalyst and titanium citrate as bulk reductant. From Ramasubramanian's work it was observed that the degradation rate of PCE increased tremendously when the DMF concentration was increased from 0 to 5% and then dropped drastically at 10% DMF. Similar results were observed in the case of methanol, although the increase in degradation rate of PCE at 5% methanol was not as high as that observed for 5% DMF. Figure 2.7c compares the rate constants of PCE degradation in the presence of Fe (III) Cl- TPP with DMF and methanol as cosolvents as reported by Ramasubramanian (2007).

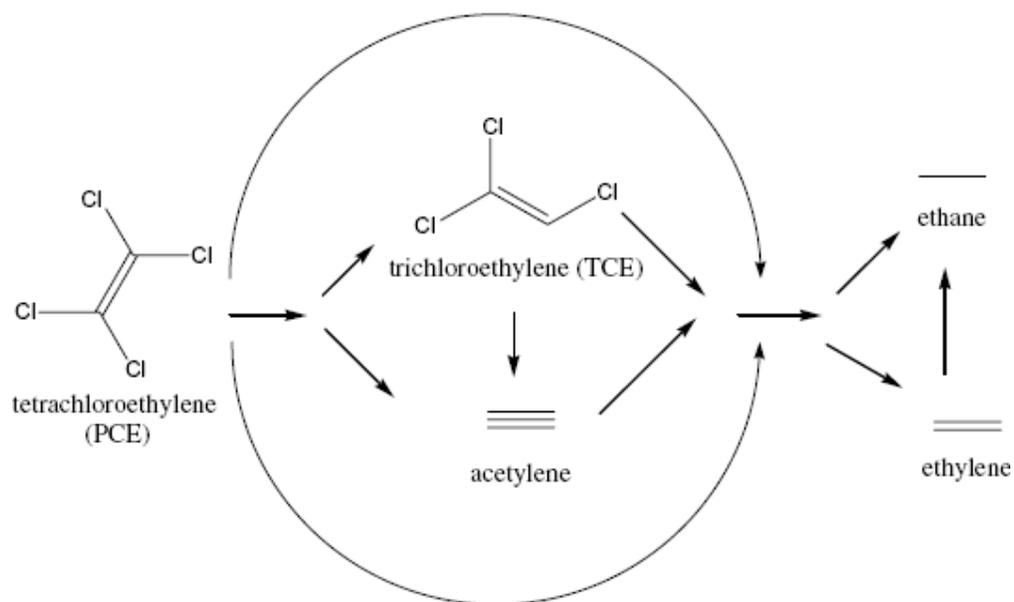


Figure 2.7.a Proposed reaction pathway for reduction of PCE catalyzed by Ni-TPP and 5% (v/v) DMF (cosolvent) with titanium citrate as bulk reductant (Dror and Schlautman, 2004).

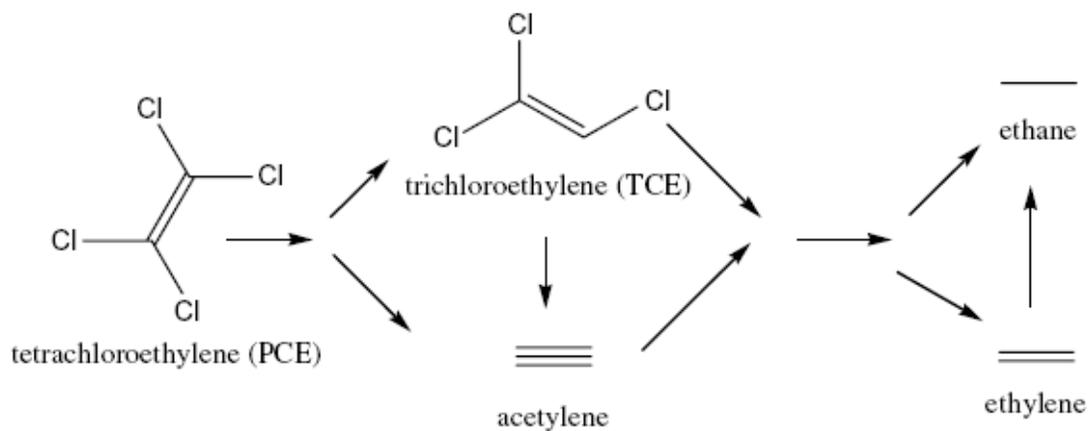


Figure 2.7.b Proposed reaction pathway for reduction of PCE catalyzed by vanadium oxide-TPP (VO-TPP) and 5% (v/v) DMF (cosolvent) with titanium citrate as bulk reductant (Dror and Schlautman, 2004).

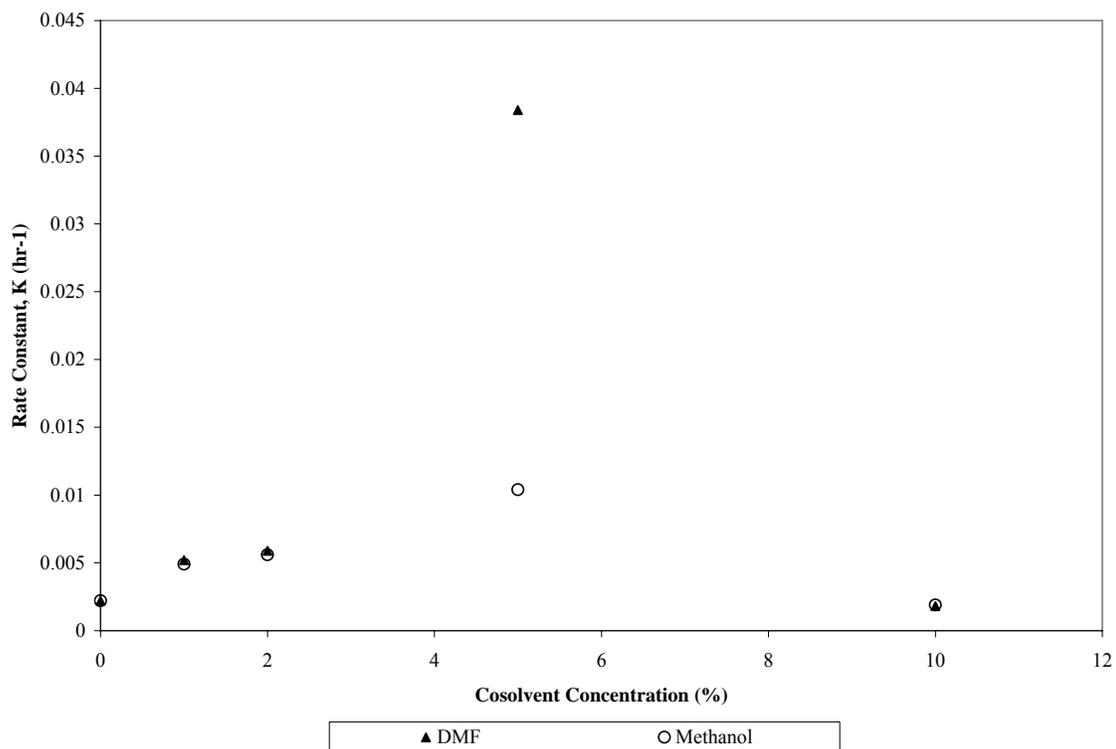


Figure 2.7.c Comparison of rate constants of PCE degradation in the presence of Fe (III) Cl TPP with DMF and methanol as cosolvents (Ramasubramanian, 2007)

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals

5, 10, 15, 20- Tetraphenyl-21H, 23H- porphine iron(III)chloride synthetic (Fe-TPP), 5, 10, 15, 20- Tetraphenyl- 21H, 23H porphine nickel (II) synthetic, sodium citrate dehydrate (>99.9%, ACS reagent), sodium dithionite, sodium bicarbonate, tetrachloroethylene (PCE), trichloroethylene (TCE), cis-DCE, t-DCE, VC, dimethyl formamide (DMF), titanium(III)chloride, sodium hydroxide pellets (98%), and TRIS (99% titration) were obtained from Aldrich Chemical. Methanol (99.9%, HPLC grade) was purchased from Burdick and Jackson. All chemicals obtained were of sufficiently high purity and thus were used without further purification.

De-ionized water purified by a Milli-Q water system (18 M Ω .cm) and purged with nitrogen for 12 hours was used for all experiments. A redox indicator solution, resazurin, was kept in the anaerobic chamber at all times to monitor oxygen contamination. The solution turns pink in the presence of oxygen and colorless at an E_h less than -110 mV (Jacob, 1970)..

pH of solutions was measured using a 420A model pH meter, using a combination pH electrode. The pH meter was calibrated with NBS buffer solutions before every use.

Preparation of Metalloporphyrin Stock solution

A concentrated 2 mM stock solution of Fe (III) Cl-TPP was prepared in pure DMF. Aliquots of this stock were added to varying water-DMF mixtures (2, 3, 5, 7.5, and 10% DMF) all with a final concentration of 10 μ M Fe (III) Cl-TPP. In order to make 0% DMF solutions of 10 μ M Fe (III) Cl-TPP, 0.7 mg of Fe (III) Cl-TPP was added directly to the reactor bottles. The processes described above were carried out in an anaerobic chamber.

A concentrated 2 mM stock of Ni-TPP was also prepared in pure DMF. The solution containing Ni-TPP was sonicated for an hour, thereby facilitating its complete dissolution in pure DMF. Aliquots of this stock were added to varying water-DMF mixtures (2, 5 and 10% DMF) to obtain a final concentration of 10 μ M Ni-TPP. In order to make 0% DMF solutions containing 10 μ M Ni-TPP, 0.67 mg of Ni-TPP was added to the reactor bottles directly. Similar to the above procedure, this process was carried out in an anaerobic chamber.

3.2 Reductant Solutions

The detailed preparation of bulk reductants/electron donors is discussed in the following sections.

Preparation of titanium (III) citrate solutions

The bulk electron donor, titanium (III) citrate, was prepared as described by Smith and Woods (1994). The processes described below were carried out in an anaerobic chamber. A stock solution of 250 mM titanium (III) citrate was prepared in 660 mM TRIS (pH 8.2). Titanium chloride (60 mL) was added to a mixture of 16 g of TRIS, 29.4

g of sodium citrate and 80 mL deoxygenated water. The pH of the solution was adjusted to 8.2 by the addition of 10 N NaOH. The solution was then diluted to 1000 mL using deionized deoxygenated water, giving a solution of 50 mM titanium (III) citrate in 0.13 M TRIS buffer. While diluting the solution, care was taken to maintain the pH at 8.2 (i.e., pH of the solution was checked before and after diluting the solution).

Similar to the above procedure, titanium (III) citrate was prepared with 0.13 M sodium bicarbonate buffer instead of TRIS. Sodium bicarbonate buffer (10.93 g) was added to the titanium (III) citrate slurry and the solution was made up to 1000 mL. While diluting the solution care was taken to maintain the pH at 8.2.

Preparation of sodium dithionite solutions

Deoxygenated water (200 mL) was added to a mixture of 6.01 g of sodium dithionite and 10.93 g of sodium bicarbonate or 16g of TRIS. The pH of the solution was adjusted to 8.5 by the addition of 10 N NaOH. The solution was then diluted to 1000 mL using de-ionized deoxygenated water, giving a solution of 34.5 mM sodium dithionite in 0.13 M sodium bicarbonate/TRIS buffer. This process was carried out in an anaerobic chamber.

3.3 Experimental design

Batch reactors (160 mL serum vials, crimp sealed with teflon lined septa) were prepared in an anaerobic chamber. The dechlorination reactions were carried out with different cosolvent (i.e., DMF) fractions. Each reaction bottle initially contained 10 μ M porphyrin, 50 mM titanium citrate or 34.5 mM sodium dithionite, and the apparent concentration of pH buffer with varying DMF fractions in a total solution volume of 100

mL, leaving 60 mL of anaerobic headspace in each bottle. The reactor bottles were immediately capped in the anaerobic chamber. PCE stock prepared in methanol (97% methanol in PCE stock) was added to each reactor bottle outside of the anaerobic chamber. Precise determination of the quantity of stock (50 μ L) added to each reactor bottle was made gravimetrically. The reactor bottle was weighed prior to addition and after the addition of PCE stock. The initial aqueous phase concentration of PCE in the reactor bottles was 20 mg/L (i.e., 19.3 μ mol/bottle or 120.6 μ M). The control systems were prepared as follows: one without bulk reductant (titanium citrate/sodium dithionite), one without the metalloporphyrin (Fe-TPP and Ni-TPP) and cosolvent, one without metalloporphyrin (Fe-TPP and Ni-TPP) and one without cosolvent (DMF). These were prepared in a similar manner to the reaction bottles. All vials were placed on a shaker table at 175 rpm and room temperature. Headspace samples of 0.5 mL were taken from each reaction bottle with a gas tight syringe (VALCO precision sampling syringe, 1 mL, using sideport needles (0.029''x .012''x 2'')) at selected time intervals for analysis (i.e., bottles were re-sampled over time). The reactor could be considered at equilibrium between the two phases (aqueous and gaseous phase) and homogeneous throughout each phase as the reactors were well mixed (Gossett, 1987). All reactor vials were prepared in triplicate. For experiments comparing electron donors, dithionite was used to replace Ti (III) citrate using sodium bicarbonate or TRIS as the buffer in the presence of Fe (III) Cl-TPP and 5% DMF. In experiments where the effects of buffers on the degradation of PCE were evaluated, systems containing 34.5 mM dithionite and 0.13 M TRIS were compared to systems containing 34.5 mM dithionite and 0.13 M sodium bicarbonate buffer in the

presence of Fe (III) Cl TPP and 5% DMF. Also systems containing 50 mM titanium (III) citrate and 0.13 M TRIS were compared to systems containing 50 mM titanium (III) citrate and 0.13 M sodium bicarbonate in the presence of Fe(III) Cl-TPP and 5% DMF. The concentration of reagents in reaction bottles is as shown in Table 3.1. The overall experimental design is shown in the form of a flowsheet in Figure 3.3a-c.

Table 3.1 Concentrations of reagents in reaction bottles for the dechlorination reaction

DMF concentration (% v/v)	0%	2%	3%	5%	7.5%	10%
PCE (mg/L)	20	20	20	20	20	20
Fe (III) Cl-TPP/ Ni-TPP (μ M)	10	10	10	10	10	10
Ti (III) citrate (mM)	50	50	50	50	50	50
Sodium dithionite (mM)	34.5	34.5	34.5	34.5	34.5	34.5
TRIS/Sodium bicarbonate buffer	0.13	0.13	0.13	0.13	0.13	0.13

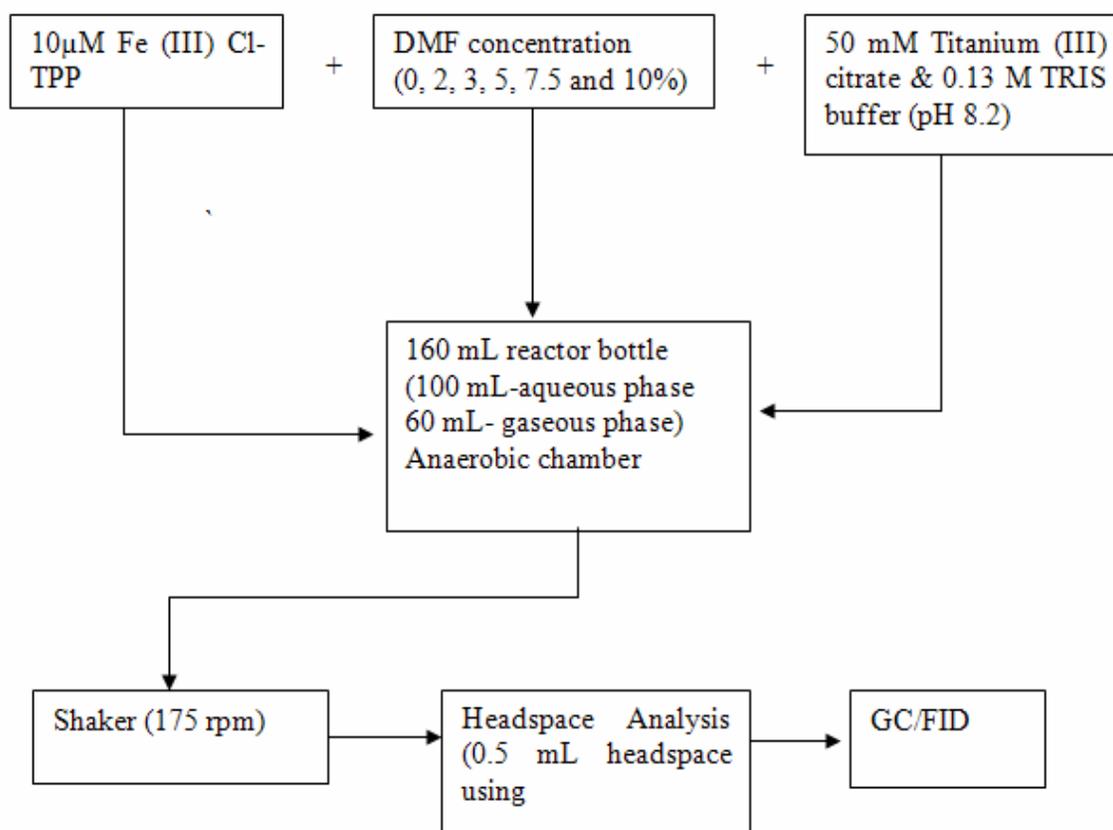


Figure 3.3.a Experimental design for DMF effect on PCE degradation rate catalyzed by Fe(III) Cl-TPP

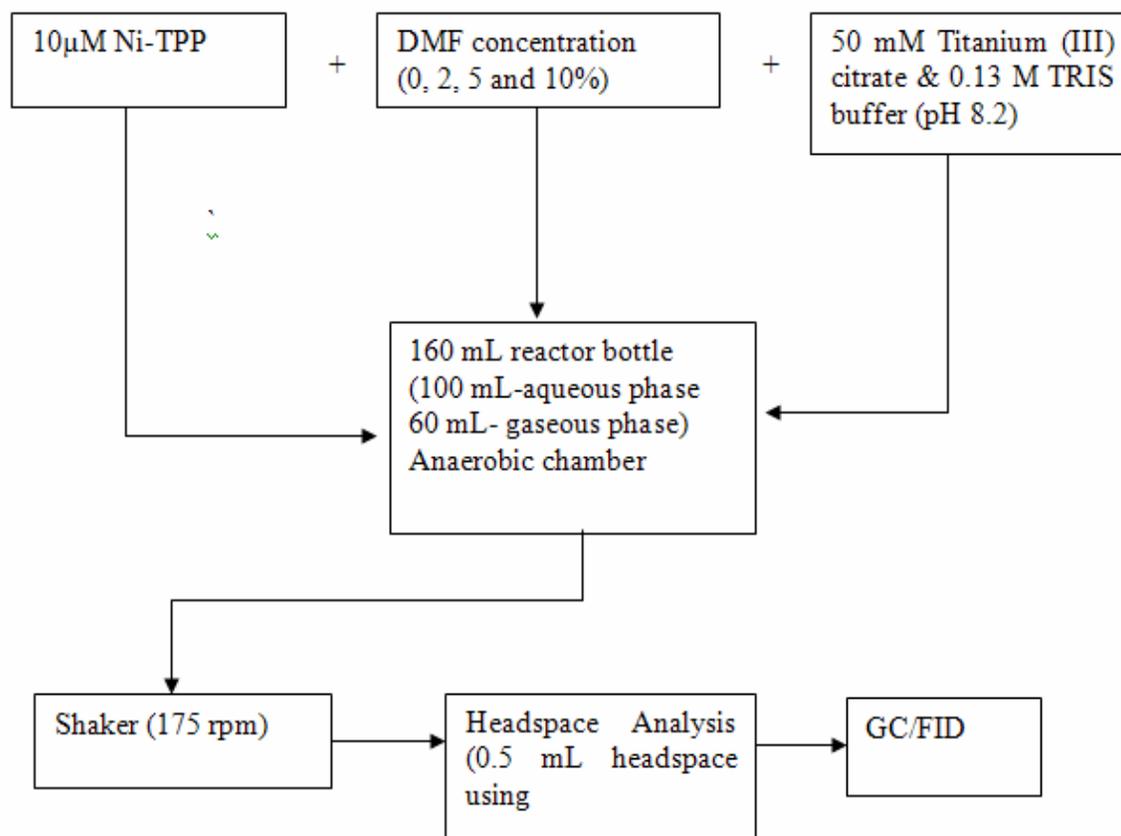


Figure 3.3.b Experimental design for DMF effect on PCE degradation rate catalyzed by Ni-TPP

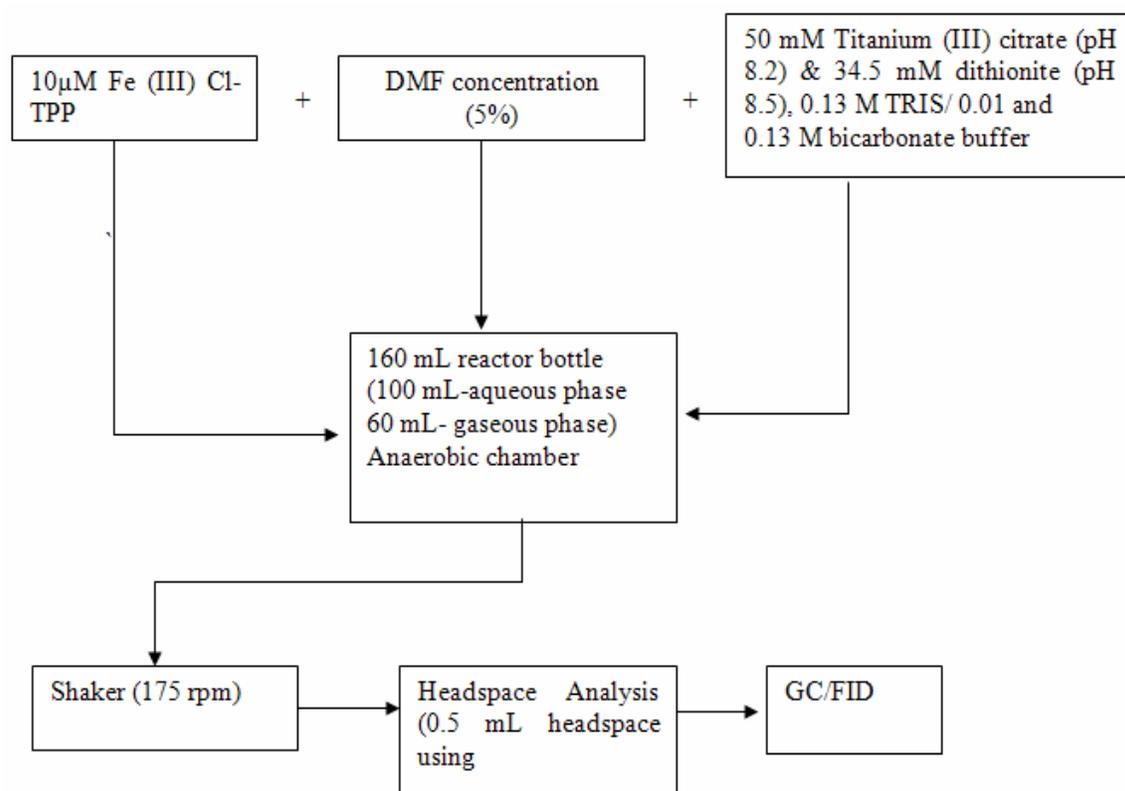


Figure 3.3.c Experimental Design for effect of reductants and pH buffers on PCE degradation rates catalyzed by Fe (III) Cl-TPP

3.4 Analytical methods

External standards containing PCE, TCE were injected separately into a gas chromatograph (GC) equipped with an RTX-5 column (30m, 0.53-mm i.d.; Agilent Technologies, Palo Alto, CA, USA) with a flame ionization detector (HP 5890 GC- FID; Hewlett Packard, Palo Alto, CA, USA) to identify retention times of reaction products formed. This column did not allow for the quantification of gases such as acetylene, ethene and ethane.

External standards containing PCE and TCE were made for each cosolvent fraction containing 0, 2, 3, 5, 7.5 and 10% DMF separately in batch reactors with a final volume of 100 mL aqueous solution and 60 mL headspace. One calibration curve each for PCE and TCE from one of the external standards run for 5% DMF is shown in Figure 3.4a and 3.4b. The carrier gas was helium and the oven temperature program consisted of holding at 40°C for 5 min, ramping at 10 °C/min to 200°C and holding at 200°C for a minute. The detector was maintained at 310°C.

The response factors for PCE and TCE with increasing DMF concentrations are shown in Table 3.2. Analytical details like the detection limit of PCE and TCE and the concentration range of standards used are shown in Table 3.3. Samples used to measure the detection limit were made similar to standards in the absence of DMF (cosolvent). PCE and TCE stocks were made in methanol and 50 µL of stock were injected into reactor bottles to make respective samples to measure detection limits. The detection limit was obtained by making 7 consecutive analyses of standards containing 10 µmol/bottle of PCE and 1 µmol/bottle of TCE and using the following equation:

$$DL = S * t_{(n-1, 1-\alpha)}$$

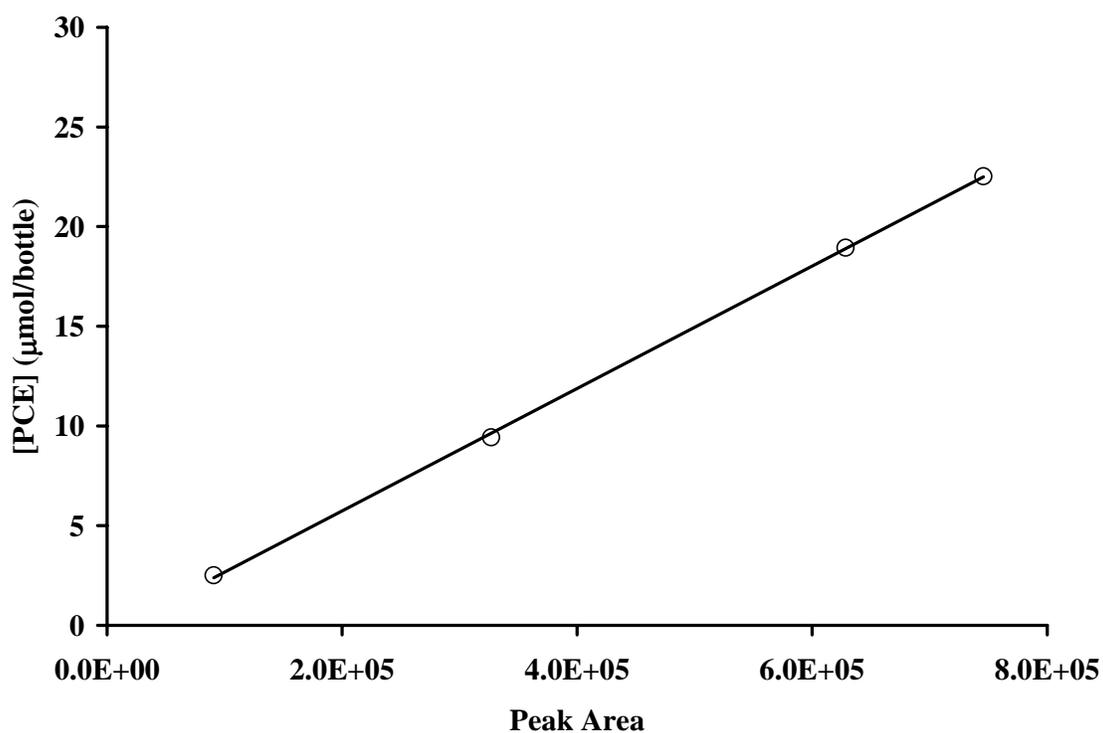
where

S = standard deviation of the replicate analyses

$t_{(n-1, 1-\alpha)}$ = student-t value for the 99% confidence level with $n-1$ degree of freedom, (e.g., $t_{(6,0.99)}=3.143$ for 7 replicates)

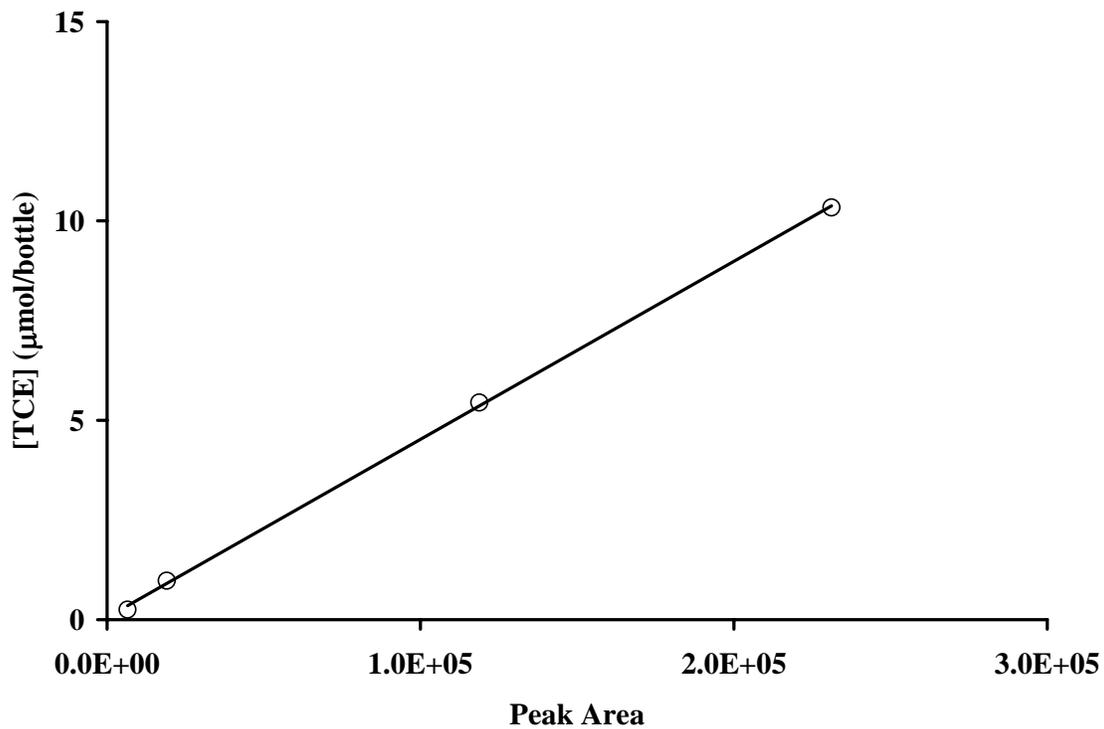
n = number of replicates

$\alpha = 0.01$, confidence level is $1-\alpha=0.99$



Response factor for PCE (μmol/bottle/peak area)	3.07E-5
R^2	0.99

Figure 3.4.a Calibration curve for PCE in 5% DMF



Response factor for TCE (μmol/bottle/peak area)	4.46E-5
R ²	0.99

Figure 3.4.b Calibration curve for TCE in 5% DMF

Table 3.2 Effect of DMF concentrations on response factors

DMF Concentration	[PCE]		[TCE]	
	Response factor ($\mu\text{mol}/\text{bottle}/\text{peak}$ area)	R^2	Response factor($\mu\text{mol}/\text{bottle}/\text{peak}$ area)	R^2
0%	2.48E-5	0.99	3.48E-5	0.99
2%	2.68E-5	0.99	4.00E-5	0.99
3%	2.71E-5	0.99	4.76E-5	0.99
5%	3.07E-5	0.99	4.48E-5	0.99
7.5%	3.91E-5	0.99	5.77E-5	0.99
10%	4.52E-5	0.99	6.47E-5	0.99

Table 3.3 Summary of analytical details

Detection limit	Concentration range for standards	No of standards
PCE 0.27 $\mu\text{mole}/\text{bottle}$ TCE 0.12 $\mu\text{mole}/\text{bottle}$	PCE- 2.5 – 24 $\mu\text{mol}/\text{bottle}$ TCE- 0.25-11 $\mu\text{mole}/\text{bottle}$	4 4

3.5 Kinetic modeling

Pseudo-first order kinetics was used to fit experimental data and calculate rate constants. *Microsoft Excel 2003* was used to fit experimental data to the pseudo first order rate expressions and to perform standard t- tests.

The detailed procedure used for data analysis is as follows:

1. Natural log transformation of PCE concentration data
2. Linear regression of $\ln [\text{PCE}]$ versus time is performed.
3. The slope (i.e., the pseudo first order rate constant) for each replicated experimental system (triplicate) and 95% confidence interval using *Microsoft excel 2003* is obtained.
4. An average rate constant from the 3 replicate values is calculated. Uncertainties of the three replicates are propagated to obtain the 95% confidence interval for the overall average rate constant using the Root Mean Square Method (Rosselot, 2006).

3.6 Metalloporphyrin absorbance systems

10 μM Fe (III) Cl- TPP and Ni- TPP solutions were prepared with varying cosolvent fractions (2, 3, 5, 7.5 and 10% DMF). Fe (III) Cl- TPP and Ni-TPP stock (2 mM) were prepared in pure DMF. These absorbance systems did not contain the pH buffer or electron donors that was present in the dechlorination systems. References contained the same amount of co-solvent but no metalloporphyrin. Table 3.4 shows the preparation of sample and reference solutions.

The sample and reference solutions each were transferred to quartz cells of 1 cm path length. The absorbance of the solutions was measured with a UV visible spectrophotometer (Cary Varian 50 Bio). The spectra range was from 300 to 650 nm and the step size was 1 nm.

Table 3.4 Solution preparation for UV-Visible absorbance measurements

	Sample solutions					Reference solutions				
Co-solvent concentration (%v/v)	2	3	5	7.5	10	2	3	5	7.5	10
Amount of Fe-TPP/Ni-TPP (ml)	0.2	0.2	0.2	0.2	0.2	0	0	0	0	0
Amount of pure co-solvent added (ml)	0.6	1	1.8	2.8	3.8	0.8	1.2	2.0	3.0	4.0
Amount of water added (ml)	39.2	38.8	38	37	36	39.2	38.8	38	37	36
Total solution volume (ml)	40	40	40	40	40	40	40	40	40	40
Fe-TPP/Ni-TPP (μM)	10	10	10	10	10	0	0	0	0	0

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Metalloporphyrin mediated reductive dechlorination of PCE

The abiotic dechlorination of PCE using metalloporphyrins and their close derivatives (e.g., Vitamin B₁₂) have been widely studied (Dror and Schlautman, 2003; Marks et al., 1989). However most studies have utilized only water-soluble porphyrins. Dror and Schlautman (2003) studied the use of insoluble metalloporphyrin catalysts to abiotically degrade PCE and observed that addition of 5% co-solvent activated and dissolved the otherwise inactive catalyst, thereby enhancing the degradation rate of PCE (Dror and Schlautman, 2003). The present study extends the work of Dror and Schlautman (2003) by more closely investigating DMF concentrations on PCE degradation catalyzed by two metalloporphyrins (Fe (III) Cl-TPP and Ni-TPP). This study also investigated effects of different bulk electron donors and buffers to obtain optimal environmental conditions for the metalloporphyrin mediated degradation of PCE

4.2 Cosolvent effect on reductive dechlorination of PCE catalyzed by Fe-(III) Cl-TPP

The effect of varying DMF fractions (0%, 2%, 3%, 5%, 7.5% and 10% (v/v) DMF) on the reductive dechlorination of PCE catalyzed by 10 μ M Fe (III)-Cl TPP was examined first. Summary results are shown in Figure 4.2a where the symbols shown represent average values. Table 4.1 summarizes apparent pseudo first order rate constants. Individual results for each DMF concentration are shown in Figures 4.2b-g.

These plots show the degradation of PCE over a time course of 144 hours. As can be seen, the degradation of PCE can be modeled as pseudo first order kinetics. Symbols in Figure 4.2b-g represent actual values obtained from triplicate experimental samples. The uncertainty in first order rate constants were estimated by calculating 95% confidence limits based on propagating the corresponding uncertainties from each replicated experiment (as shown in Appendix A). The root mean square method was used for the propagation of uncertainty. The variation of first order rate constants with increasing cosolvent concentrations is presented in Figure 4.2h.

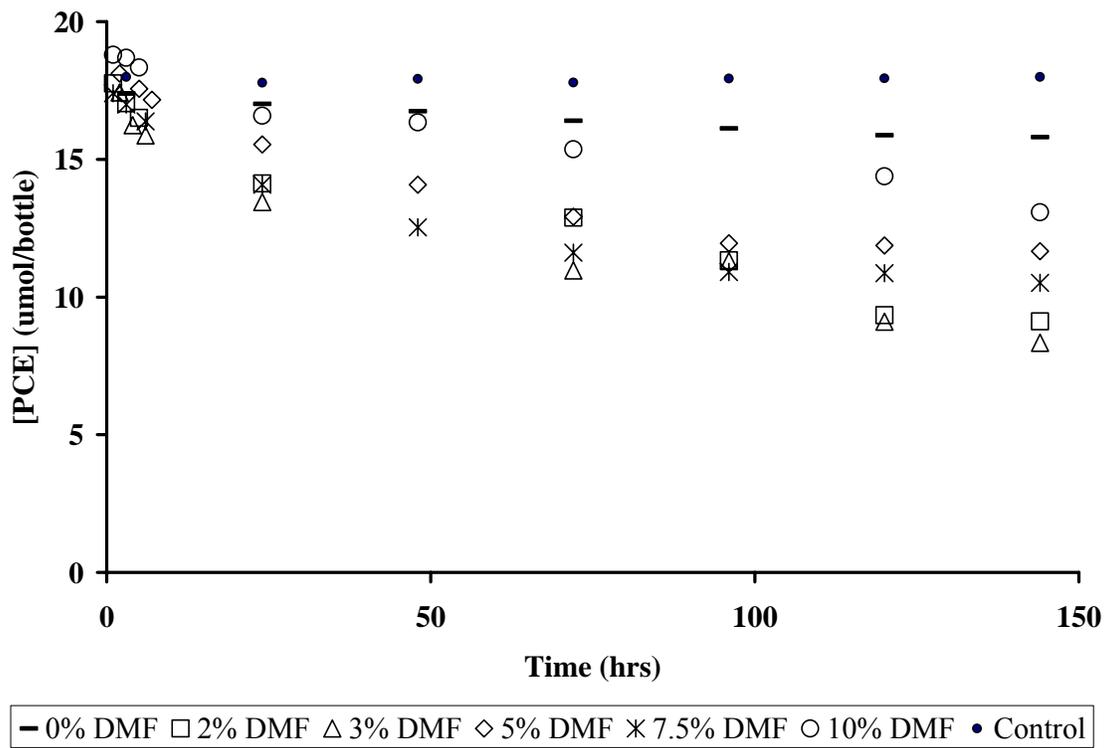
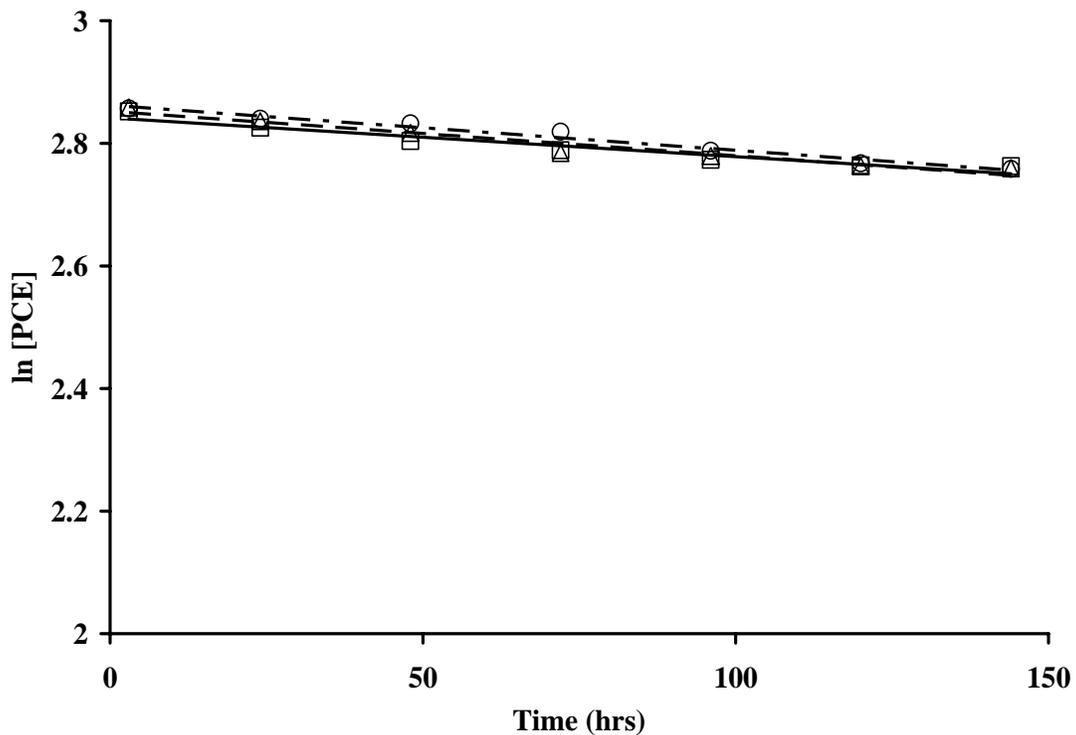


Figure.4.2.a Effect of DMF concentration on PCE degradation with 10 μ M Fe(III)Cl TPP. Data points represent average values. Controls do not contain titanium citrate.

Table.3.1 Observed rate constants (k_{obs}) for pseudo first order degradation of PCE using 50 mM titanium citrate as the bulk reductant catalyzed by 10 μ M Fe (III)-Cl TPP with varying amounts of DMF.

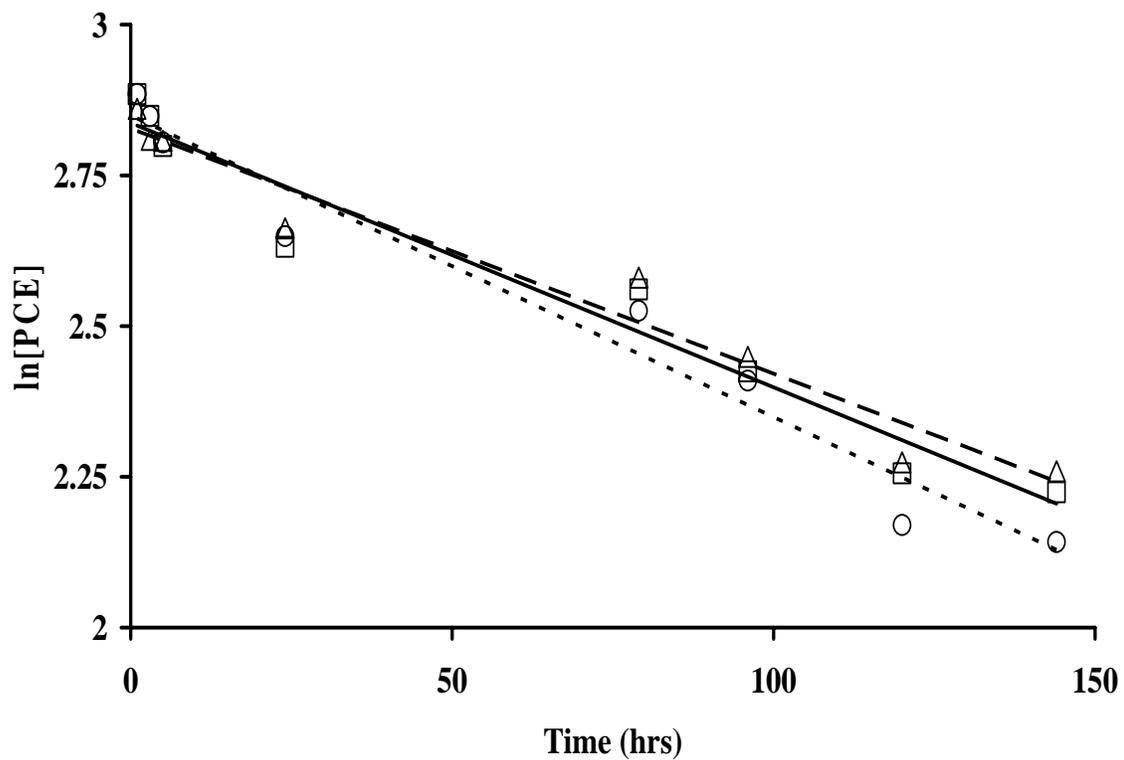
Amount of cosolvent (%v/v)	k_{obs} (hr ⁻¹) ^a
0%	(0.70 \pm 0.10) x10 ⁻³ ^a (0.60, 0.80) x10 ⁻³ ^b
2%	(4.49 \pm 0.53) x10 ⁻³ ^a (3.96, 5.02) x10 ⁻³ ^b
3%	(4.72 \pm 0.61) x10 ⁻³ ^a (4.11, 5.33) x10 ⁻³ ^b
5%	(3.24 \pm 0.42) x10 ⁻³ ^a (2.82, 3.66) x10 ⁻³ ^b
7.5%	(3.59 \pm 0.66) x10 ⁻³ ^a (2.93, 4.25) x10 ⁻³ ^b
10%	(2.33 \pm 0.38) x10 ⁻³ ^a (1.95, 2.71) x10 ⁻³ ^b

^areported rate constants \pm calculated uncertainties based on propagating 95% confidence limits. ^breported rate constants values inclusive of the calculated uncertainties.



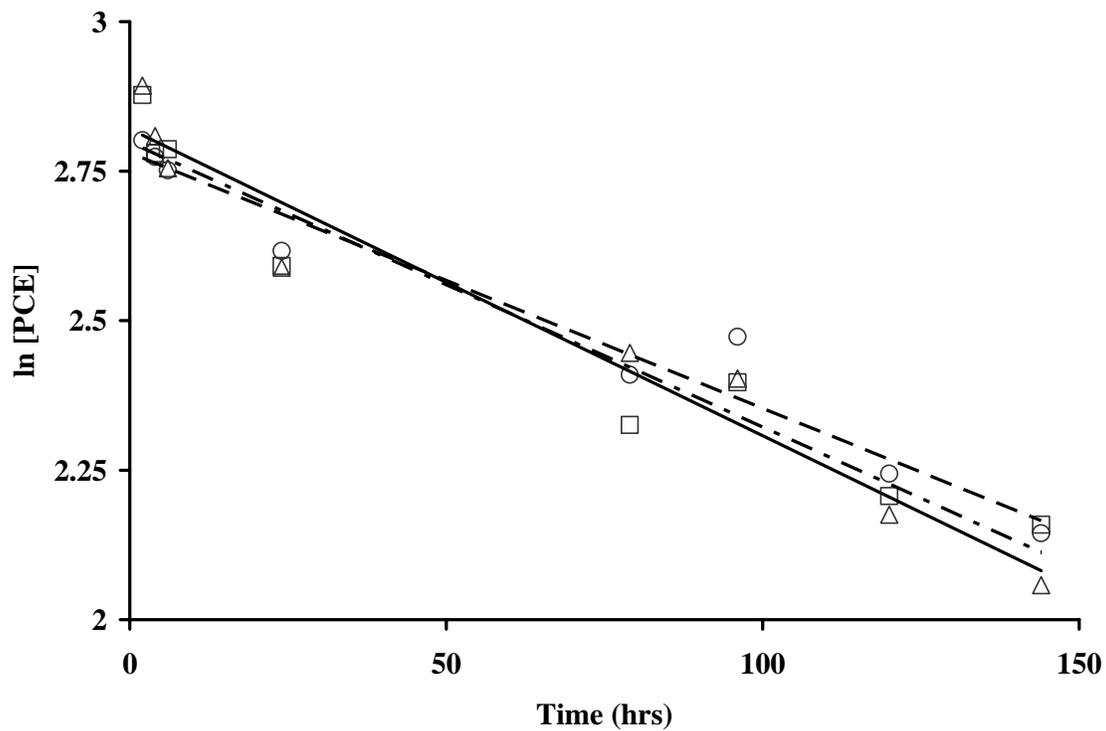
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(7.3 \pm 1.3) \times 10^{-4}$	$(6.3 \pm 2.0) \times 10^{-4}$	$(7.3 \pm 2.0) \times 10^{-4}$
Intercept	2.862 ± 0.018	2.842 ± 0.017	2.852 ± 0.017
R ²	0.97	0.93	0.95

Figure 4.2.b Reduction of PCE with 10 μ M Fe(III) Cl⁻ TPP in the absence of DMF



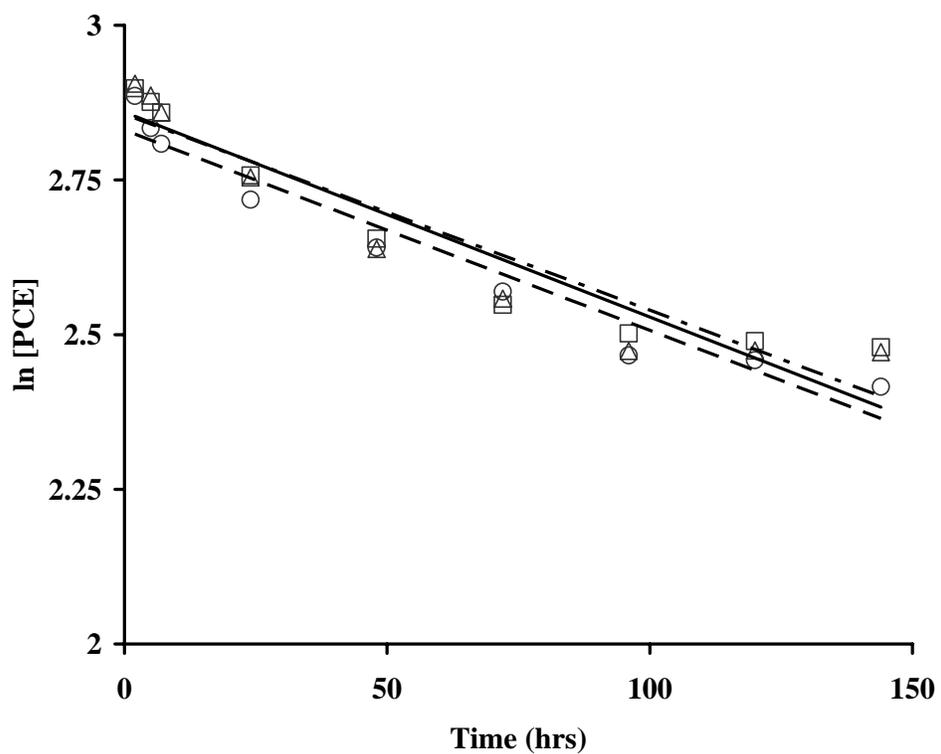
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(5.0 \pm 1.0) \times 10^{-3}$	$(4.4 \pm 1.0) \times 10^{-3}$	$(4.1 \pm 0.8) \times 10^{-3}$
Intercept	2.849 ± 0.077	2.837 ± 0.078	2.828 ± 0.067
R^2	0.96	0.95	0.96

Figure 4.2.c Reduction of PCE with 10 μ M Fe(III) Cl- TPP in the presence of 2% DMF



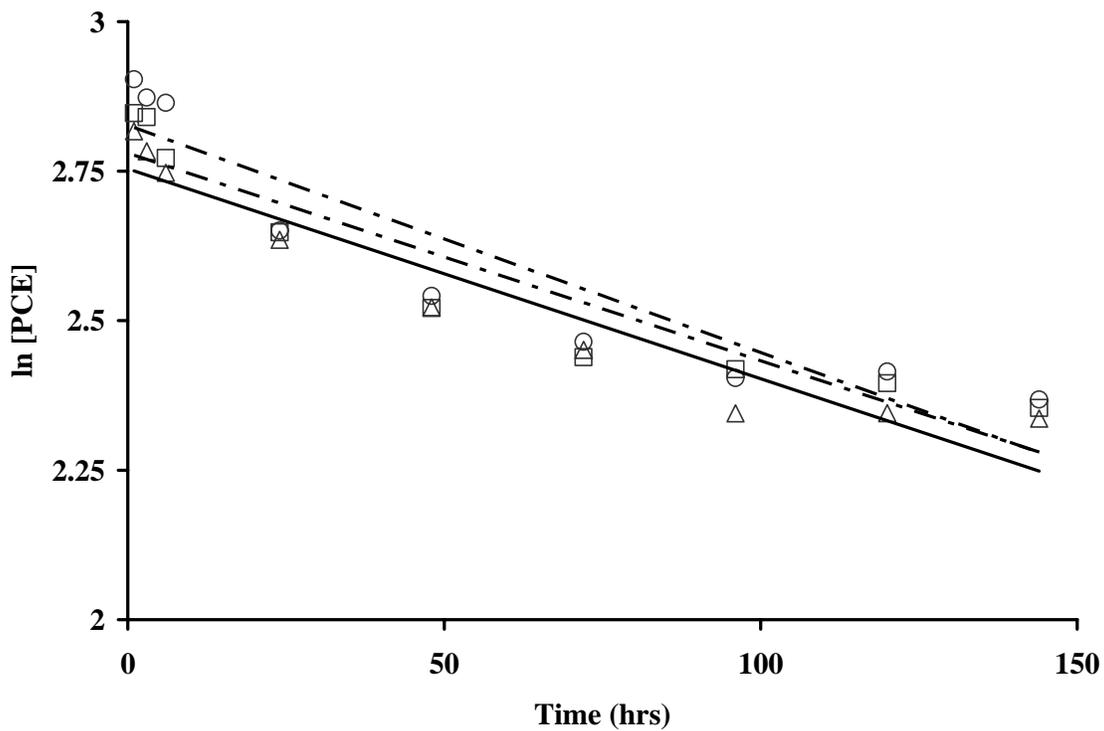
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(4.3 \pm 0.87) \times 10^{-3}$	$(4.8 \pm 1.2) \times 10^{-3}$	$(5.1 \pm 1.1) \times 10^{-3}$
Intercept	2.780 ± 0.069	2.797 ± 0.094	2.820 ± 0.088
R ²	0.96	0.94	0.96

Figure 4.2.d Reduction of PCE with 10 μ M Fe(III) Cl- TPP in the presence of 3% DMF



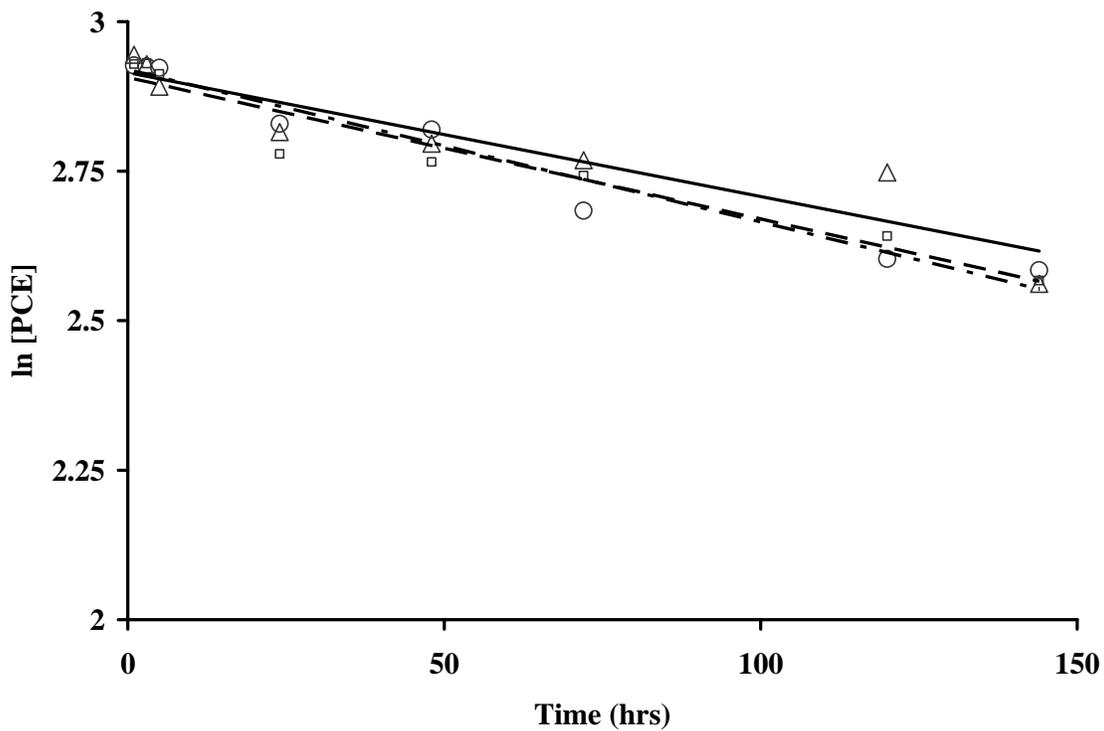
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(3.2 \pm 0.7) \times 10^{-3}$	$(3.17 \pm 0.5) \times 10^{-3}$	$(3.31 \pm 0.9) \times 10^{-3}$
Intercept	2.830 ± 0.052	2.856 ± 0.068	2.859 ± 0.073
R ²	0.95	0.91	0.91

Figure 4.2.e Reduction of PCE with 10 μ M Fe(III) Cl- TPP in the presence of 5% DMF



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(3.8 \pm 1.3) \times 10^{-3}$	$(3.5 \pm 1.1) \times 10^{-3}$	$(3.5 \pm 0.9) \times 10^{-3}$
Intercept	2.826 ± 0.102	2.779 ± 0.086	2.754 ± 0.073
R^2	0.86	0.88	0.91

Figure 4.2.f Reduction of PCE with $10 \mu\text{M}$ Fe(III) Cl- TPP in the presence of 7.5% DMF



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(2.6 \pm 0.5) \times 10^{-3}$	$(2.4 \pm 0.6) \times 10^{-3}$	$(2.1 \pm 0.8) \times 10^{-3}$
Intercept	2.920 ± 0.038	2.906 ± 0.044	2.914 ± 0.060
R ²	0.96	0.94	0.87

Figure 4.2.g Reduction of PCE with 10 μ M Fe(III) Cl- TPP in the presence of 10% DMF

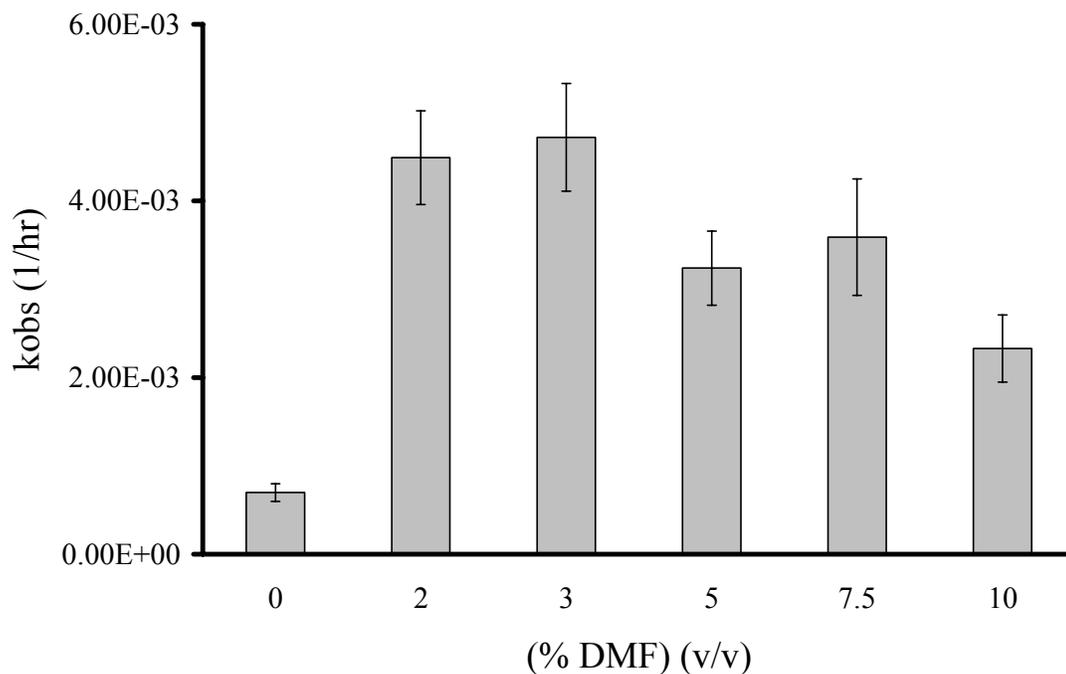


Figure 4.2.h Effects of increasing cosolvent concentration on the degradation rate of PCE catalyzed by 10 μ M Fe (III)Cl- TPP. The y-axis represents pseudo first order rate constants. Error bars represent uncertainty values calculated based on 95% confidence limits.

It was observed that the addition of DMF to an insoluble metalloporphyrin Fe(III) Cl-TPP increased the degradation rate of PCE. This finding is in accordance with a previous study which showed that the addition of 5% co-solvent dissolves and activated insoluble and inactive metalloporphyrin catalysts (Dror and Schlautman, 2003). Previously our research group observed a large increase in PCE degradation rate from 1% DMF to 5% DMF followed by a sharp decline at 10% DMF (with respect to 5% DMF) in the presence of 10 μ M Fe (III) Cl-TPP (Ramasubramanian, 2007). This finding is not in agreement with the simple hypothesis advanced by Dror and Schlautman (2003) because

(1) the metalloporphyrin did not stay in solution (e.g; flocs of Fe(III) Cl-TPP were formed) and (2) increasing DMF concentration did not consistently increase the catalyzed degradation rate of PCE. The present study was formulated with the aim of building on the results of Ramasubramanian (2007) to elucidate the process by which the addition of co-solvent affects PCE degradation. As a first step the rate of PCE degradation was determined for various DMF concentrations in the presence of two different metalloporphyrins, with more closely spaced DMF concentrations being tested (0, 2, 3, 5, 7.5 and 10% DMF). The degradation rate at 2, 3, 5, 7.5 and 10% DMF were higher than at 0% DMF. The degradation rate was highest at 3% DMF and remained relatively constant at 2% DMF and declined for higher concentrations of DMF. These results have been further discussed in section 4.5. It is also important to test whether increasing co-solvent concentrations in the absence of Fe (III)Cl-TPP would contribute to an increase in degradation rate.

4.3 Cosolvent effect on reductive dechlorination of PCE in the absence of Fe-(III) Cl-TPP

Presumably, cosolvents can enhance the rate of PCE degradation either by increasing the solubility of the organic pollutant or by increasing the solubility of an insoluble metalloporphyrin catalyst or by affecting some other component(s) of the reductive dechlorination reaction. Therefore, it is important to determine whether addition of DMF in the absence of Fe (III) Cl TPP enhances PCE degradation. Summary results are shown in Figure 4.3a where symbols show average values. The rate constants for PCE degradation in the absence of Fe(III) Cl-TPP are summarized in Table 4.2.

Individual results for each DMF concentration are shown in Figures 4.3b-g for the degradation of PCE over 144 hours. Symbols represent actual values from triplicate experimental samples. These plots show the degradation of PCE over a time course of 144 hours. Degradation rate constants in the presence and absence of Fe (III) Cl-TPP for increasing DMF concentrations are compared in Figure 4.3h. The data analysis procedure is the same as previously described for experiments conducted with Fe(III) Cl-TPP present (section 4.2).

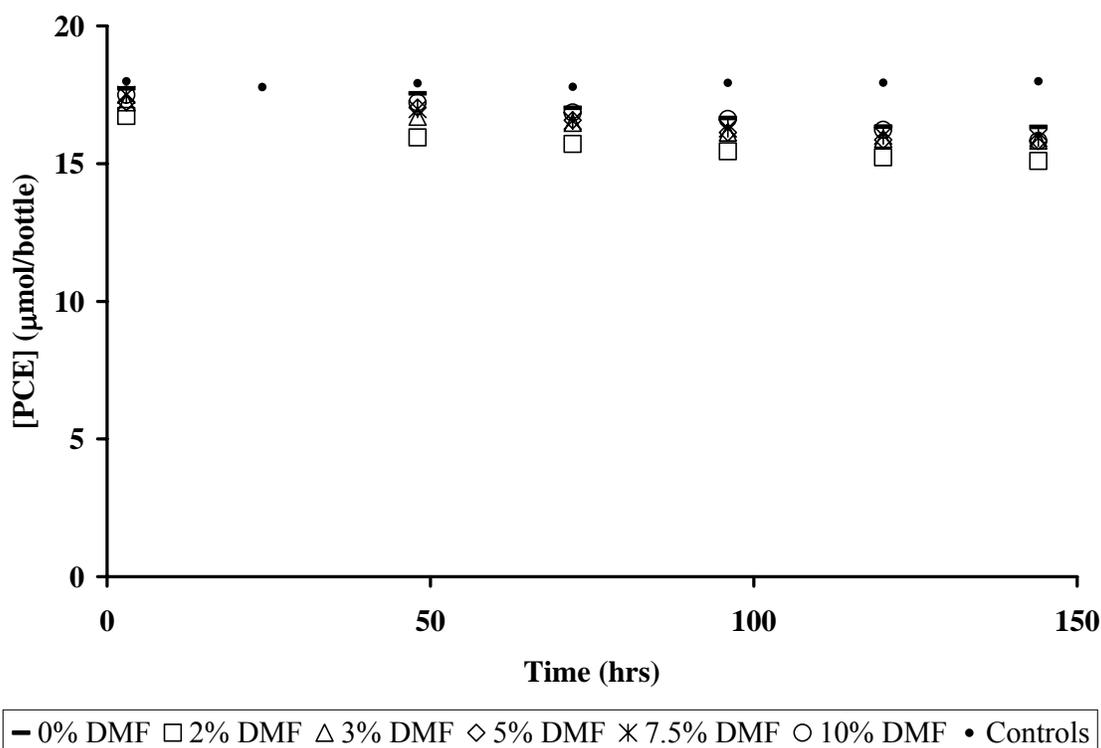
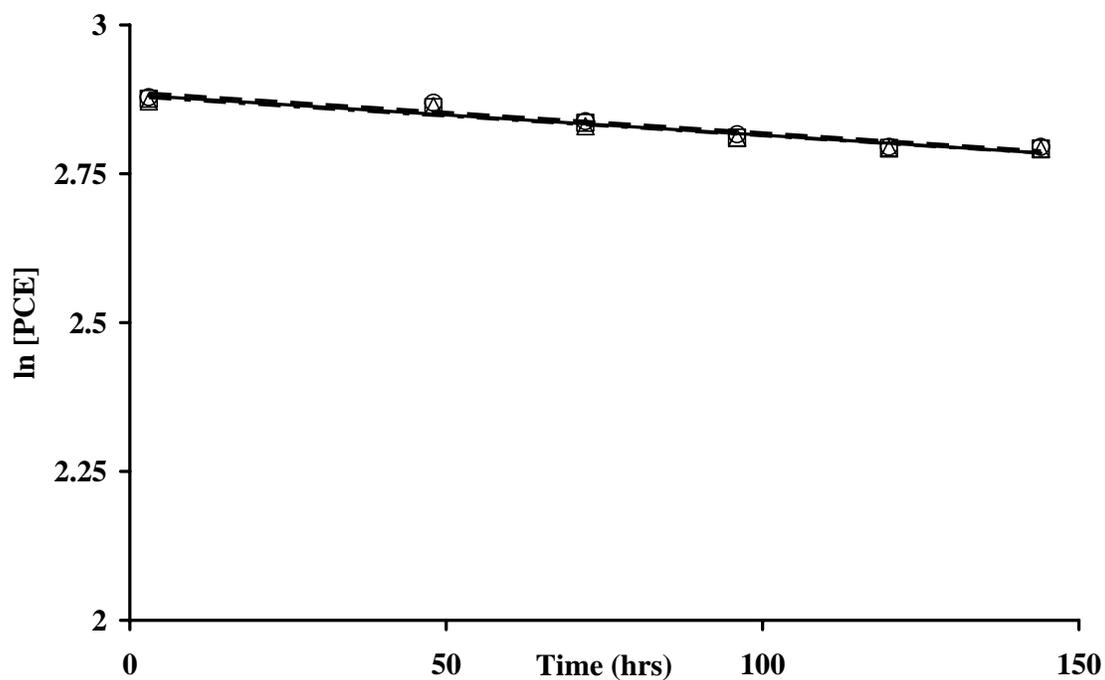


Figure 4.3.a Effect of DMF concentration on PCE degradation in the absence of Fe(III)Cl TPP. Data points represent average values.

Table 4.2 Observed rate constants (k_{obs}) for pseudo first order degradation of PCE using 50 mM titanium citrate as the bulk reductant with varying DMF concentrations in the absence of Fe (III)-Cl TPP

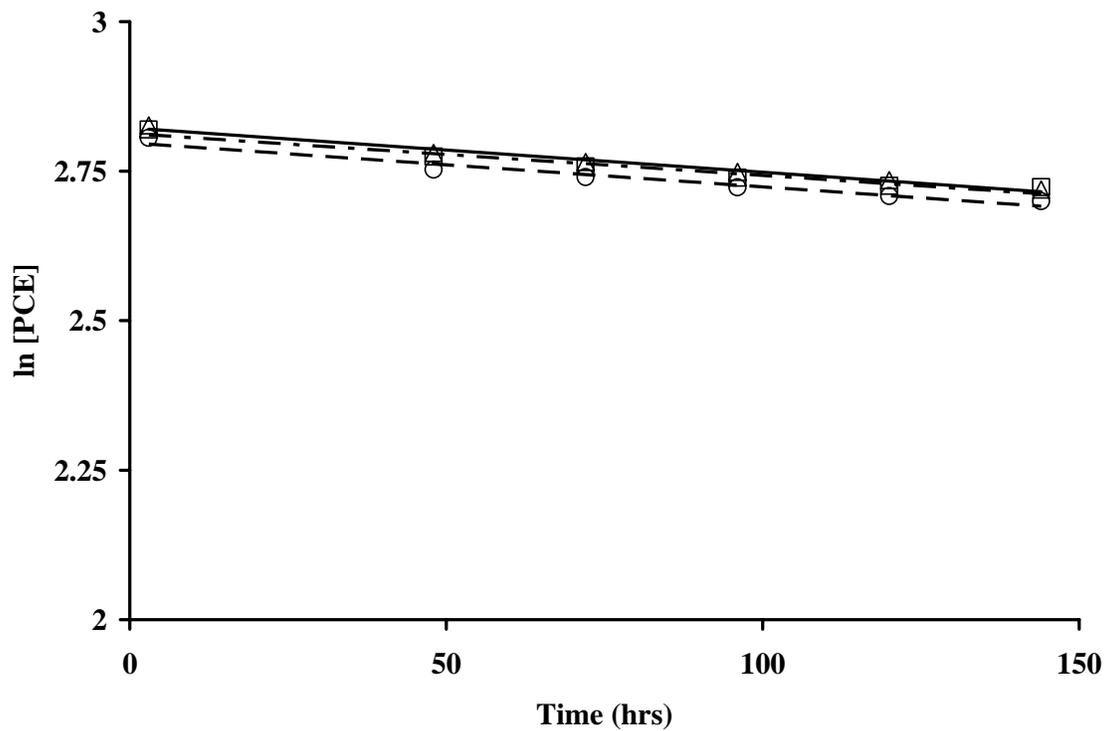
Amount of co-solvent (% v/v)	Observed rate constant k_{obs} (hr^{-1}) ^a
0%	$(6.7 \pm 1.0) \times 10^{-4}$ ^a $(5.7, 7.7) \times 10^{-4}$ ^b
2%	$(7.2 \pm 1.1) \times 10^{-4}$ ^a $(6.1, 8.3) \times 10^{-4}$ ^b
3%	$(6.3 \pm 1.1) \times 10^{-4}$ ^a $(5.2, 7.4) \times 10^{-4}$ ^b
5%	$(6.9 \pm 1.5) \times 10^{-4}$ ^a $(5.4, 8.4) \times 10^{-4}$ ^b
7.5%	$(7.0 \pm 1.1) \times 10^{-4}$ ^a $(5.9, 8.1) \times 10^{-4}$ ^b
10%	$(7.2 \pm 1.2) \times 10^{-4}$ ^a $(6.0, 8.4) \times 10^{-4}$ ^b

^areported rate constants \pm calculated uncertainties based on propagating 95% confidence limits. ^breported rate constant values inclusive of the calculated uncertainties.



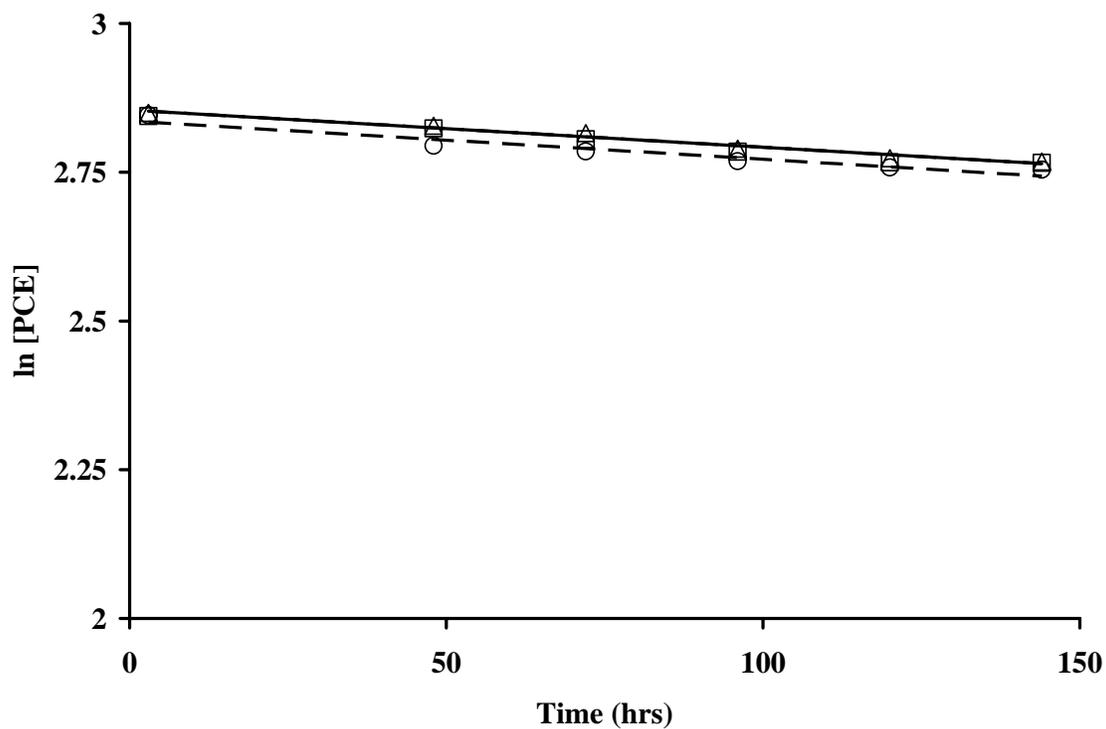
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(6.9 \pm 2.5) \times 10^{-4}$	$(6.8 \pm 2.2) \times 10^{-4}$	$(6.6 \pm 2.5) \times 10^{-4}$
Intercept	2.886 ± 0.023	2.882 ± 0.020	2.880 ± 0.023
R ²	0.93	0.95	0.93

Figure 4.3.b Reduction of PCE in the absence of DMF and Fe(III) Cl-TPP.



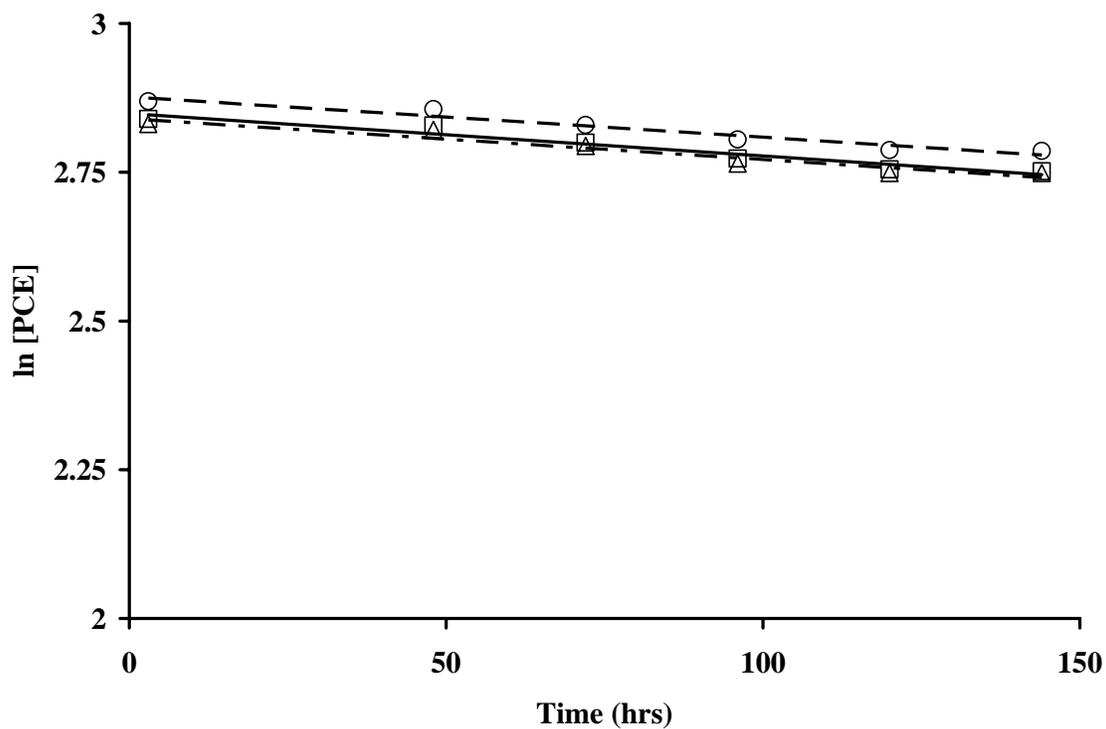
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(7.4 \pm 2.1) \times 10^{-4}$	$(7.0 \pm 2.1) \times 10^{-4}$	$(7.4 \pm 1.3) \times 10^{-4}$
Intercept	2.797 ± 0.020	2.813 ± 0.020	2.822 ± 0.012
R ²	0.96	0.95	0.98

Figure 4.3.c Reduction of PCE in the presence of 2% DMF and absence of Fe (III) Cl-TPP



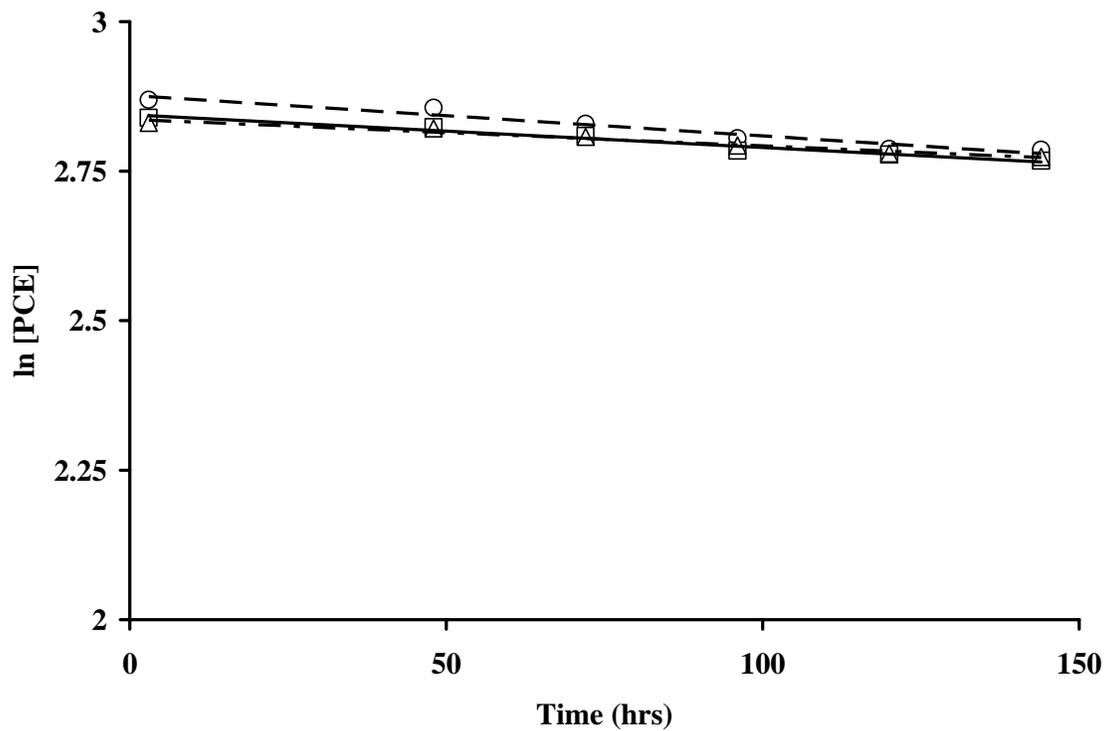
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(6.4 \pm 2.5) \times 10^{-4}$	$(6.1 \pm 1.50) \times 10^{-4}$	$(6.3 \pm 1.4) \times 10^{-4}$
Intercept	2.836 ± 0.023	2.847 ± 0.011	2.859 ± 0.013
R^2	0.93	0.97	0.97

Figure 4.3.d Reduction of PCE in the presence of 3% DMF and absence of Fe (III) Cl-TPP.



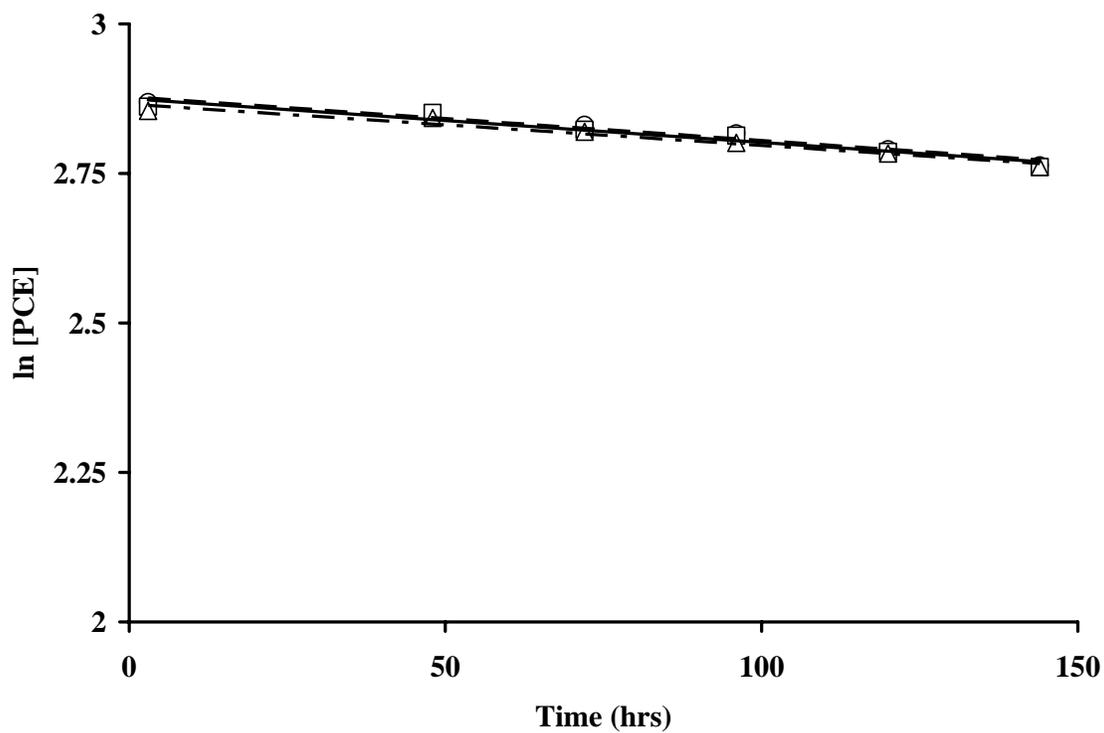
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(6.8 \pm 2.6) \times 10^{-4}$	$(7.1 \pm 2.5) \times 10^{-4}$	$(6.9 \pm 2.7) \times 10^{-4}$
Intercept	2.840 ± 0.025	2.850 ± 0.023	2.876 ± 0.021
R^2	0.95	0.94	0.93

Figure 4.3.e Reduction of PCE in the presence of 5% DMF and absence of Fe (III) Cl-TPP



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(7.3 \pm 2.3) \times 10^{-4}$	$(7.2 \pm 1.1) \times 10^{-4}$	$(6.6 \pm 1.1) \times 10^{-4}$
Intercept	2.862 ± 0.022	2.864 ± 0.011	2.860 ± 0.019
R^2	0.95	0.99	0.95

Figure 4.3.f Reduction of PCE in the presence of 7.5% DMF and absence of Fe (III) Cl-TPP



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(7.3 \pm 1.9) \times 10^{-4}$	$(7.3 \pm 2.4) \times 10^{-4}$	$(6.9 \pm 1.9) \times 10^{-4}$
Intercept	2.878 ± 0.018	2.875 ± 0.022	2.866 ± 0.0173 b
R ²	0.97	0.94	0.96

Figure 4.3.g Reduction of PCE in the presence of 10% of DMF and absence of Fe (III) Cl-TPP

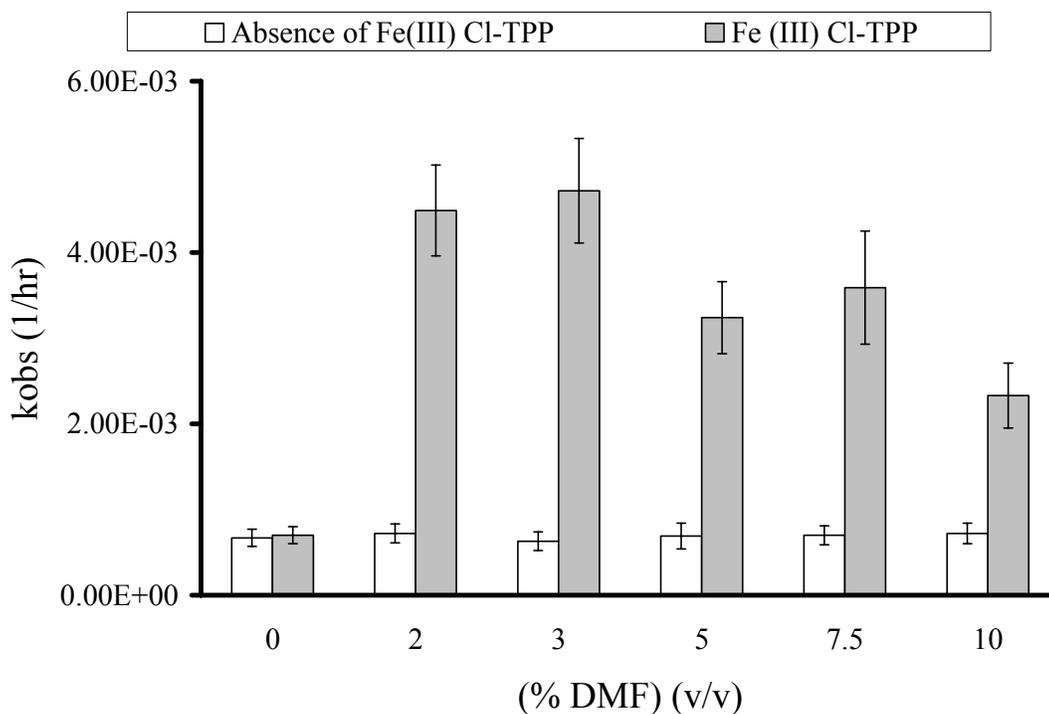


Figure 4.3.h Comparison of PCE degradation rates in the presence and absence of Fe (III)Cl-TPP. The y-axis represents pseudo first order rate constants. Error bars represent uncertainty values calculated based on propagating 95% confidence limits.

From Figure 4.3h and Table 4.2 it is evident that the addition of increasing DMF concentrations in the absence of Fe (III)-Cl TPP does not have any substantial effect on the degradation rate of PCE when compared to the first order rate constants in the presence of Fe (III)-Cl TPP. Therefore, DMF in the absence of Fe (III)-Cl TPP does not contribute to an increase in the degradation rate of PCE.

4.4 Cosolvent effect on reductive dechlorination of PCE in the presence of Ni (II)- TPP

The effect of varying DMF concentrations (0, 2, 5 and 10% (v/v) DMF) on the reductive dechlorination of PCE catalyzed by 10 μ M Ni-TPP was studied. This section will compare PCE degradation rates catalyzed by Fe-TPP with that of Ni-TPP with

increasing DMF concentrations. Summary results obtained from all experiments are shown in Figure 4.4a where symbols shown represent average values. The apparent pseudo first order rate coefficients are summarized in Table 4.3. Individual results for each DMF concentration are shown in Figures 4.4b-e. Symbols in Figure 4.4b-e represent actual values from triplicate experiments. These plots show the degradation of PCE over a time course of 144 hours. Figure 4.4f shows the variation of rate constants with increasing DMF concentrations. Figure 4.4g compares the first order rate constants in the presence of Fe (III) Cl- TPP to that of Ni-TPP with increasing co-solvent concentrations. The data analysis procedure used was the same as previously described for experiments conducted with Fe (III) Cl-TPP in section 4.2.

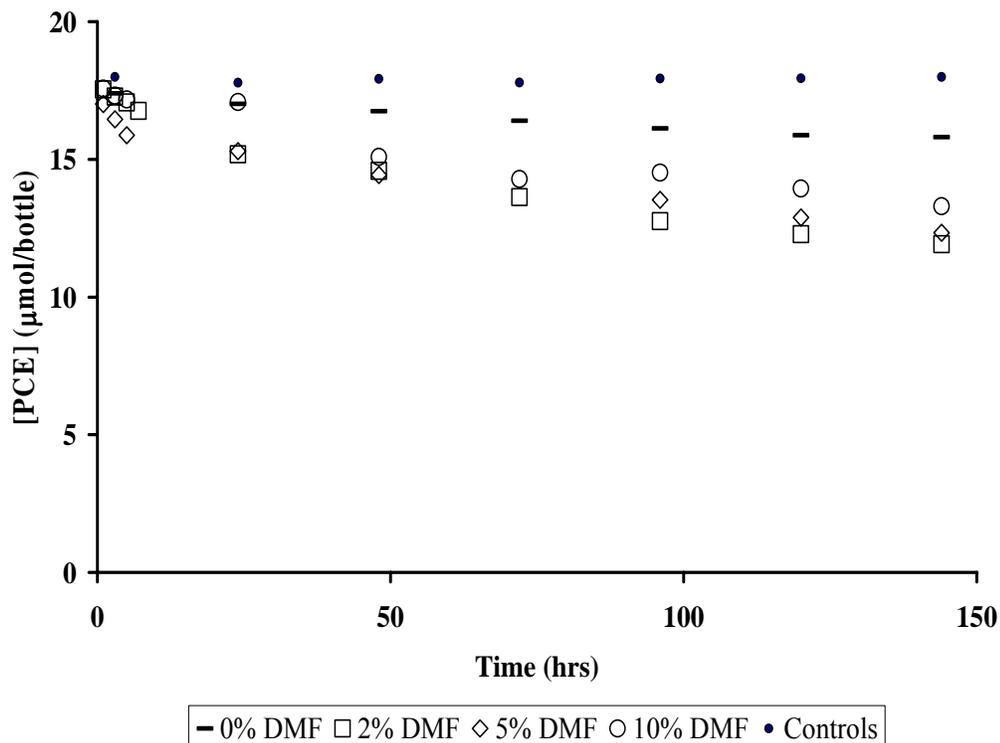
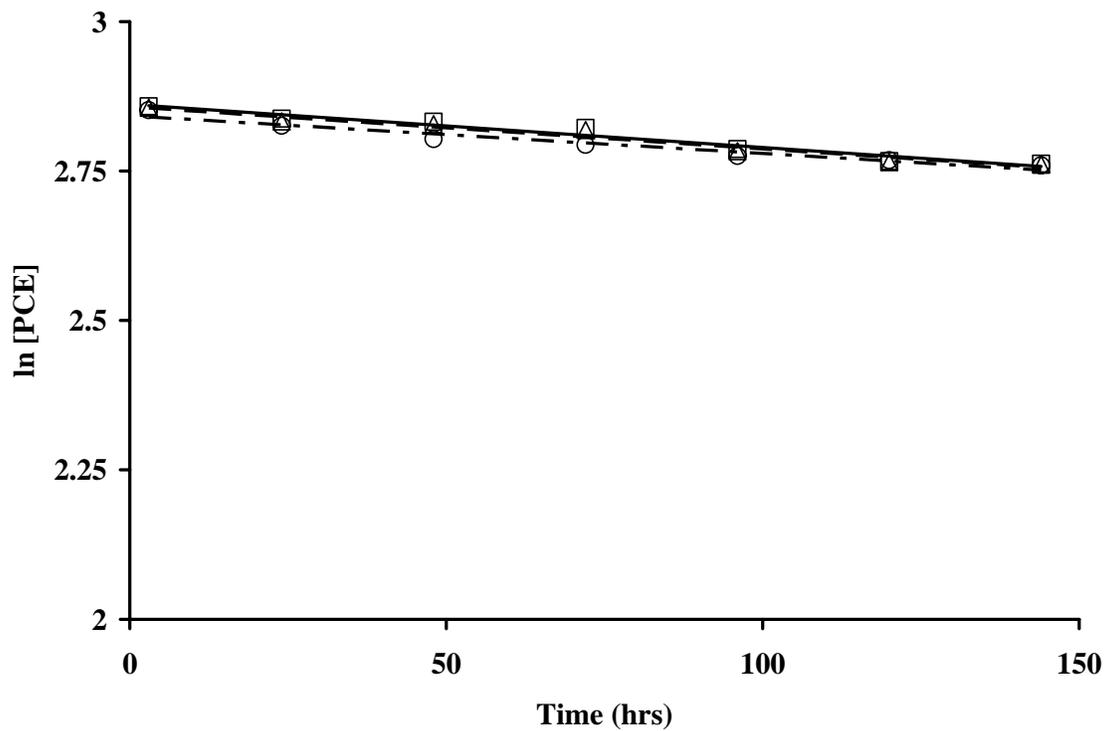


Figure 4.4.a Effect of cosolvent concentration on PCE degradation with 10 μ M Ni (II) TPP. Data points represent average values. The controls do not contain titanium citrate.

Table 4.3 Observed rate constants (k_{obs}) for pseudo first order degradation of PCE using 50mM titanium citrate as the bulk reductant catalyzed by 10 μ M Ni(II) TPP with varying amounts of cosolvent present

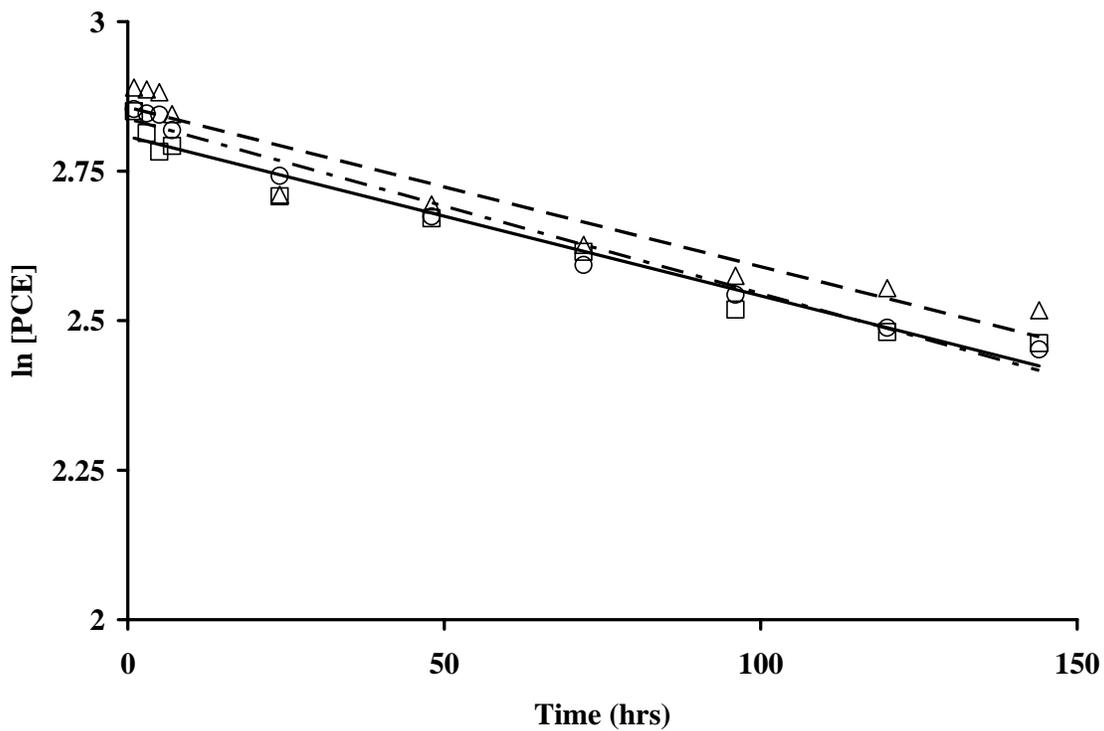
Amount of co-solvent	k_{obs} (hr ⁻¹) ^a
0%	(0.7 \pm 0.2) $\times 10^{-3}$ ^a (0.5, 0.9) $\times 10^{-3}$ ^b
2%	(2.8 \pm 0.3) $\times 10^{-3}$ ^a (2.5, 3.1) $\times 10^{-3}$ ^b
5%	(2.1 \pm 0.3) $\times 10^{-3}$ ^a (1.8, 2.4) $\times 10^{-3}$ ^b
10%	(1.9 \pm 0.3) $\times 10^{-3}$ ^a (1.6, 2.2) $\times 10^{-3}$ ^b

^areported rate constants \pm calculated uncertainties based on propagating 95% confidence limits. ^breported rate constant values inclusive of the calculated uncertainties.



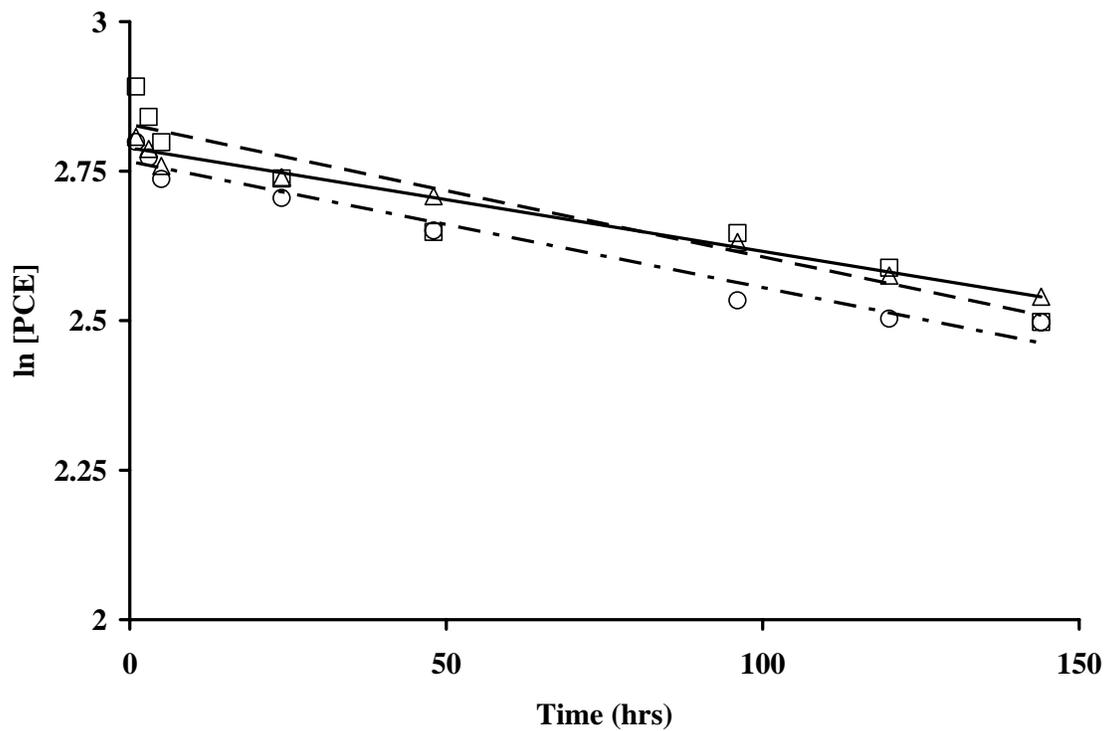
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(6.3 \pm 1.6) \times 10^{-4}$	$(7.2 \pm 1.7) \times 10^{-4}$	$(7.0 \pm 1.7) \times 10^{-4}$
Intercept	2.861 ± 0.014	2.865 ± 0.015	2.857 ± 0.015
R ²	0.95	0.96	0.96

Figure 4.4.b Reduction of PCE catalyzed by 10 μ M Ni- TPP in the absence of DMF



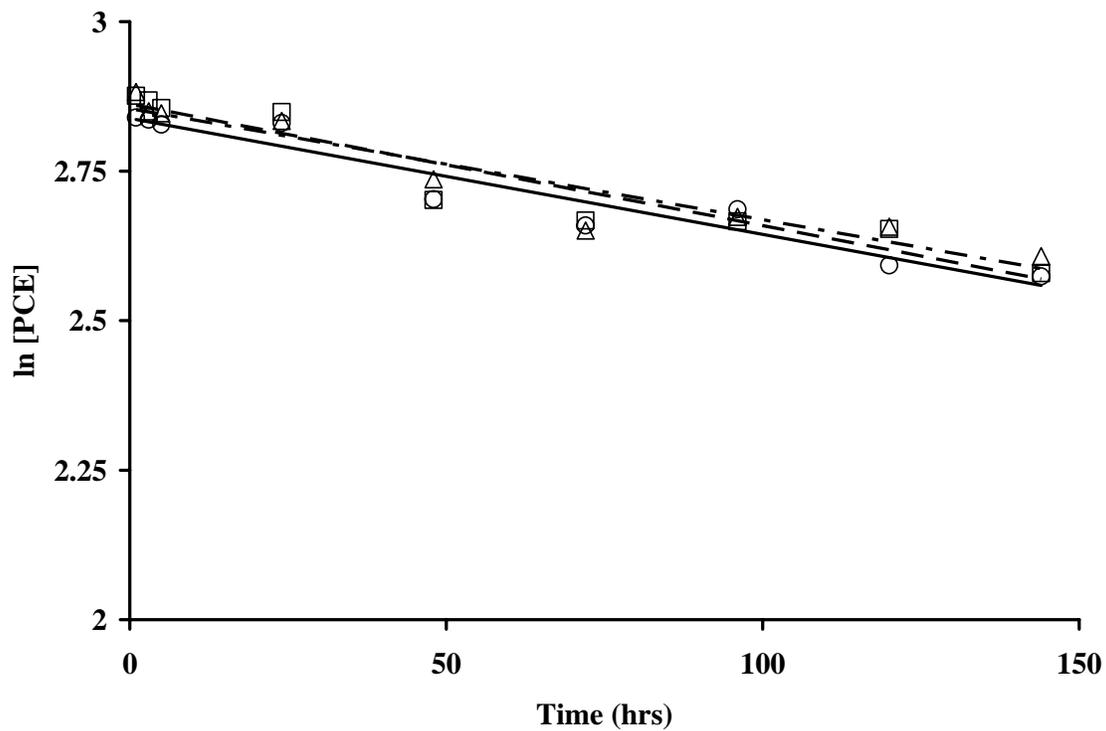
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(2.9 \pm 0.4) \times 10^{-3}$	$(2.67 \pm 0.4) \times 10^{-3}$	$(2.7 \pm 0.7) \times 10^{-3}$
Intercept	2.837 ± 0.026	2.807 ± 0.030	2.866 ± 0.053
R ²	0.98	0.97	0.90

Figure 4.4.c Reduction of PCE catalyzed by 10 μ M Ni- TPP in the presence of 2% DMF



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(2.2 \pm 0.5) \times 10^{-3}$	$(2.3 \pm 0.9) \times 10^{-3}$	$(1.7 \pm 0.2) \times 10^{-3}$
Intercept	2.766 ± 0.032	2.834 ± 0.066	2.788 ± 0.016
R ²	0.96	0.87	0.98

Figure 4.4.d Reduction of PCE catalyzed by 10 μ M Ni (II)-TPP in the presence of 5% DMF



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(1.9 \pm 0.5) \times 10^{-3}$	$(2.0 \pm 0.6) \times 10^{-3}$	$(1.90 \pm 0.5) \times 10^{-3}$
Intercept	2.838 ± 0.036	2.862 ± 0.043	2.855 ± 0.041
R^2	0.93	0.91	0.91

Figure 4.4.e Reduction of PCE catalyzed by $10 \mu\text{M}$ Ni (II)-TPP in the presence of 10% DMF

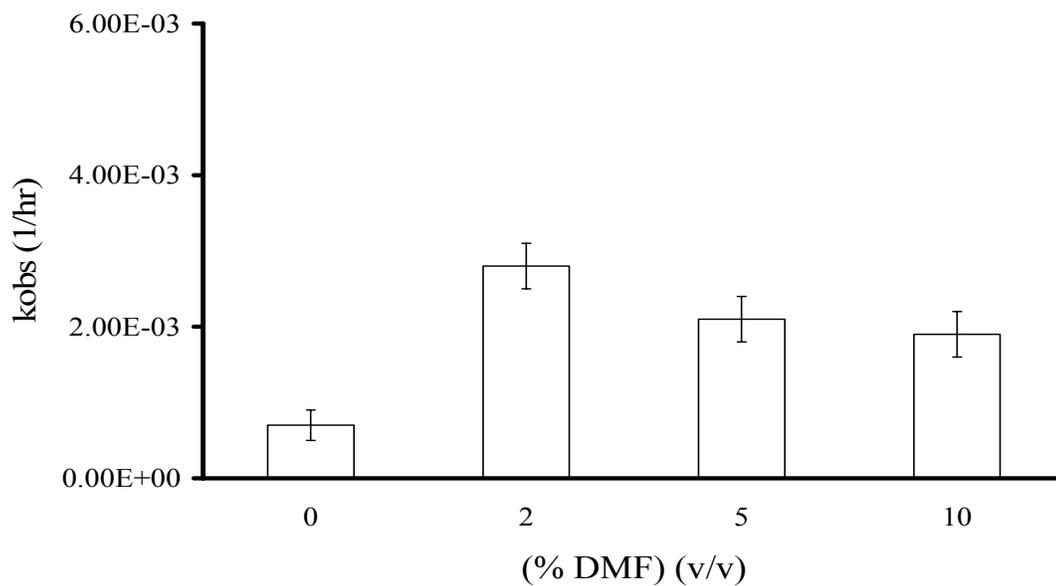


Figure 4.4.f Effect of increasing DMF concentration on the degradation rate of PCE in the presence of $10 \mu\text{M}$ Ni-TPP. The y-axis represents pseudo first order rate constants. Error bars represent uncertainty values calculated based on propagating 95% confidence limits

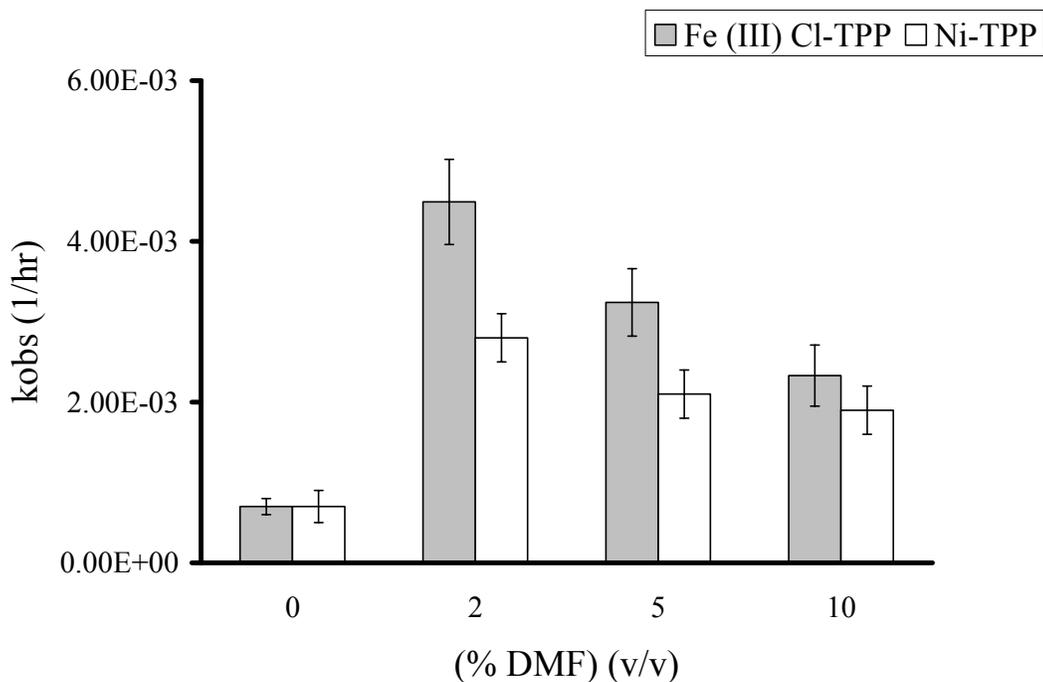


Figure 4.4.g Comparison of degradation rate of PCE with increasing co-solvent concentration in the presence of 10 μ M Fe (III)Cl- TPP and Ni-TPP. The y-axis represents pseudo first order rate constants. Error bars represent uncertainty values calculated based on 95% confidence limits.

The effects of DMF concentration (0, 2, 5 and 10%) were also tested for PCE degradation in the presence of Ni-TPP. PCE degradation rates were significantly higher for 2, 5 and 10% DMF than for 0% DMF. The degradation rate was the highest for 2% DMF and decreased for higher co-solvent concentrations. These Ni-TPP results are consistent with the results obtained in section 4.2 for Fe (III) Cl-TPP. The efficacy of Ni-TPP as a catalyst was compared to Fe (III)Cl-TPP. Fe (III) Cl-TPP was observed to be more effective than Ni-TPP in catalyzing the degradation of PCE. However, these results did not agree with the findings reported by Dror and Schlautman (2003) who stated that complete degradation of PCE occurred in 40 hrs in the presence of Ni-TPP at 5% DMF

whereas only 30% of PCE degraded in 168 hrs in the presence of Fe (III) Cl-TPP and 5% DMF, suggesting that Ni-TPP was more effective as a catalyst than Fe (III) Cl-TPP.

While Dror and Schlautman's (2003) research studied the degradation of PCE catalyzed by Ni-TPP in the presence of 5% DMF, we performed experiments that not only sampled multiple DMF concentrations but also looked at different measures of PCE degradation (for e.g., percentage degraded, concentration and degradation rate). Though Dror and Schlautman (2003) used the same analytical technique, the degradation of PCE was calculated relative to the total peak area counts of other degradation products formed whereas we quantified the amount of PCE degraded based on the external standards/response factors of PCE. Therefore, our findings may give a more robust account of PCE degradation compared to other findings.

4.5 Metalloporphyrin dimers

It has been shown that the addition of an organic solution containing a hydrophobic metalloporphyrin like Fe (III)TPP-Cl to an aqueous solution of high pH, leads to the formation of μ -oxo dimers ((FeTPP)₂O) (Kasuno et al., 2005; Fleischer and Srivastava, 1969). Iron porphyrins are known to dimerize in aqueous solutions (Smith, 1975). In the case of protoporphyrin IX, the ferric form exists as dimers in basic solution whereas the ferrous form exists either as dimers or monomers depending on the pH (Bednarski and Jordan, 1957). Dimers have been shown to possess remarkable electron transfer properties (Yushmanov et al., 1996). Therefore, it was hypothesized that the increase in degradation rate observed upon addition of co-solvent may be explained by formations of metalloporphyrin dimers.

To test for the presence of dimers, UV-Vis absorbance of Fe (III) Cl-TPP was measured in the presence of varying DMF concentrations (pure DMF, 2, 3, 5, 7.5 and 10% DMF). The spectra are shown in Figure 4.5b along with the characteristic absorption spectra of FeTPP-Cl and (FeTPP)₂O (Figure 4.5a) that have been previously reported (Cheng et al., 1981). Table 4.4 shows the visible absorption spectra of Fe(III)Cl-TPP and (FeTPP)₂O obtained by different researchers.

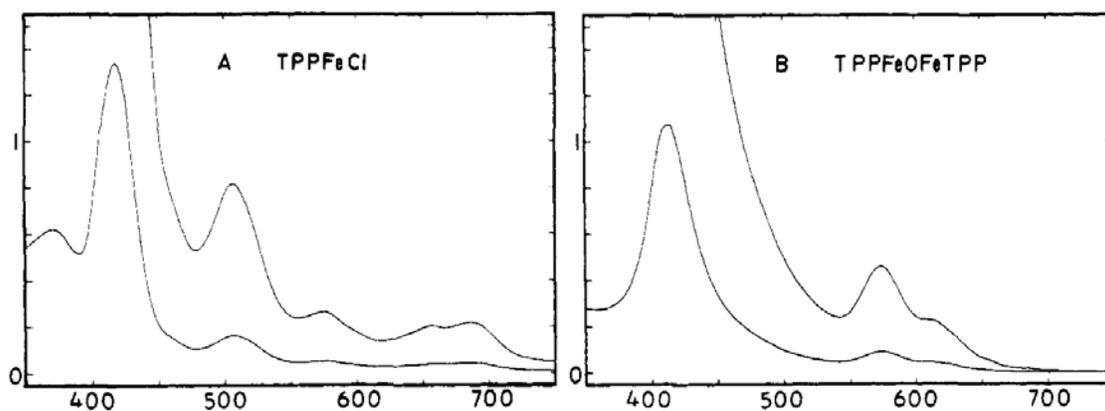


Figure 4.5.a Characteristic spectrum of Fe (III)Cl-TPP and (FeTPP)₂O in toluene (Cheng et al., 1981). The other spectra in each of these figures are merely “blowups” or magnified by some unknown/unreported amount.

Table 4.4 Visible absorption spectrum of Fe (III) Cl-TPP and (FeTPP)₂O

Compound	Solvent	Peak (nm)	Reference
Fe(III)Cl-TPP	CHCl ₃	380	(Fleischer et al., 1970)
		417	
		511	
		577	
		658	
		690	
Fe(III) Cl-TPP	Toluene	419	(Cheng et al., 1981)
		506	
		572	
		656	
		690	
(FeTPP) ₂ O	Benzene	408	(Fleischer et al., 1970)
		571	
		612	
(FeTPP) ₂ O	DMF	408	(Kadish et al., 1975)
		570	
(FeTPP) ₂ O	Toluene	412	(Cheng et al., 1981)
		574	
		610	
Fe (III)Cl-TPP	Pure DMF, 2, 3, 5, 7.5 AND 10% DMF	409	Spectra obtained from our analysis
		571	
		613	

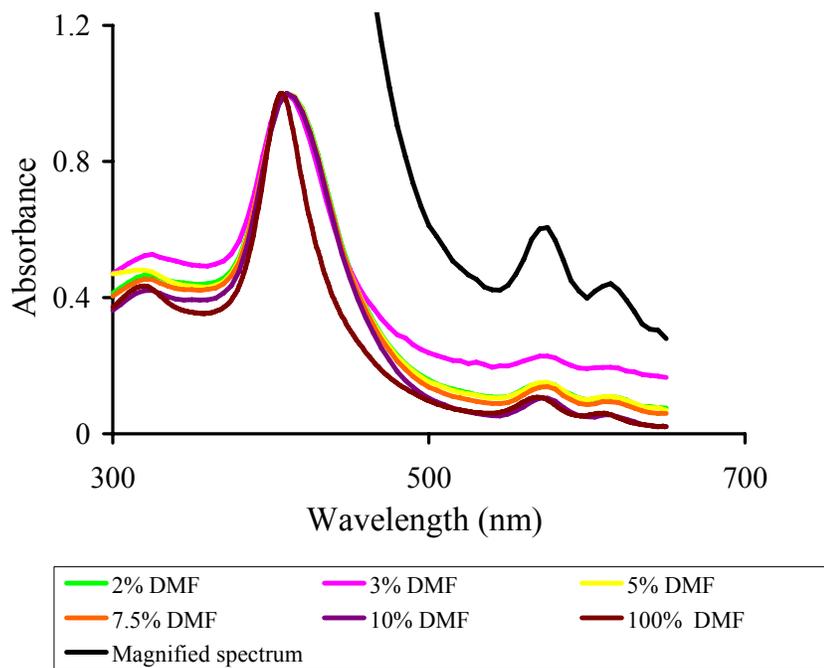


Figure 4.5.b UV-Vis spectra of Fe (III) Cl-TPP in 2, 3, 5, 7.5, 10 and 100% DMF. The second spectrum in the figure is a mere “blowup” or magnified by 2.5 times the original absorbance.

Peaks for Fe (III)TPP-Cl in toluene were observed at 419, 506, 572, 656 and 690 nm and for that of (FeTPP)₂O were observed at 412, 574 and 610 nm (Cheng et al., 1970). The peak 506- 510 nm is characteristic of monomeric Fe (III) porphyrins and the peak at 570 nm is characteristic of dimers (Yushmanov et al., 1996). However, the absorption spectrum measured here for Fe (III)Cl-TPP in pure DMF (i.e., similar to the metalloporphyrin stock solution) was not similar to the spectra of Fe(III) Cl-TPP in toluene obtained by Cheng et al. (1981). Rather, the spectrum of Fe(III) Cl-TPP in pure DMF and 2, 3, 5, 7.5 and 10% DMF looked very similar to the absorption spectrum of (Fe-TPP)₂O in toluene. The absence of any peak around 510 nm strongly suggests the absence of monomers while the presence of peaks around 570 nm suggests μ -oxo dimers are present in our experimental system. This presence of dimers may help explain why Fe(III) Cl-TPP was able to increase the rate of degradation in the presence of DMF.

No evidence was found in the literature regarding possible formation of dimers for experimental systems containing Ni-TPP. Therefore, it is unknown if Ni-TPP formed dimers in our experimental system.

4.6 Effect of different bulk electron donors on the reductive dechlorination of PCE in the presence of Fe (III) Cl- TPP

The effects of two different bulk electron donors (50 mM titanium citrate versus 34.5 mM sodium dithionite) were studied on the reductive dechlorination of PCE catalyzed by 10 μ M Fe (III) Cl- TPP in the presence of 5% DMF. Of the various concentrations tested (11.5, 34.5, 68.9 and 137.8 mM dithionite solutions), 34.5 mM dithionite was found to be most effective in degrading PCE and was therefore chosen for our experimental system (Nzengung et al., 2001). Concentrations of dithionite greater

than 34.5 mM did not proportionally increase the degradation of PCE. This may have been due to the consumption of protons in competing reactions, for example the sulfoxyl radical ($\text{SO}_2\cdot^-$) may react with the protons to form hydrogen sulfite and sulfate (Nzengung et al., 2001) (Please refer back to section 2.6).

Summary results are shown in Figures 4.6a-b for average values. Results from individual experiments are shown in Figures 4.6c-e. . Apparent first order rate constants are summarized in Table 4.5. PCE degradation rates in the presence of dithionite at different buffer (bicarbonate) concentrations are compared in Figure 4.6f. The data analysis procedure is the same as previously described experiments in section 4.2. Rate constants in the presence of bulk reductants- titanium citrate and dithionite are compared in Figure 4.6g.

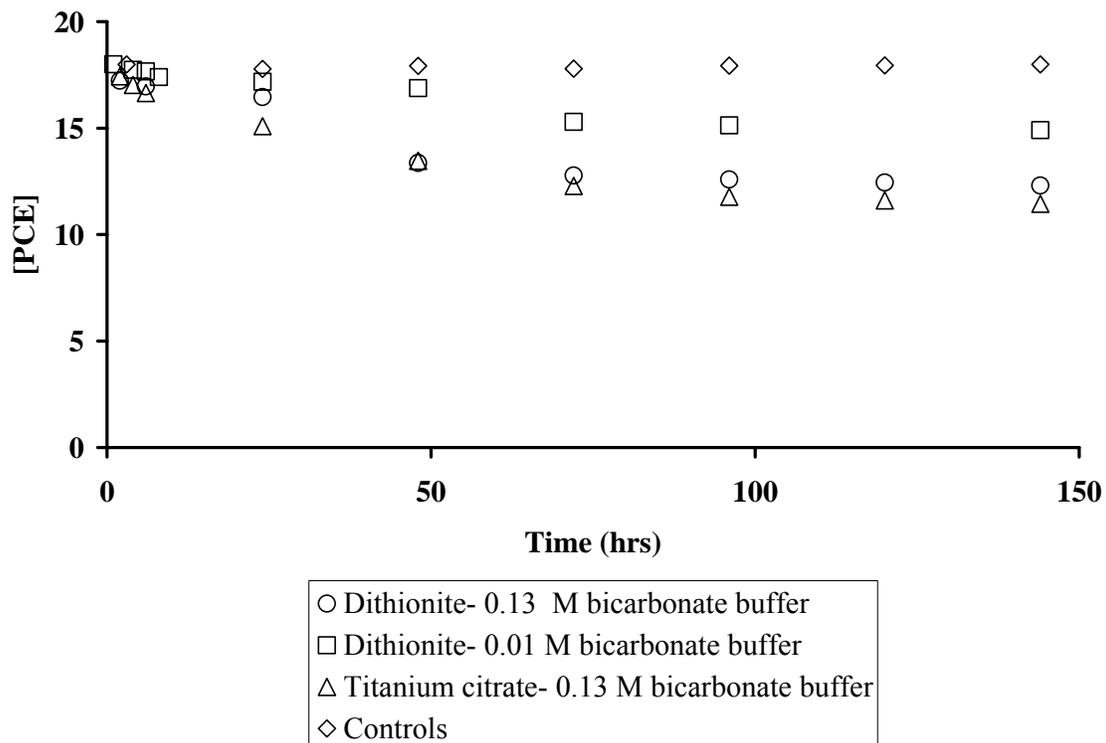


Figure 4.6.a Effect of different bulk reductants (titanium citrate and dithionite on the degradation of PCE catalyzed by Fe (III)Cl-TPP in the presence of 5% DMF. Controls do not contain dithionite or titanium citrate

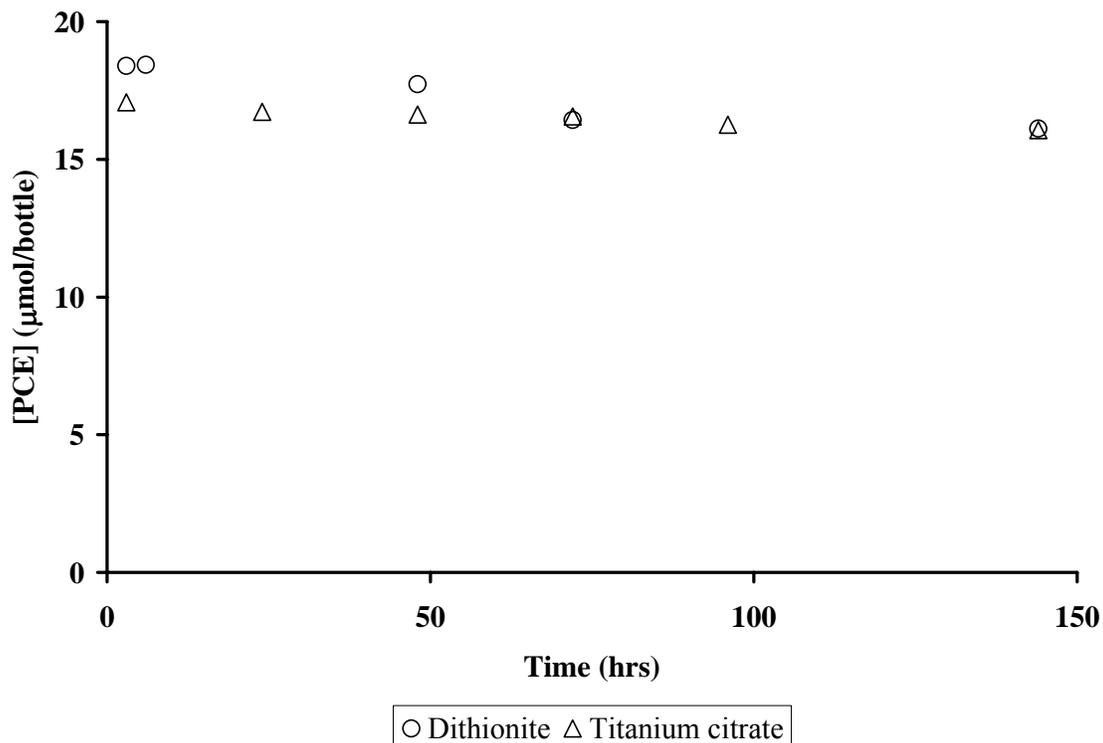
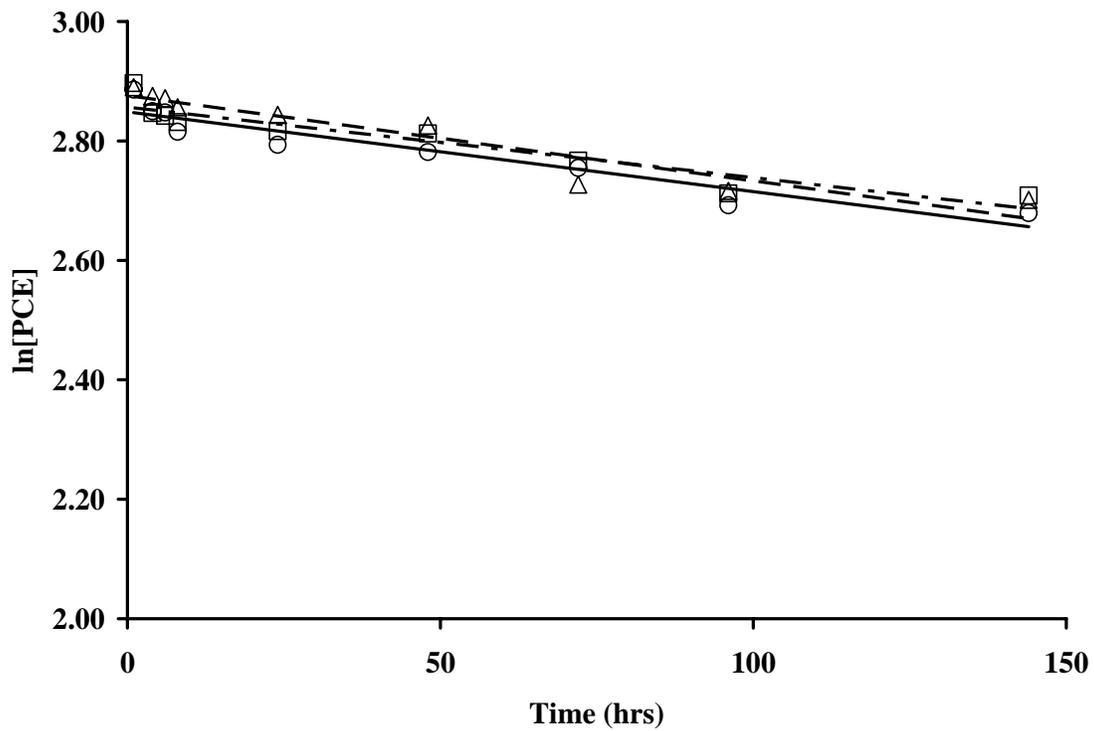


Figure 4.6.b Effect of different bulk reductants (titanium citrate and dithionite on the degradation of PCE in the absence of Fe (III)Cl-TPP 5% DMF.

Table 4.5 Observed rate constants (k_{obs}) for pseudo first order disappearance of PCE using titanium citrate and dithionite as the bulk reductant catalyzed by $10\mu\text{M}$ Fe(III) Cl TPP in the presence of 5% DMF.

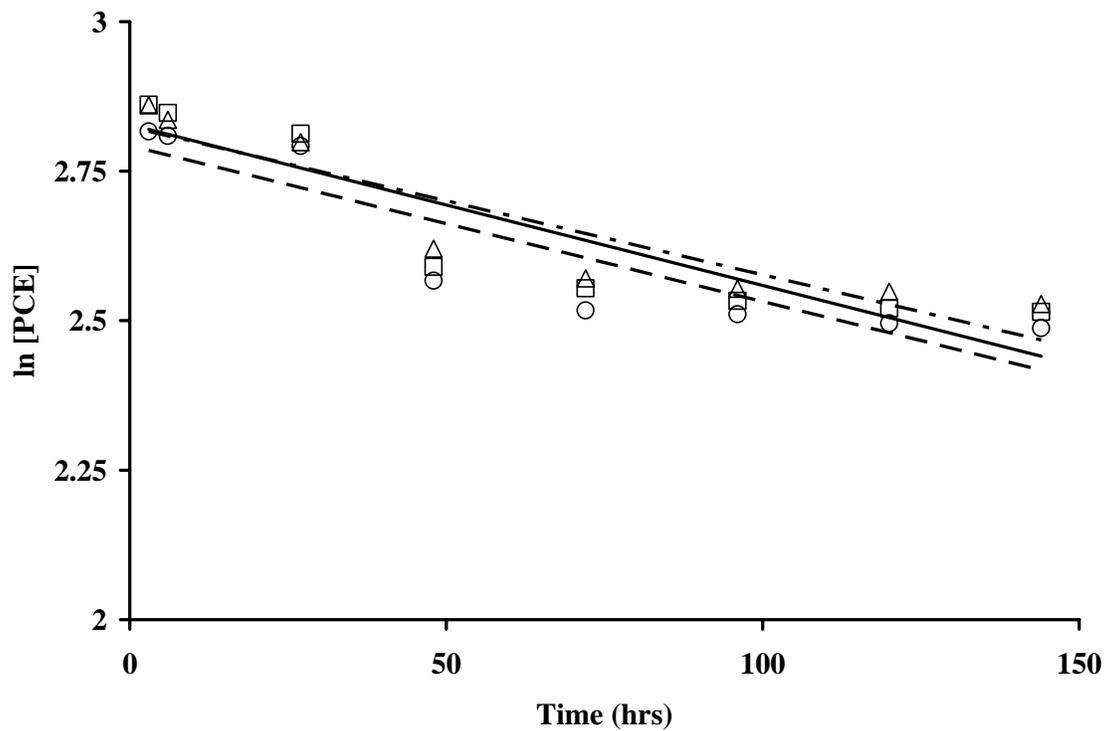
Bulk electron donor	$k_{\text{obs}} (\text{hr}^{-1})^{\text{a}}$
Titanium citrate (0.13 M bicarbonate buffer)	$(3.1 \pm 0.5) \times 10^{-3} \text{ }^{\text{a}}$ $(2.6, 3.6) \times 10^{-3} \text{ }^{\text{b}}$
Sodium dithionite (0.13 M bicarbonate buffer)	$(2.7 \pm 0.7) \times 10^{-3} \text{ }^{\text{a}}$ $(2.0, 3.4) \times 10^{-3} \text{ }^{\text{b}}$
Sodium dithionite (0.01 M) bicarbonate buffer	$(1.3 \pm 0.2) \times 10^{-3} \text{ }^{\text{a}}$ $(1.1, 1.5) \times 10^{-3} \text{ }^{\text{b}}$

^areported rate constants \pm calculated uncertainties based on propagating 95% confidence limits. ^breported rate constants inclusive of the calculated uncertainties.



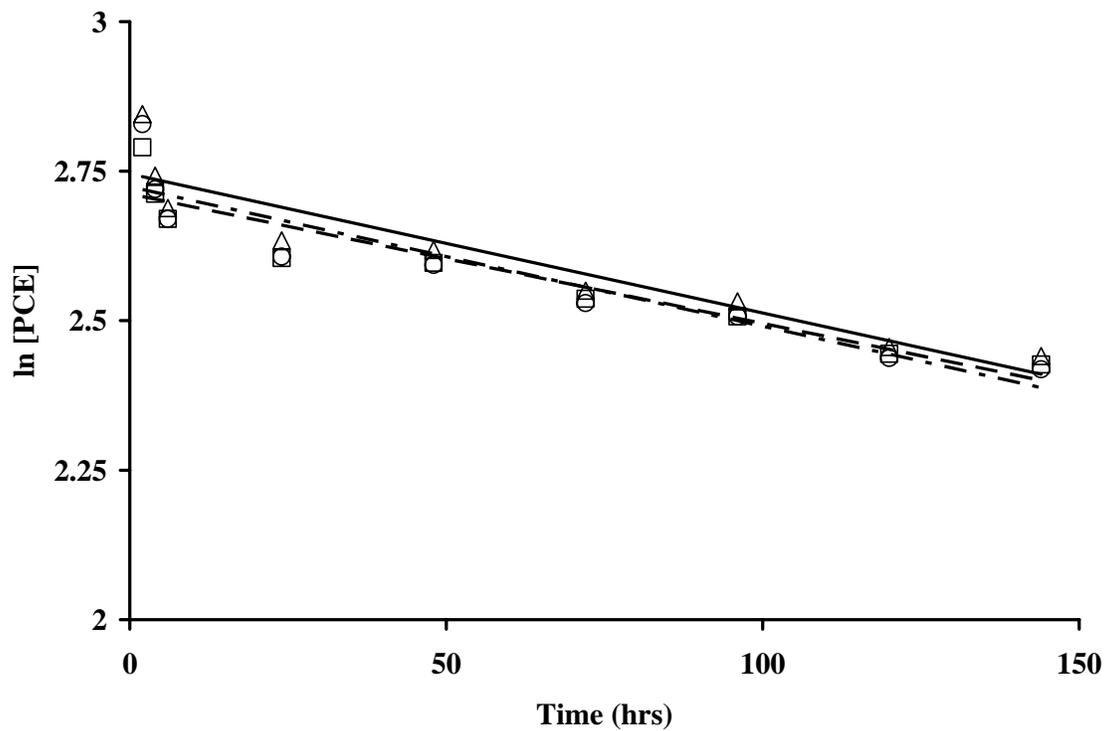
	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(1.3 \pm 0.4) \times 10^{-3}$	$(1.2 \pm 0.4) \times 10^{-3}$	$(1.4 \pm 0.4) \times 10^{-3}$
Intercept	2.848 ± 0.027	2.856 ± 0.025	2.875 ± 0.020
R ²	0.89	0.88	0.91

Figure 4.6.c Reduction of PCE in the presence of 34.5 mM sodium dithionite, 0.01M buffer and 5% DMF catalyzed by 10 μ M Fe (II)Cl-TPP



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(2.9 \pm 1.1) \times 10^{-3}$	$(2.7 \pm 0.13) \times 10^{-3}$	$(2.5 \pm 1.1) \times 10^{-3}$
Intercept	2.805 ± 0.087	2.827 ± 0.103	2.824 ± 0.087
R ²	0.88	0.81	0.84

Figure 4.6.d Reduction of PCE in the presence of 34.5 mM sodium dithionite, 0.13 M buffer and 5% DMF catalyzed by 10 μ M Fe (III)Cl-TPP



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(3.3 \pm 0.9) \times 10^{-3}$	$(3.1 \pm 0.9) \times 10^{-3}$	$(3.0 \pm 0.9) \times 10^{-3}$
Intercept	2.775 ± 0.070	2.827 ± 0.070	2.828 ± 0.066
R ²	0.91	0.90	0.91

Figure 4.6.e Reduction of PCE using titanium citrate as the bulk reductant, 0.13 M sodium bicarbonate buffer, catalyzed by Fe (III) Cl- TPP in the presence of 5% DMF.

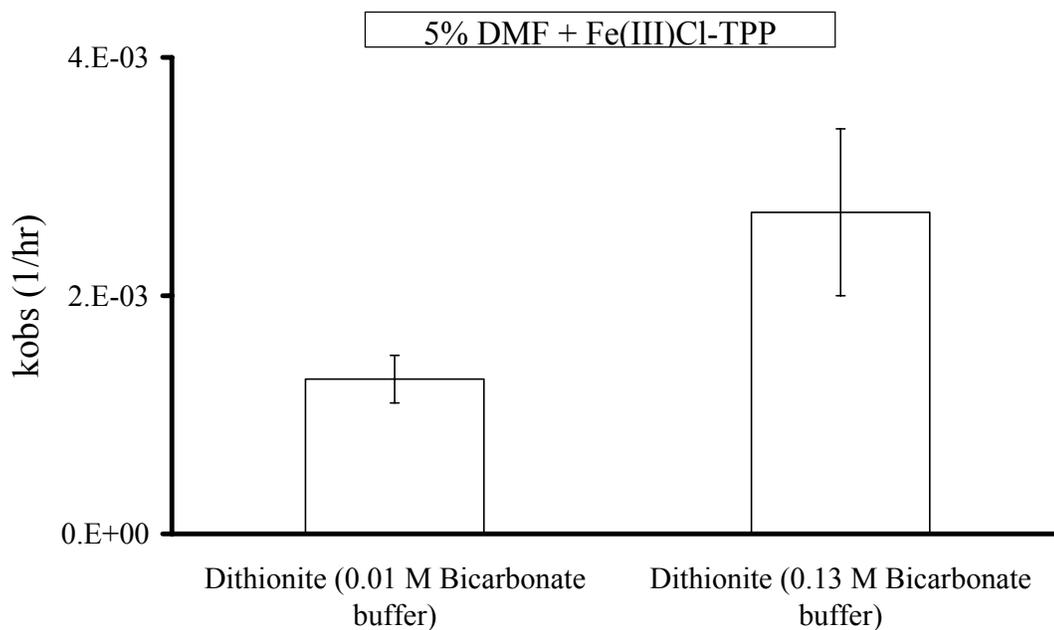


Figure 4.6.f Comparison of the degradation rate of PCE using dithionite and two different bicarbonate buffer concentrations (0.01M and 0.13 M) in the presence of Fe(III) Cl-TPP and 5% DMF. The y-axis represents pseudo first order rate constants. Error bars represent uncertainty values calculated based on propagating 95% confidence limits.

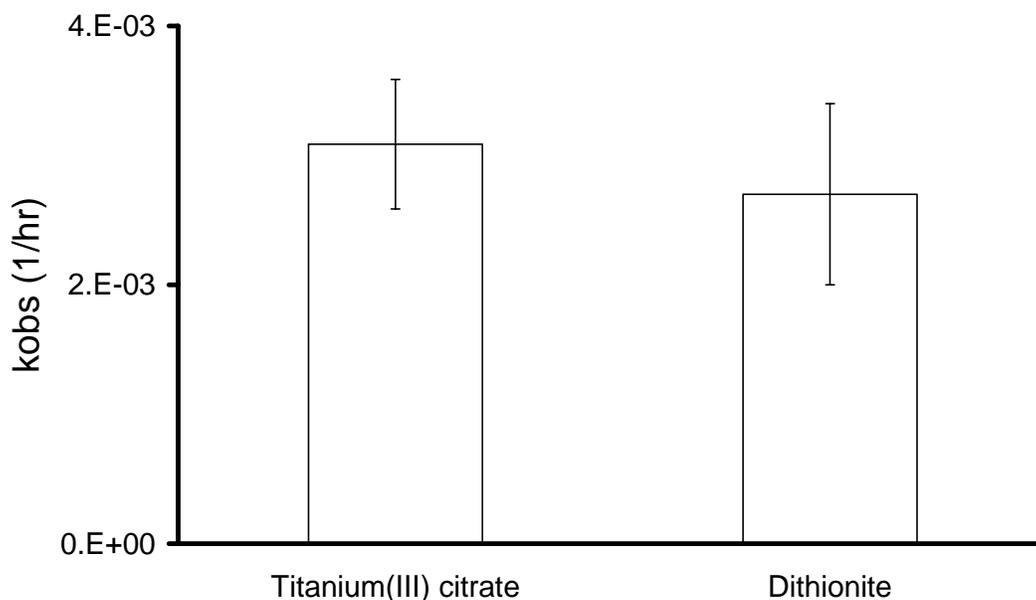


Figure 4.6.g Comparison of the degradation rate of PCE using dithionite and titanium citrate using 0.13 M bicarbonate buffer in the presence of Fe(III) Cl-TPP and 5% DMF. The y-axis represents pseudo first order rate constants. Error bars represent uncertainty values calculated based on 95% confidence limits.

The degradation rate for PCE was observed to be relatively constant for titanium citrate and dithionite in the presence of 0.13 M bicarbonate buffer. Additionally, the degradation rate was observed to be significantly lower for dithionite containing low bicarbonate concentration (0.01 M) than systems containing dithionite with relatively high bicarbonate concentrations (0.13 M). This difference may be attributed to pH changes that occurred during the degradation reaction. For example, systems containing dithionite as electron donor, the pH decreased from 8.5 to 6.4 in the presence of 0.01 M bicarbonate buffer concentration whereas, it only decreased from 8.5 to 8.0 in the

presence of 0.13 M bicarbonate buffer concentration (0.13 M). These results are consistent with those obtained by Nzengung et al. (2001) who demonstrated better degradation in well-buffered dithionite solutions versus un-buffered dithionite solutions. These results may be explained by the faster degradation of dithionite observed at low pH. PCE degradation stops when dithionite dissociates completely and/or is inhibited by the accumulation of oxysulfur anions which change the ionic strength of the solution (Nzengung et al., 2001).

4.7 Effect of different buffers on the reductive dechlorination of PCE in the presence of Fe (III) Cl- TPP

The effect of different buffers (TRIS and sodium bicarbonate- 0.13 M) was studied on the degradation rate of PCE in the presence of each reductant (dithionite and titanium citrate) catalyzed by Fe (III) Cl-TPP. Summary results are shown in Figures 4.7a-b for average values. Pseudo first order rate constants are summarized in Table 4.6. Individual results for experiments are shown in Figures 4.7c-d. Symbols in Figures 4.7c-d represent actual values from all triplicates. Figures 4.7e-f show the variation of first order rate constants in the presence of different buffers catalyzed by Fe(III)Cl-TPP in the presence of 5% DMF.

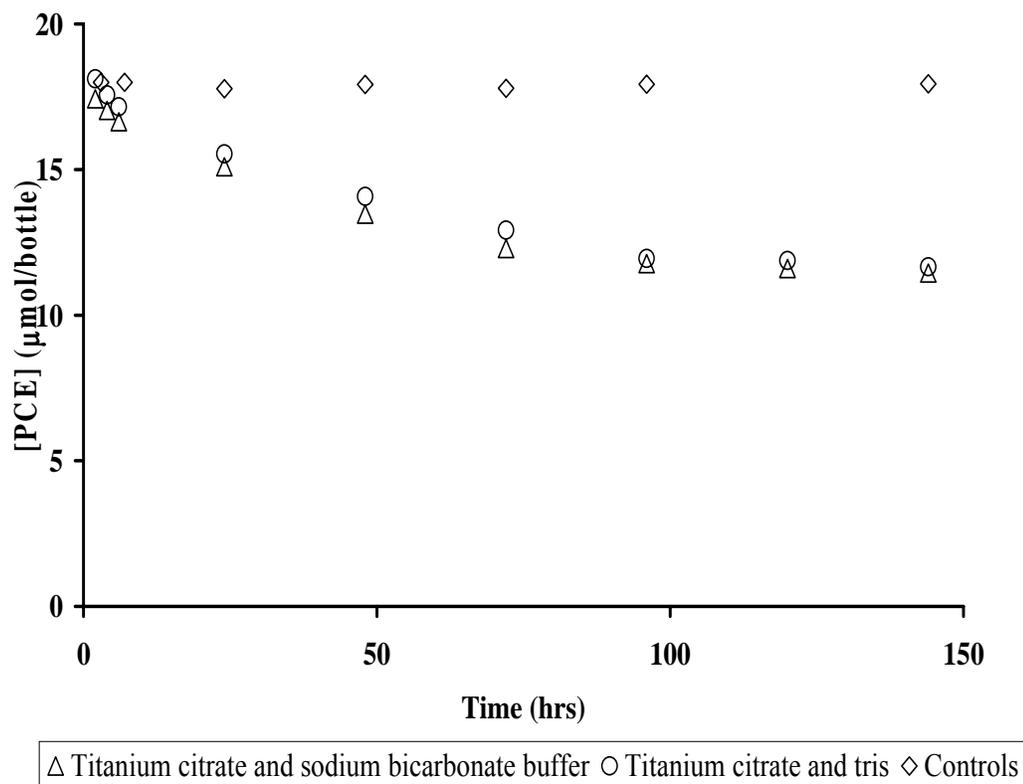


Figure 4.7.a Effect of TRIS and sodium bicarbonate buffer on the degradation of PCE using titanium citrate as the bulk reductant, catalyzed by Fe (III) Cl-TPP in the presence of 5% DMF. Symbols represent average values. Controls do not contain titanium citrate.

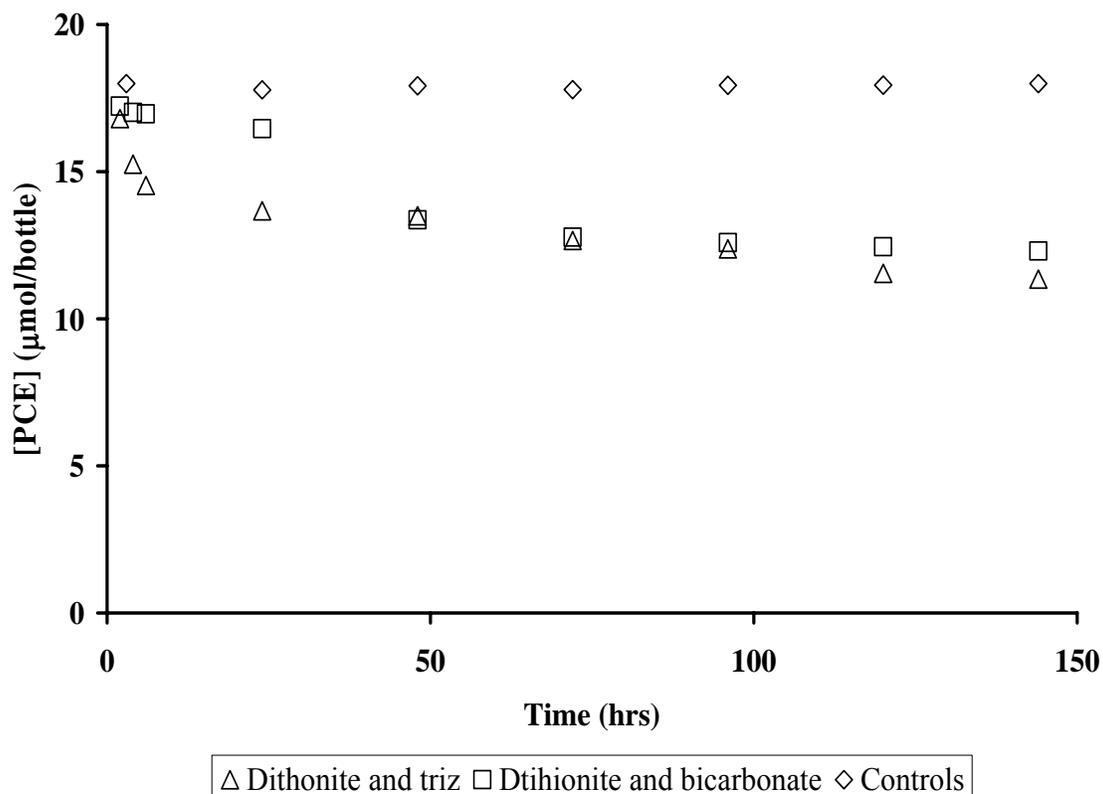
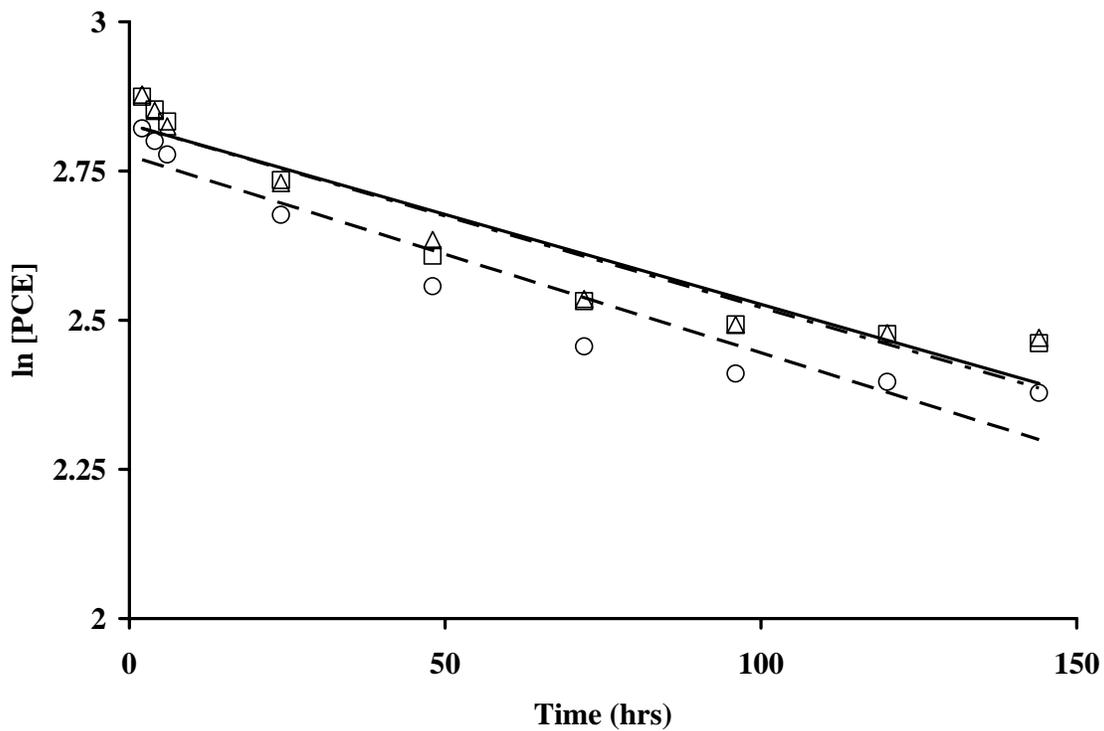


Figure 4.7.b Effect of TRIS and sodium bicarbonate buffer on the degradation of PCE using dithionite as the bulk reductant, catalyzed by Fe (III) Cl-TPP in the presence of 5% DMF. Symbols represent average values. Controls do not contain dithionite.

Table 4.6 Observed rate constants (k_{obs}) for pseudo first order degradation of PCE using different buffers (TRIS and sodium bicarbonate) using different bulk reductants (titanium citrate and dithionite) catalyzed by Fe(III) Cl-TPP in the presence of 5% DMF.

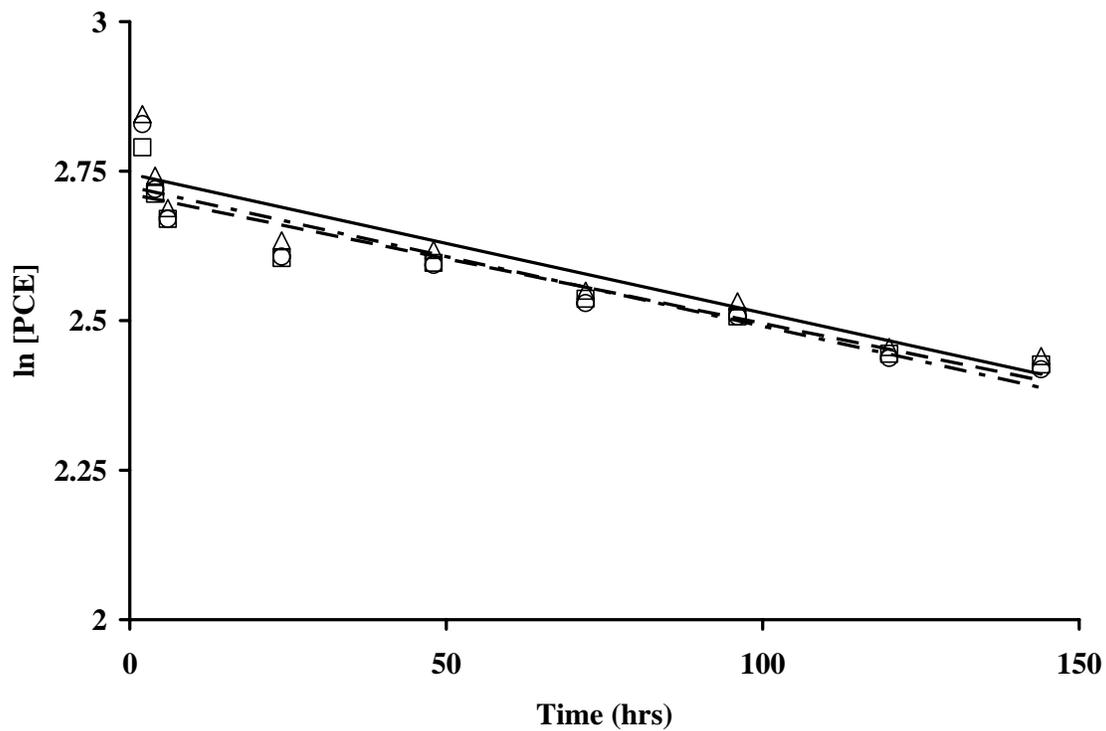
Bulk reductant and buffer	k_{obs} (hr^{-1}) ^a
50 mM Titanium citrate and 0.13 M TRIS	$(3.2 \pm 0.4) \times 10^{-3}$ ^a $(2.8, 3.6) \times 10^{-3}$ ^b
50 mM Titanium citrate and 0.13 M bicarbonate	$(3.1 \pm 0.5) \times 10^{-3}$ ^a $(2.6, 3.6) \times 10^{-3}$ ^b
34.5 mM Dithionite and 0.13 M bicarbonate	$(2.7 \pm 0.7) \times 10^{-3}$ ^a $(2, 3.4) \times 10^{-3}$ ^b
34.5 mM Dithionite and 0.13 M TRIS	$(2.3 \pm 0.4) \times 10^{-3}$ ^a $(1.9, 2.7) \times 10^{-3}$ ^b

^areported rate constants \pm calculated uncertainties based on propagating 95% confidence limits. ^breported rate constants inclusive of the calculated uncertainties.



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(2.3 \pm 0.8) \times 10^{-3}$	$(2.2 \pm 0.7) \times 10^{-3}$	$(2.3 \pm 0.8) \times 10^{-3}$
Intercept	2.723 ± 0.063	2.712 ± 0.050	2.745 ± 0.061
R ²	0.87	0.90	0.87

Figure 4.7.c Reduction of PCE using dithionite as the bulk reductant, TRIS buffer catalyzed by Fe (III) Cl-TPP in the presence of 5% DMF.



	Replicate 1 □	Replicate 2 ○	Replicate 3 △
Slope	$(3.3 \pm 0.9) \times 10^{-3}$	$(3.1 \pm 0.9) \times 10^{-3}$	$(3.0 \pm 0.9) 10^{-3}$
Intercept	2.775 ± 0.070	2.827 ± 0.070	2.828 ± 0.066
R ²	0.91	0.90	0.91

Figure 4.7.d Reduction of PCE using titanium citrate as the bulk reductant, sodium bicarbonate buffer, catalyzed by Fe (III) Cl- TPP in the presence of 5% DMF

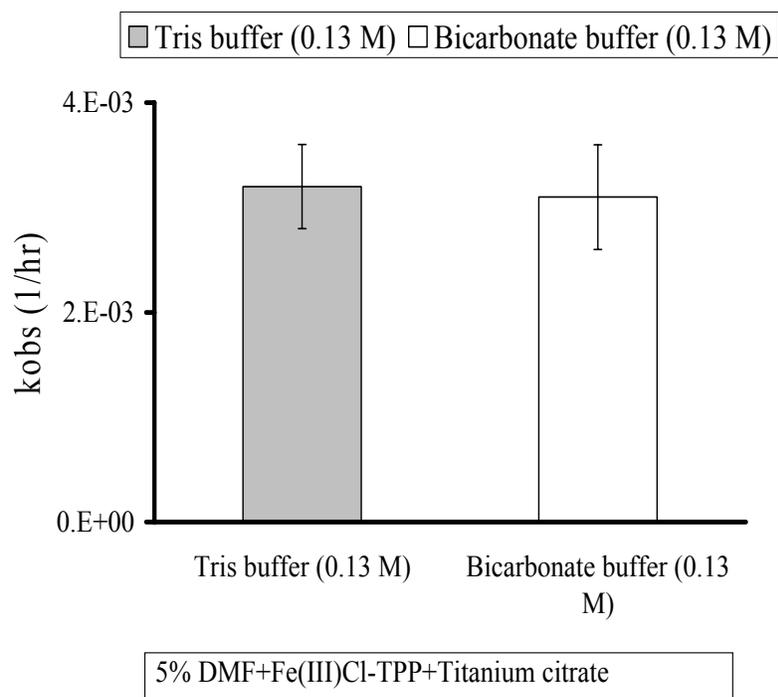


Figure 4.7.e Comparison of the effects of TRIS and sodium bicarbonate buffer on the degradation rate using titanium citrate as the bulk reductant catalyzed by Fe (III)Cl-TPP. Error bars represent uncertainty values calculated based on 95% confidence limits.

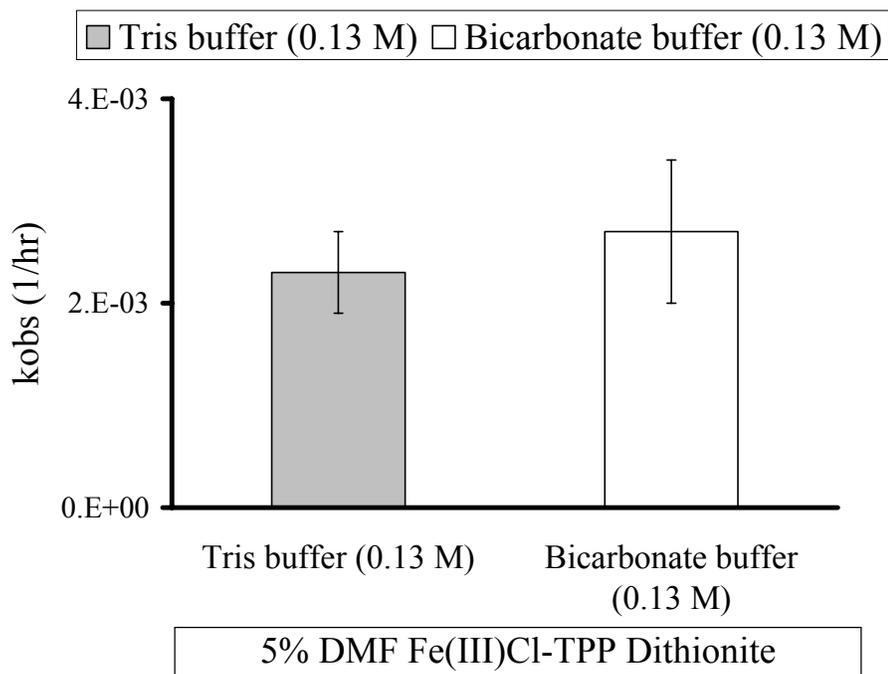


Figure 4.7.f Comparison of the effects of TRIS and sodium bicarbonate buffer on the degradation rate using dithionite as the bulk reductant catalyzed by Fe (III)Cl-TPP. Error bars represent uncertainty values calculated based on 95% confidence limits.

From the above data it is observed that the use of different buffers in the presence of both titanium citrate and dithionite did not result in a significant difference on the degradation rate of PCE.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The primary objective of this study was to test the effect of increasing DMF concentration on the rate of PCE degradation catalyzed by the water insoluble metalloporphyrins Fe (III) Cl-TPP and Ni-TPP. A secondary objective was to study the effect of different electron donors and buffers to determine optimal environmental conditions necessary for porphyrin mediated reductive dechlorination of PCE.

The addition of 2% DMF activated both Fe(III) Cl-TPP and Ni-TPP, thereby resulting in an increase in the PCE degradation rate. However, when the DMF concentration was increased beyond 3% the degradation rate began to decrease. Therefore, the “solubility hypothesis” first advanced by Dror and Schlautman (2003) does not appear to fully explain all aspects of how the presence of co-solvents activates water-insoluble metalloporphyrins for the catalyzed degradation of PCE.

Fe(III)Cl-TPP was found to be a more effective catalyst than Ni-TPP for the degradation of PCE, presumably because it can form dimers in water-DMF mixtures. Metalloporphyrins containing Fe as the central metal have been shown to form dimers that possess remarkable electron transfer properties. In the present study, UV-Vis spectra of Fe (III) Cl-TPP in 2, 3, 5, 7.5, 10, and 100% DMF displayed absorption bands characteristic of μ -oxo dimers as reported in the literature.

In the second part of the study, different bulk electron donors (titanium citrate and dithionite) and buffers (TRIS and sodium bicarbonate) were compared to determine the

optimal environmental conditions for porphyrin mediated PCE degradation. Titanium (III) citrate was found to be as effective an electron donor as dithionite. No difference in PCE degradation rates were observed when adequate concentrations of TRIS versus sodium bicarbonate buffers were tested. However, dithionite solutions containing relatively high bicarbonate buffer concentration facilitated faster degradation of PCE when compared to dithionite solutions containing low concentrations of bicarbonate buffer.

The overall conclusions of this study are:

- Addition of 2% DMF enhanced the Fe(III) Cl-TPP and Ni-TPP catalyzed degradation of PCE. However, PCE degradation did not consistently increase with higher DMF concentrations.
- Fe(III)Cl-TPP likely exists as μ -oxo dimers in DMF-water mixtures. No evidence of monomers was observed based on comparisons with reported absorption spectra. No evidence in the literature was found for μ -oxo dimer formation for Ni-TPP, so it was not possible to make comparisons for its measured UV-visible absorption spectra.
- In our experimental system, Fe (III)Cl-TPP is a more effective catalyst than Ni-TPP for catalyzing PCE degradation.
- Titanium citrate is as effective an electron donor as dithionite for catalyzing PCE degradation.
- Use of adequate amounts of different buffers (TRIS and bicarbonate) did not produce any significant difference in PCE degradation rates.

- Well buffered dithionite solutions degraded PCE faster than dithionite solutions containing low buffer concentrations.

Results from this study shed additional light on the effects of adding a cosolvent to enhance the degradation of PCE in the presence of otherwise water-insoluble metalloporphyrin catalysts. However, further study is needed to fully understand the processes involved, particularly when higher cosolvent concentrations are used. While the present study makes use of DMF as a cosolvent for all experiments, testing the utility of more easily degradable co-solvents to facilitate PCE degradation would be of practical relevance. Further study may be done to research the use of surfactants and cyclodextrins to activate the metalloporphyrin catalyst.

APPENDIX A

DETAILED PROCEDURE FOR DATA ANALYSIS

The detailed procedure used for data analysis is as follows:

1. Log transform PCE concentration data
2. Linear regression of $\ln [\text{PCE}]$ vs time is performed.
3. The slope (i.e., the pseudo first order rate constant) for each replicated experimental system (triplicate) and 95% confidence interval using Microsoft excel 2003 is obtained.
4. An average rate constant from the 3 replicate values is calculated. Uncertainties of the three replicates are propagated to obtain the 95% confidence interval for the average rate constant using the Root Mean Square Method.

$$U_R = ((u_1 df/dx_1)^2 + (u_2 df/dx_2)^2 + \dots + (u_n df/dx_n)^2)^{1/2}$$

For example, the triplicate values of rate constants (obtained from experiments where dithionite is used as the electron donor and TRIS is used as the pH buffer in the presence of Fe (III)Cl-TPP and 5% DMF) and their corresponding uncertainties are as follows:

$$A_1 = (2.330 \pm 0.820) \times 10^{-3}; A_2 = (2.160 \pm 0.650) \times 10^{-3}; A_3 = (2.320 \pm 0.790) \times 10^{-3}$$

The overall uncertainty

$$U_R = 1/3 \times ((0.820 \times 10^{-3})^2 + (0.650 \times 10^{-3})^2 + (0.790 \times 10^{-3})^2)^{1/2} = (4.37 \times 10^{-4})$$

$$A = (A_1 + A_2 + A_3) / 3 = (2.330 + 2.160 + 2.320) / 3 = 2.27$$

Therefore, the overall rate constant $a = (2.27 \pm 0.44) \times 10^{-3}$

APPENDIX B

ABSORPTION SPECTRA FOR NI-TPP IN 2, 5 AND 10% DMF

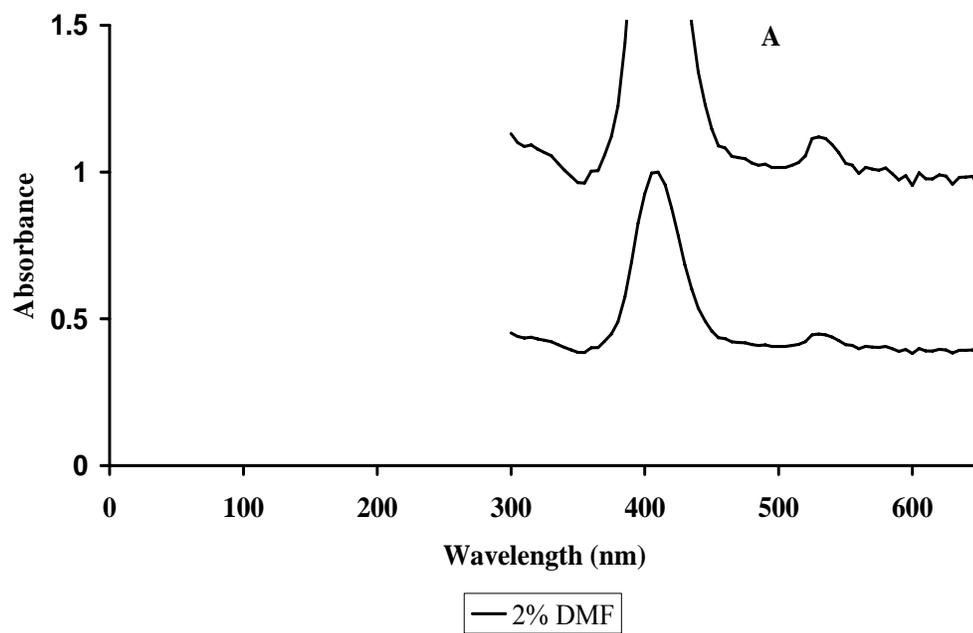


Figure B.a Absorption spectrum of Ni-TPP in 2% DMF. The second spectra in each of these figures are merely “blowups” or magnified by 2.5 times the original absorbance values.

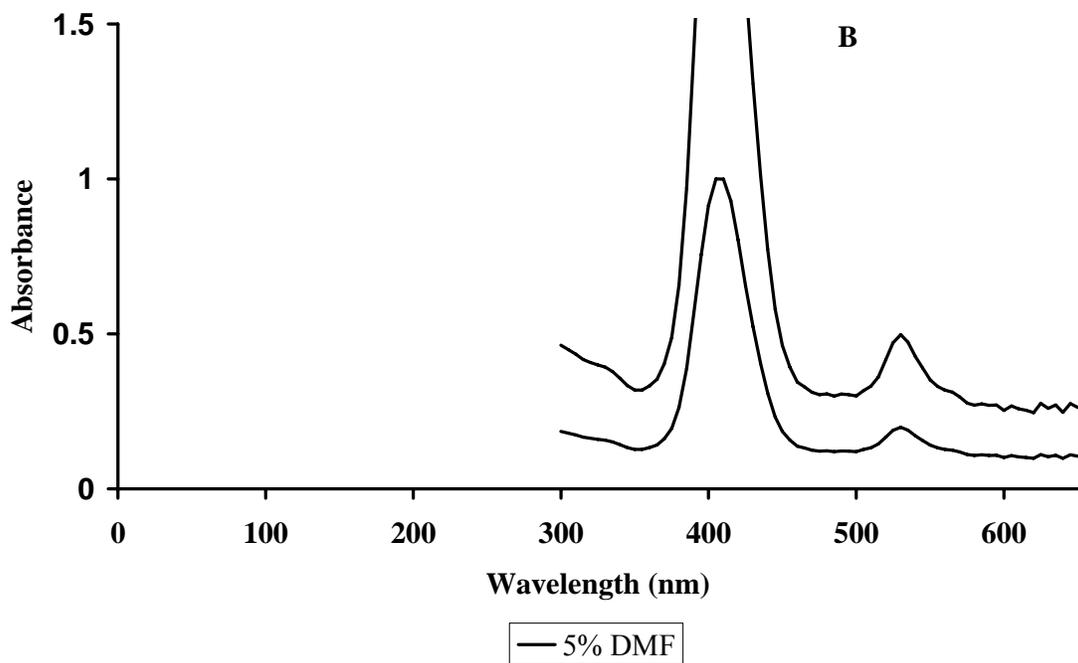


Figure B.b Absorption spectrum of Ni-TPP in 5% DMF. The second spectra in each of these figures are merely “blowups” or magnified by 2.5 times the original absorbance values.

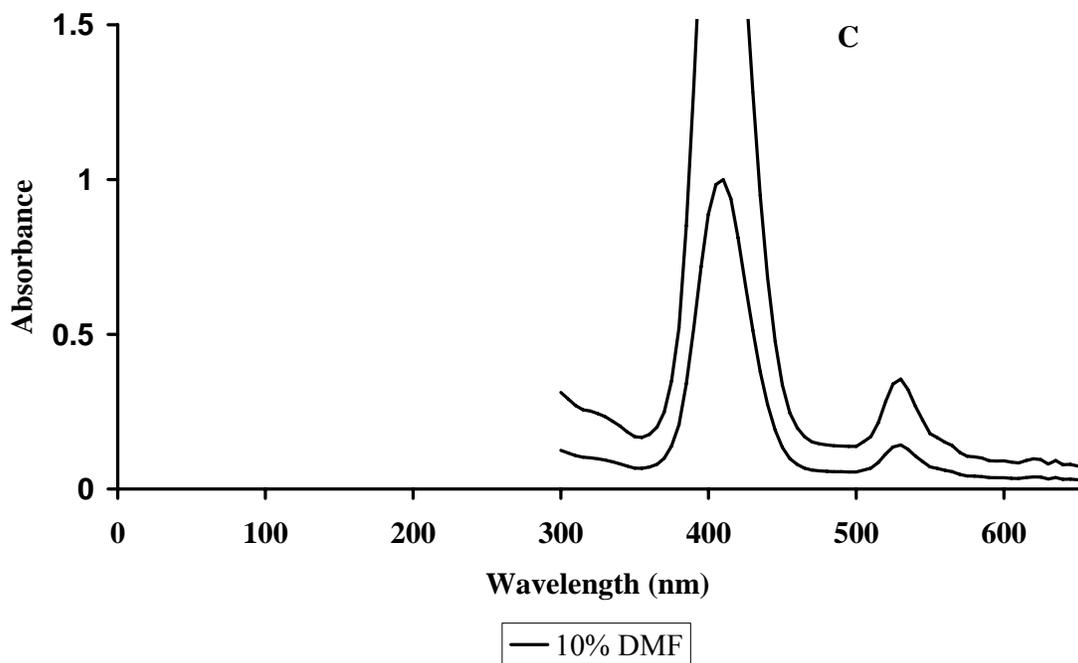


Figure B.c Absorption spectrum of Ni-TPP in 10% DMF. The second spectra in each of these figures are merely “blowups” or magnified by 2.5 times the original absorbance values

APPENDIX C

COMPARISON OF PREVIOUS RESULTS WITH EXISTING DATA

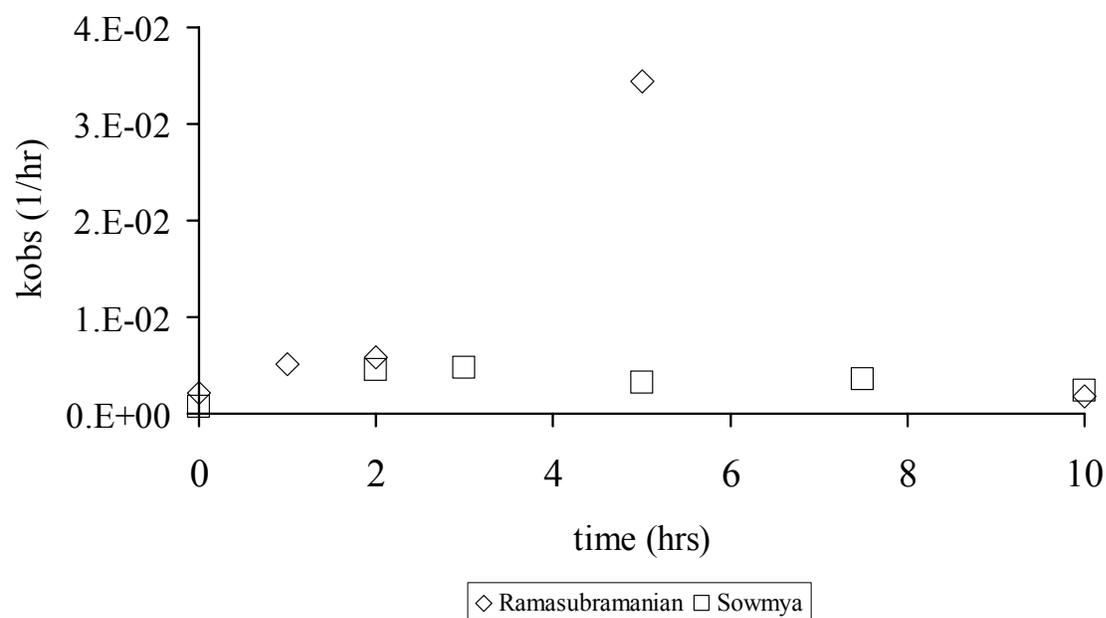


Figure C.a Comparison of PCE degradation rates in the presence of increasing DMF concentrations catalyzed by Fe (III) Cl-TPP from previous results and existing data

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