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# COSOLVENT EFFECTS ON THE REDUCTIVE DECHLORINATION OF TETRACHLOROETHYLENE CATALYZED BY IRON TETRAPHENYL PORPHYRIN CHLORIDE

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COSOLVENT EFFECTS ON THE REDUCTIVE DECHLORINATION OF  
TETRACHLOROETHYLENE CATALYZED BY IRON TETRAPHENYL  
PORPHYRIN CHLORIDE

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A Thesis  
Presented to  
the Graduate School of  
Clemson University

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

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by  
Lavanya Ramasubramanian  
December 2007

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Accepted by:  
Dr. Mark Schlautman, Committee Chair  
Dr. Elizabeth Carraway  
Dr. David Freedman

## ABSTRACT

Abiotic electron transfer mediated reductive dechlorination reactions have been studied extensively in the past decade. Porphyrins and metalloporphyrins are common electron transfer mediators used. Past studies have shown that some metalloporphyrins play a key role in increasing the rate of reaction in the presence of cosolvents. There have also been suggestions that organic cosolvents enhance the rate of reduction by increasing the solubility of metalloporphyrins.

The primary objective of this project was to examine the effect of cosolvents on the metalloporphyrin-catalyzed reductive dechlorination of tetrachloroethylene (PCE). Subsequently, experiments were also conducted to test the hypothesis that metalloporphyrin solubility is linked to the rate of degradation of PCE. PCE degradation mediated by iron tetrphenyl porphyrin chloride [Fe (III)-Cl TPP] was studied using various volume concentrations (0, 1, 2, 5 and 10%) of dimethylformamide (DMF) and methanol. The rate of PCE degradation increased with increase in cosolvent concentration up to 5% but decreased considerably when the cosolvent concentration was 10%. The increase in reaction rate up to 5% DMF or methanol may be due to an increase in solubility of the Fe (III)-Cl TPP with increasing cosolvent concentration. The decrease in reaction rate from 5 to 10% cosolvent concentration however was not consistent with the expected enhanced solubility of Fe (III)-Cl TPP.

The solubility of metalloporphyrins was investigated using absorbance measurements and the Beer-Lambert Law. Fe (III)-Cl TPP absorbance was expected to increase with increasing cosolvent concentration marking an increase in concentration of

metalloporphyrin with increasing solubility. However, the absorbance values did not show the expected trend and formation of flocs were noticed in all the samples. These flocs may be related to dimers which are known to form when Fe (III)-Cl TPP is present in a mixture of water and an organic solvent. The increase in dechlorination reaction rate up to 5% cosolvent concentration might be attributed to the catalytic activity of dimers.

Although the reason for the increase in PCE dechlorination reaction rate with increasing DMF and methanol concentration up to 5% and then subsequent decrease at 10% could not be experimentally established, sufficient evidence was obtained in this study which precludes Fe (III)-Cl TPP solubility as being solely responsible for the “solubility hypothesis” advanced by Dror and Schlautman (2004a, 2004b).

## DEDICATION

I dedicate this work to the Almighty and my family.

## ACKNOWLEDGMENTS

First and foremost, I would like to express my gratitude to my thesis advisor and committee chairperson, Dr. Mark Schlautman, who gave me an opportunity to work on this project. I thank him for his invaluable guidance, motivation and assistance, not only in my research but also otherwise, which has been a great source of encouragement.

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## CHAPTER 1

### INTRODUCTION

Chlorinated hydrocarbons have been used extensively for years in agricultural and industrial applications. Accidental discharges and disposals are the main sources of chlorinated hydrocarbon pollution. The high stability of the carbon-chlorine(C-Cl) bond, common to all organo-Cl compounds makes them highly persistent in the environment (Schwarzenbach et al., 2003). Due to their persistent nature they tend to contaminate aquatic and soil systems (Schwarzenbach et al., 2003). Bioaccumulation of anthropogenic chlorinated compounds has been observed in areas remote from human settlements (Simonich and Hites, 1995; Blais et al., 1998). Once a chlorinated compound is released to the environment it finds its way into the air, water and soil systems. Such widespread distribution of these compounds is attributed to their high stability and long-range transport in the environment.

Among chlorinated hydrocarbons, chlorinated ethenes such as perchloroethylene (PCE) and trichloroethylene (TCE) are often detected as groundwater pollutants. PCE is a non-flammable volatile organic compound (VOC) and finds extensive use in the dry cleaning and metal degreasing processes (Kawauchi and Nishiyama, 1989; ATSDR, 1995). PCE is the only chlorinated ethene that resists aerobic biodegradation (Holliger, 1995). Pure phase PCE can leach through the soil and, being denser than water, can sink to the bottom of an aquifer. Owing to its aqueous solubility PCE dissolves in water resulting in contamination of groundwater. Chlorinated ethenes can undergo reductive

dechlorination under anaerobic conditions to form harmless end products, such as ethene and ethane (Holliger, 1995). Zero-valent metals, electrochemical processes and bioremediation are widely used for the dechlorination of chlorinated ethenes (Fritsch and McNeill, 2005). These reductive dechlorination reactions are often catalyzed by tetrapyrrole cofactors such as corrinoids, porphyrins and cofactor F<sub>430</sub> (Holliger and Schraa, 1994). Catalysis involving vitamin B<sub>12</sub> has been widely studied due to its involvement in natural systems (Fritsch and McNeill, 2005).

Abiotic reductive dechlorination of oxidized organic and inorganic contaminants has attracted researchers in the past two decades due to its advantages over biological reduction. Biological reduction is possible but is generally slow and requires appropriate conditions for microbial activity and growth. High chlorinated ethene concentrations at contaminated sites can be toxic to the microorganisms (Mikesell and Boyd, 1986; Morris et al., 1993) and the presence of other contaminants such as Cr (VI) is known to inhibit microbial activity (Richard and Bourg, 1991; Krishnamurthy and Wilkens, 1994).

Abiotic electron-mediated reductive dechlorination systems have attracted considerable interest for chlorinated hydrocarbon remediation because they generally do not have the limitations associated with bioremediation (Assaf-Anid et al., 1994; Gantzer and Wackett, 1991; Schwarzenbach et al., 1990). Numerous laboratory studies have shown that abiotic reductive transformations of relatively oxidized organic compounds can be enhanced by electron shuttle systems (i.e., electron mediators; Larson and Weber, 1983). The rate of the reaction is increased when an electron mediator is used. The bulk reductant rapidly reduces the mediator, which in turn transfers electrons to the final

electron acceptor (i.e. the contaminant) thus enhancing the rate of the reaction. The oxidized mediator is regenerated by the bulk reductant to start the reaction over again.

Porphyrins and other tetrapyrrole macrocycles are common electron transfer mediators and are known to catalyze reductive dechlorination reactions of a variety of chlorinated contaminants (Dror and Schlautman, 2003, 2004a). Reductive dechlorination of chlorinated ethenes, catalyzed by the porphyrin derivative, corrin Vitamin B<sub>12</sub> has been commonly studied (Gantzer and Wackett, 1991; Chiu and Reinhard, 1995; Burris et al., 1996; Burris et al., 1998; Woods et al., 1999). Metalloporphyrins are one of the most common electron mediators and are well known for their electron transfer role in various redox systems. Metalloporphyrin derivatives with a variety of core metals have been used in reductive dechlorination reactions (Dror and Schlautman, 2003). Past studies have dealt mainly with using soluble porphyrins for reductively dechlorinating the pollutants as only soluble porphyrins have shown to be reactive as electron transfer shuttles. Thus aqueous solubility of metalloporphyrins appears to play a vital role in reductive dechlorination reactions. For metalloporphyrins with limited solubility, the use of water-miscible cosolvents has been suggested as a promising approach to enhance the solubility of metalloporphyrins (Dror and Schlautman, 2004a, 2004b).

Cosolvents are highly water-soluble organic solvents that completely change the solvation properties of an aqueous phase. Cosolvents have been widely used in enhancing the solubility of hydrophobic compounds like chlorinated ethenes, PCBs, chlorinated methanes etc. thus enhancing their remediation processes (Li and Andren, 1994, 1995; Zhai et al., 2006). Often the contaminated soil is washed with a mixture of water and water miscible cosolvents (Li et al., 1996). Recent research has shown a cosolvent effect

on metalloporphyrin catalyzed reductive dechlorination of PCE, where PCE was completely transformed in 24 hours when DMF or pyridine was used as a cosolvent to solubilize the metalloporphyrin whereas no reaction was observed in the absence of a cosolvent (Dror and Schlautman, 2004b).

Previous studies by Dror and Schlautman (2004a, 2004b) were limited to examining the effect of cosolvent on the reductive dechlorination of PCE. A 5% cosolvent system showed an increase in the rate of reaction. It was concluded that this was due to an increase in solubility of metalloporphyrin with the addition of cosolvent. The objective of this study was to study the effect of cosolvent concentration on reductive dechlorination of PCE and also experimentally test the assumption that the increase in rate of reaction was actually due to the solubility of metalloporphyrins.



## CHAPTER 2

### LITERATURE REVIEW AND RESEARCH OBJECTIVE

#### 2.1 Perchloroethylene

Chlorinated ethenes, especially PCE and TCE are the most commonly detected pollutants in groundwater (Doherty, 2000) and are listed in the United States Environmental Protection Agency (U.S. EPA) priority pollutants list (Fritsch and McNeill, 2005). PCE has been identified at 54% of the U.S. EPA's Superfund sites (He et al., 2003). The maximum contaminant limit (MCL) for PCE is 5 ppb (U.S. EPA).

##### 2.1.1 Sources of PCE

PCE is a commercially important chlorinated hydrocarbon and is also a chemical intermediate in the manufacture of refrigerants. PCE has excellent solvent characteristics and is widely used as a dry cleaning agent. PCE is also used in textile processing as a scouring solvent that removes oil from fabrics. In addition, PCE has applications in vapor and liquid degreasing. Due to its capability of dissolving many organic compounds, some inorganic compounds, and high melting pitches and waxes, PCE is used to clean and dry contaminated metal parts and other fabricated material. It also is used to remove soot from industrial boilers (ATSDR, 1995).

PCE enters the air by evaporation from dry cleaning or other industrial processes. PCE can also enter the atmosphere during disposal of sewage sludge and industrial wastes containing PCE. PCE is present in the vinyl liners in asbestos-cement water pipelines used for water distribution, causing water pollution. PCE gets into groundwater

mainly through leaks and spills and may travel through the soil and contaminate groundwater (ATSDR, 1995).

### 2.1.2 Fate and transport of PCE in the environment

The fate of PCE in the environment is determined by its physicochemical properties as well as the specific environmental characteristics. The properties that determine its distribution in the environment are listed in Table 2.1. The high specific gravity of pure PCE allows it to sink to the bottom of an aquifer and to slowly dissolve in water, thus contaminating the groundwater. PCE has a moderate octanol/water distribution coefficient ( $K_{ow}$ ), predicting hydrophobicity and moderate adsorption to soil (Watts, 1996). When exposed to the atmosphere, PCE is likely to partition into the air because of its relatively high volatility. PCE has a relatively high vapor density, suggesting that the volatilized compound stays closer to the ground (Watts, 1996).

Table 2.1 Physical properties of PCE

Parameter	Values	Reference
Water solubility (mg/l) @ 25°C	150	Ladaa et al., 2001
Specific gravity @ 24°C	1.623	Roy et al., 2002
Octanol/ water partition coefficient (log $K_{ow}$ )	3.4	ATSDR, 1995
Vapor pressure (mm Hg) @ 20°C	14	Poulsen and Kueper, 1992
Henry's Law constant (@ 25°C)	0.682	Ladaa et al., 2001

### 2.1.3 Health effects

PCE degradation products include TCE, the isomers of dichloroethylene (DCE) (*cis*-DCE, *trans*-DCE and 1,1-DCE), vinyl chloride (VC), acetylene, ethene and ethane. PCE and some of its degradation products are considered carcinogens or suspected carcinogens, and are hazardous materials. Exposure to high concentrations of PCE may be a threat to liver, kidney and nervous systems. Studies in animals showed that PCE can cause liver and kidney damage and/or cancer (ATSDR, 1995). The health effects of PCE and its daughter products are summarized in Table 2.2.

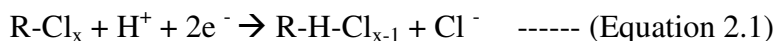
Table 2.2 Health effects of PCE and its daughter products

Compound	MCL	Health Effects	Carcinogen?	Reference
PCE	5 ppb	Respiratory and ocular irritation, cerebral cortical depression, increased urinary lysozyme activity and liver damage, vomiting, narcotic effects.	Yes	<a href="http://www.atsdr.cdc.gov/">http://www.atsdr.cdc.gov/</a> <a href="http://www.epa.gov/">http://www.epa.gov/</a>
TCE	5 ppb	Headaches, lung irritation, dizziness, impaired heart function, nerve, kidney, and liver damage and death, nausea, impaired immune system function, impaired fetal development in pregnant women, Skin rashes.	Yes	<a href="http://www.atsdr.cdc.gov/">http://www.atsdr.cdc.gov/</a> <a href="http://www.epa.gov/">http://www.epa.gov/</a>
1,1 -DCE	7 ppb	Liver and kidney damage, central nervous system depression.	No	<a href="http://www.atsdr.cdc.gov/">http://www.atsdr.cdc.gov/</a> <a href="http://www.watersafetestkits.com/pdf">http://www.watersafetestkits.com/pdf</a>
c-DCE	70 ppb	Nauseous, depression of the central nervous.	No	<a href="http://www.atsdr.cdc.gov/">http://www.atsdr.cdc.gov/</a> <a href="http://www.watersafetestkits.com/pdf">http://www.watersafetestkits.com/pdf</a>
t-DCE	100 ppb			
VC	2 ppb	Dizziness or sleepiness, headache, liver changes, nerve damage.	Yes	<a href="http://www.atsdr.cdc.gov/">http://www.atsdr.cdc.gov/</a> <a href="http://www.watersafetestkits.com/pdf">http://www.watersafetestkits.com/pdf</a>

#### 2.1.4 Remediation of PCE

PCE can undergo biotic and abiotic transformations. Common abiotic transformations are hydrolysis, nucleophilic substitution, and elimination (Schwarzenbach, 2003). Biodegradation of chlorinated ethenes can occur aerobically or anaerobically (Vogel et al., 1987; Nielson et al., 1990; Wackett et al., 1992), with the exception of PCE which is resistant to aerobic biodegradation (Holliger, 1995).

PCE undergoes reductive dechlorination under anaerobic conditions to give harmless end - products such as ethene or ethane. However, under aerobic conditions, PCE is not amenable to undergo microbial degradation whereas its anaerobic daughter products, TCE and DCEs can be degraded cometabolically (Jayaraj et al., 2003). Reductive dechlorination takes place in the presence of electron donating species, which exchange an electron for a chlorine atom. Equation 2.1 shows a typical reductive dechlorination reaction (Assaf Anid et al., 1992). This reaction involves the transfer of two electrons to R-Cl, the release of chlorine as chloride, and scavenging of a proton from solution.



Abiotic reductive dechlorination of PCE using zero valent iron technology is one of the most commonly studied techniques. It has been used in the remediation of groundwater contaminated with chlorinated hydrocarbons (Song and Carraway, 2006). It has also been used for treatment of waste effluents produced during removal of NAPLs from subsurface source zones using cosolvents (Clark et al., 2003). Abiotic reductive

dechlorination utilizing electron mediators has received growing attention over the past decade. Studies have shown that the presence of these electron mediators helps to speed up the rates of reduction by the bulk reductants (Gantzer and Wackett, 1991).

## 2.2 Porphyrins and Metalloporphyrins

Porphyrins are ubiquitous, naturally occurring compounds consisting of four pyrrole-type rings joined by four methine bridges to give a macrocycle (Fig 2.1). Porphyrins are aromatic macrocycles that are highly conjugated and have a number of resonance forms. There are nominally 22  $\pi$ -electrons, of which only 18 are included in delocalization pathway. This is in conformation with Huckel's  $4n + 2$  rule of aromaticity, where  $n = 4$ . Thus, of the two peripheral double bonds of the porphyrins, one can undergo addition reaction to form porphyrin derivatives like, chlorins, corrins, bacteriochlorins, without loss of aromaticity (Smith, 1975).

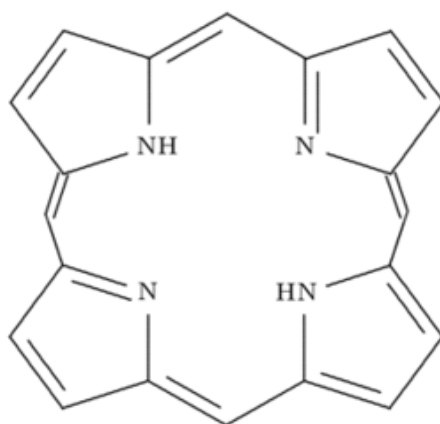


Fig 2.1: Basic porphyrin structure (adapted from Smith, 1975, Milgrom, 1997).

Porphyrins play a variety of roles in the metabolism of living organisms. Heme [iron (II) protoporphyrin IX complex] is the prosthetic group in hemoglobins and myoglobins (Fig 2.2). These are responsible for oxygen transport and storage in living tissues (Milgrom, 1997). Heme is also found in the enzyme peroxidase. This enzyme is responsible for catalyzing the oxidation of substrates by peroxide. Cytochrome, a heme containing protein, serves as an electron carrier in the electron transport chain (Smith, 1975). When one of the pyrole units in the porphyrin group is reduced it leads to a class of porphyrin derivative called the chlorins. Chlorophylls, belong to this class of porphyrin derivatives and are found in plants and algae, where they play an important role in photosynthesis (Fig 2.3). Further reduction of chlorins gives rise to another class of porphyrin derivatives called the bacteriochlorins. The well known vitamin B<sub>12</sub> contains a porphyrin like unit called a corrin (Fig 2.4).

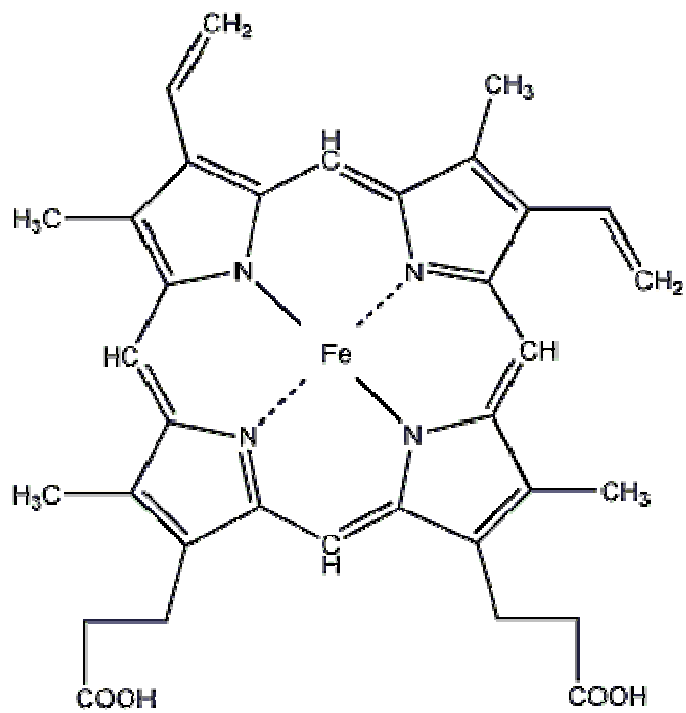


Fig 2.2: Heme (adapted from Milgrom, 1997)

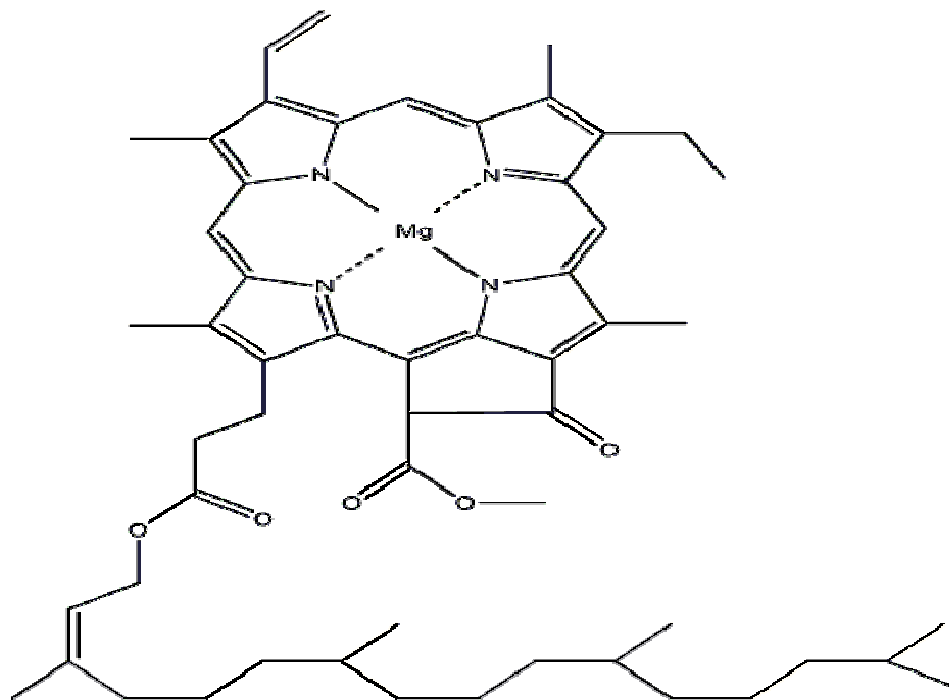


Fig 2.3: Chlorophyll a (adapted from Milgrom, 1997)



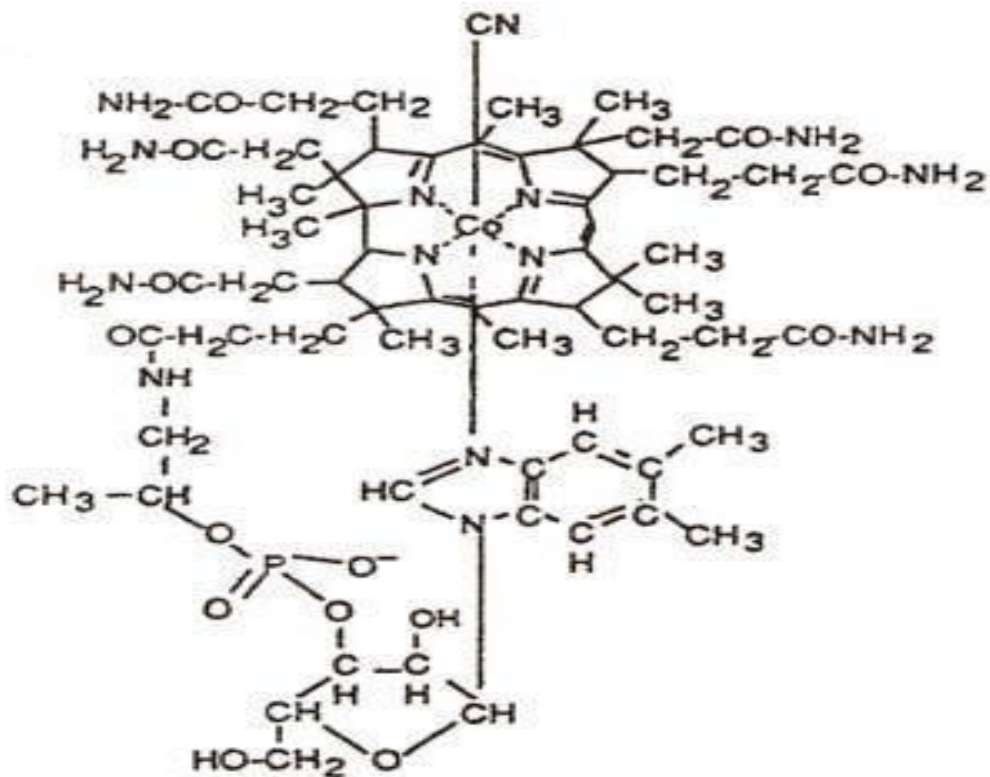


Fig 2.4: Cyanocobalamin (Gantzer and Wackett, 1991)

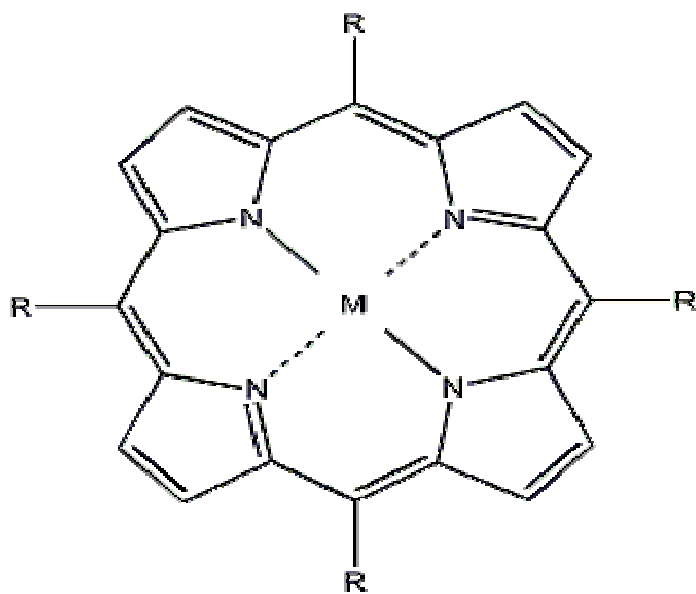
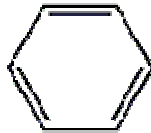
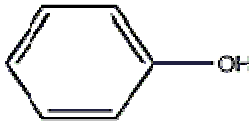
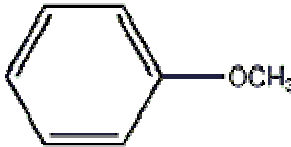
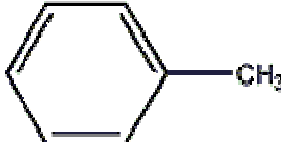
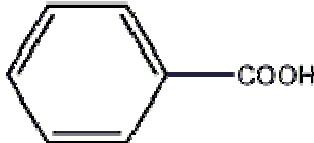
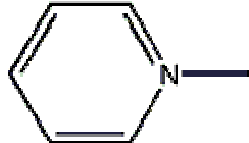
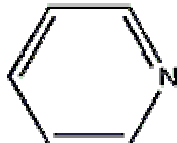


Fig 2.5: Porphyrin, with central metal atom (M) and functional groups (R) (adapted from Dror and Schlautman, 2003)

Table 2.3: Porphyrins with various functional groups (R) (Dror and Schlautman, 2003)

Porphyrin	Abbreviation	Functional group ( R )	Molecular Weight
Tetraphenyl porphine	TPP		614.75
5,10,15,20 (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 p-tolyl 21H, 23H porphine	T(p-toly)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

Porphyrins generally exist as free bases or as metal complexes. Porphyrins readily combine with metals, coordinating with them in the central metal cavity (Fig 2.5). Iron-, zinc-, nickel-, magnesium-, manganese-, vanadium oxide-, copper- and cobalt-containing porphyrins are the commonly known metal inserted in porphyrins (Smith, 1975). Various functional groups can be added to the basic porphyrin structure to give new compounds. Some of the synthetic porphyrins available are cobalt (Co)-TPP, nickel (Ni)-TPP, Co-TMPyP, iron (Fe) (III) - TPP chloride and many more (Table 2.3). Also, a large fraction of naturally-occurring porphyrins are bound to solids such as kerogens and/or minerals. The most abundantly found porphyrins on earth are the geoporphyrins (Barwise and Roberts, 1984; Harradine and Maxwell, 1998). The majority of these porphyrins are insoluble in water, and as a result, they are found together with natural organic matter or as accumulated crystalline materials in sediment pores and voids.

Metalloporphyrins are derivatives of porphyrins in which the metal acts as a Lewis acid, accepting a lone pair of electrons on the centrally located nitrogen atom to form a coordination complex (Smith, 1975). The metal acts as a dipositive ion and combines with the dinegatively charged porphine ion resulting from the delocalized  $\pi$  electron system over the four nitrogen atom in the porphyrin ring. The porphine anion found in metalloporphyrins is mostly a rigid, closed, macrocyclic tetradentate dinegative chelating ligand.

Metalloporphyrins have attracted increasing attention from researchers in the treatment of priority pollutants recently due to their unique properties (Dror and Schlautman, 2004b):

- Good redox catalysts which exhibit a range of redox activities;

- Electrochemically active with any core metal;
- Porphyrins are highly stable which helps in redox reactions to proceed under severe conditions, which is otherwise limited in using alternative treatment techniques; and
- Naturally occurring metalloporphyrins are found in every type of subsurface environment which should aid in using them to treat pollutants in situ.

Porphyrins and metalloporphyrins find application in various fields due to their thermal stability, non-linear optical effects from their extended  $\pi$ -conjugated macrocyclic ring, and the variation in their physical properties that can be caused by chemical modification of their periphery. When the periphery of the porphyrin undergoes substitution, unusual liquid crystalline materials can be generated. The porphyrin ligand behaves as a base for which desirable molecular and material properties such as large dipole moments, polarizabilities, and hyperpolarizabilities can be established. The non-optical properties of porphyrins and metalloporphyrins are of special interest in areas of energy transfer with molecular control and find applications in optical communication, data storage, and signal processing (Chou et al., 2000).

Apart from their interaction with applied electric, magnetic or electromagnetic fields, porphyrins and metalloporphyrins also interact with chemical species (Chou et al., 2000). These interactions are called chemo-responsive interactions. The use of porphyrins in the development of molecular sieves and shape selective catalysts because of their porous nature is one example where porphyrins find application in chemo-responsive interactions. However there is very less development of porphyrins as chemo-responsive materials.

Metalloporphyrins catalyze a large number of reactions including biological oxidation reactions (Chou et al., 2000). For this purpose, metalloporphyrins are often covalently bonded to support materials. Common materials that have served as supports include organic polymers (Anson et al., 1985), zeolites (Persaud et al., 1987; Li et al., 1988), and silica (Battioni et al., 1989).

Porphyrins and metalloporphyrins have also been used as environmental sensors because of their inherent stability, unique optical properties, and synthetic versatility. Substantial work has been done in areas of solution and gas phase sensing (Chou et al., 2000). It is well known that heme binds to a variety of gases, such as nitric oxide, carbon dioxide and oxygen. Other gases detectable with porphyrin based sensors include ammonia, hydrazine, and nitric oxide (Malinski and Taha, 1992; Vaughan et al., 1996; Arnold et al., 1997). Porphyrin sensors for solutions species are used to detect anions and cations in solution. The anions commonly detected include nitrite (Gao et al., 1994), chloride, bromide, and nitrate (Beer et al., 1995). The ability of porphyrins to coordinate with different metals and the unique spectral signatures also allows detection of various metals (Morales-Bahnik et al., 1993). Porphyrins are also widely used to detect organic molecules. This is based on the ability of porphyrins to catalyze reduction and oxidation of organic substrates. Organohalides (Dobson and Saini, 1997), sugars (Takeuchi et al., 1997), and amines (Chou et al., 2000) are among the commonly detected organic molecules.

### 2.3 Porphyrin- and metalloporphyrin-catalyzed reductive dechlorination reactions

Various transformation reactions are enhanced when mediated by electron shuttle systems, i.e., electron transfer mediators (Larson and Weber, 1983). The most abundant electron donors in anaerobic environments include reduced inorganic iron and sulfur species (Stumm and Morgan, 1996) and it has been postulated that the presence of electron transfer mediators helps to speed up the rates of reduction by the bulk reductants. The enhancement occurs because the bulk donor rapidly reduces the mediator, which in turn transfers the electron to the acceptor, i.e., the chlorinated compound. The mediator, which gets oxidized, is regenerated by the reductant to start the reaction over again.

At most contaminated sites, the final electron acceptor is an oxidized pollutant or a chlorinated hydrocarbon. Although biological reductive dechlorination of the pollutants is possible, the reactions can be slow and require appropriate conditions for microbial activity and growth. For example, the chlorinated hydrocarbon concentration at many contaminated sites reaches a level that is toxic to the microorganisms (Mikesell and Boyd., 1990; Morris et al., 1993). There is also a chance for the microbial activity to be inhibited due to the presence of co-contaminants such as Cr (VI) (Richard and Bourg, 1991; Krishnamurthy and Wilkens, 1994).

With such limitations in biological reductive dechlorination, abiotic reductive dechlorination utilizing electron mediators has received growing attention over the past decade. Several biogeochemical substances have been proposed for use as electron mediators, including various minerals, natural organic matter, bacterial transition-metal coenzymes, and naturally occurring metalloporphyrins (Larson and Weber, 1983). Of these potential mediators, the most commonly studied to date are bacterial transition-

metal coenzymes, porphyrins and other biomimetic macrocycles (Krone et al., 1989; Marks et al., 1989; Baxter, 1990; Gantzer and Wackett, 1991). It is believed that the reactivity of an electron transfer mediator, especially the biomimetic macrocycles, is closely related to its core metal. Electron mediation is achieved by assigning oxidation states to the core metal and cycling between the various oxidation states of the metals (e.g., Fe, Co, Ni) (Assaf-Anid et al., 1994; Chiu and Reinhard, 1995; Chiu and Reinhard, 1996). In general, all biomimetic macrocycles rely on the cycling between the various oxidation states of their associated transition metals (e.g., Fe, Co, Ni) to transfer electrons. For example, in the case of hematin, the reduced central metal, Fe (II), is oxidized to Fe (III) after transferring an electron to a final electron acceptor; and Fe (III) is then converted back Fe (II) upon accepting an electron from a bulk reductant. Transition metals that have been investigated in previous studies include iron (e.g., hemin, hematin, and a variety of porphyrins: Klecka and Gonsier, 1984; Baxter, 1990; Schwarzenbach et al., 1990; Gantzer and Wackett, 1991; Chiu and Reinhard, 1995), cobalt (e.g., Vitamin B<sub>12</sub> and other cobalamins: Krone et al., 1989; Assaf-Anid et al., 1994; Chiu and Reinhard, 1995; Marks et al., 1989; Gantzer and Wackett, 1991), and nickel (e.g., coenzyme F<sub>430</sub>: Gantzer and Wackett, 1991; Krone et al., 1991).

The most common porphyrin derivative studied in the reductive dechlorination reactions is the corrin, Vitamin B<sub>12</sub>. Vitamin B<sub>12</sub> is a strong nucleophile and has been used as a mediator in the reduction of chlorinated alkanes, alkenes, polychlorinated biphenyls, chlorophenols, and chlorinated dioxins (Schwarzenbach et al., 1990; Gantzer and Wackett, 1991; Krone et al., 1991; Assaf-Anid et al., 1992; Dunnivant et al., 1992; Schanke and Wackett, 1992; Assaf-Anid, 1994; Smith and Woods, 1994; Chiu and

Reinhard, 1995; Hejman et al., 1995; Burris et al., 1996; Perlinger et al., 1996; Glod et al., 1997a,b; Burris et al., 1998; Lesage et al., 1998; Woods et al., 1999; Lesage et al., 2001; Assaf-Anid and Lin, 2002). In a study involving dechlorination of hexachlorobenzene and 2,3,4,5,6-pentachlorobiphenyl with Vitamin B<sub>12</sub>, dechlorination products were detected in system containing reduced Vitamin B<sub>12</sub> whereas they were not detected in systems containing the oxidized Vitamin B<sub>12</sub>. This showed that the degradation could occur only in anoxic environments (Assaf-Anid et al., 1992). Long term dechlorination of 2, 3, 4, 5, 6-pentachlorobiphenyl in aqueous solution and sediment with Vitamin B<sub>12</sub> produced tetra-, tri-, di- and monochlorobiphenyl (Woods et al., 1999).

Other porphyrins used previously as electron transfer mediators include tetrakis (N-methyl-4-pyridiniumyl) porphyrin (TMPyP) (Ukrainczyk et al., 1995; Lewis et al., 1995; Schwarzenbach et al., 1990), coenzyme F<sub>430</sub> (Gantzer and Wackett, 1991), hematin (Klecka and Gonsior, 1984) and protoporphyrin, uroporphyrin, coproporphyrin and hematoporphyrin (Marks et al., 1989). It has been observed that the core metal affects the reactivity of the metalloporphyrin. For example, PCE degradation did not occur when Fe-TMPyP was used whereas transformation of PCE was evident when Co-TMPyP and Ni-TMPyP were used although they followed different pathways (Dror and Schlautman, 2003). This indicates that the core metal affects the rate and product distribution of reductive dechlorination reactions. Lewis et al. (1995) also observed that porphyrins metallated with Co or Ni had higher catalytic activity than the ones metallated with Fe in the reduction of carbon tetrachloride.

While there are many types of natural and synthetic porphyrins available, the majority of previous studies have focused on soluble metalloporphyrins. (Burris et al.,



1998; Glod et al., 1997a,b; Schwarzenbach et al., 1990; Lewis et al., 1995; Burris et al., 1996; Marks and Maule, 1992; Kliewer and Morra, 1998). There are only a limited number of studies that investigated insoluble porphyrins. For example, Dror and Schlautman (2004b) used both soluble (Vitamin B<sub>12</sub>) and insoluble metalloporphyrins (cobalt-tetraphenyl porphine, Co-TPP) for the reduction of PCE. Their results indicated Co-TPP was not able to drive the reaction while there was substantial increase in reaction rate with Vitamin B<sub>12</sub>. This result suggested that solubility of metalloporphyrins is a key factor for enhancing contaminant degradation. In other words, solvation of the metalloporphyrins causes ligation of water molecules to key regions of the macrocycles or promotes a particular conformation that activates the complex enabling it to catalyze reduction reactions (Dror and Schlautman, 2003). Thus, solubility enhancement techniques could be used to enable catalytic property of metalloporphyrins.

One simple method to increase the solubility of some metalloporphyrins with carboxylic and/or phenolic acid-base groups on the periphery is pH adjustment. For example, Dror and Schlautman (2004a) observed that the rate of dechlorination mediated by T(benzoic)P and TP-OHP was increased greatly with increase in pH. Another approach to increase the metalloporphyrin reactivity was to add a small amount of organic cosolvent to solubilize the metalloporphyrin (Dror and Schlautman, 2003, 2004a, 2004b). An enhancement in the rate of reduction of PCE compared to a system without cosolvent added was observed when 5% dimethylformamide was used.

Along with the mediators noted above, quinones are also reported to exhibit electron mediating capability. Various abiotic reductive dechlorination reactions have been mediated by quinones, including the reduction of hexachloroethane (C<sub>2</sub>Cl<sub>6</sub>) (Curtis

and Reinhard, 1994; Perlinger et al., 1996; Butler and Hayes, 1998). A similar electron mediating effect was also observed from natural organic matter, and its function as an electron mediator has been attributed to the presence of quinone-type moieties (Larson and Weber, 1983).

## 2.4 Cosolvent effects on reductive dechlorination reactions

### 2.4.1 Cosolvents

Organic cosolvents are defined as highly water-soluble compounds that completely change the solvation properties of an aqueous phase. Organic cosolvents are encountered at waste disposal sites as a result of waste dumping. They are also commonly applied at remediation sites where contaminated soil is washed with a mixture of water and water miscible organic cosolvent (Li et al., 1996).

A significant amount of work has been done on the effects of cosolvents on the aqueous solubility and activity coefficient of organic pollutants (Pinal et al., 1991; Li and Andren, 1994; Li et al., 1996; Kawakami et al., 2006). Commonly used cosolvents include methanol, ethanol, propanol, acetone, dioxane, acetonitrile, dimethylsulfoxide, dimethylformamide, and glycerol. Most cosolvents used are completely water miscible organic solvents.

Cosolvent affects the solubility of an organic compound in the following ways (Schwarzenbach et al., 2003):

1. The activity coefficient of an organic solute decreases exponentially with increasing completely miscible organic solvent (CMOS) fraction.
2. Significant effect is observed only at cosolvent volume fractions greater than 5%, and below 1% the effect can be considered negligible.

3. The magnitude of the cosolvent effect is a function of the type of cosolvent and type of organic solute present.

CMOSs are small molecules possessing strong H-acceptor and/or H-donor properties. When CMOSs and water are mixed it results in the breaking of hydrogen bond between water molecules and the formation of a new hydrogen bond with mixed solvent. The functions and properties of the “mixed solvent” depend on the nature and amount of cosolvent (Schwarzenbach et al., 2003). For small and more polar organic compounds the excess free energy in pure aqueous solution is dominated by the entropy term. The enthalpy term is significant only for nonpolar solutes. Hence, in a mixture with cosolvent volume fraction less than 0.5, the increase in solubility of organic compounds with increasing water/CMOS ratio is due to increase in the excess entropy (Bustamante et al., 1998).

#### 2.4.2 Application

There has been considerable work done on increasing the solubility of an organic pollutant with low aqueous solubility, by addition of a cosolvent, thus enhancing the remediation process (Li and Andren, 1994; Li and Andren, 1995; Li et al., 1996). In a study with the oxidation of PCE by potassium permanganate, it was observed that the oxidation of PCE was enhanced by addition of acetone and tertiary butyl alcohol (Zhai et al., 2006). Researchers have used cosolvents to dissolve water insoluble porphyrins and increase their reactivity to enhance reductive dechlorination of PCE (Dror and Schlautman, 2003, 2004a, 2004b). For example, the use of (DMF), pyridine and acetone increased reactivity of nickel (Ni) -TPP, iron (Fe) -TPP chloride and vanadium oxide (VO) – TPP, which were inactive in aqueous solutions in the absence of cosolvents.

## 2.5 UV-Vis Absorption spectroscopy of metalloporphyrins

UV-Vis Absorption spectroscopy is a widely used analytical method for detecting and determining the concentration of organic and inorganic substances (Skoog et al., 1998). It measures the intensity of the absorption at different wavelengths in the ultraviolet and visible regions. The intensity of the absorption is used for calculating the concentration of the substance according to the Beer-Lambert law, represented by the following equation

$$A = \epsilon \times b \times c \text{ ----- (Equation 2.2)}$$

Where,

A : Absorbance

$\epsilon$  : Molar extinction coefficient (liter/moles/cm)

b : Path length (cm)

c : Concentration (moles/liter)

Porphyrins serve nature in variety of ways. The diversity of their functions is because of the variety of metals that bind in the “pocket” of the porphyrin ring. When the porphyrin ring is metallated the system deprotonates, forming dianionic ligand. The metal ions behave as Lewis acids and accept lone pair of electrons from the dianionic porphyrin ligand. The color of the porphyrin is due the absorption within the porphyrin ligand involving excitation of electrons from  $\pi$  to  $\pi^*$  porphyrins ring orbitals (Smith, 1975).

Porphyrins are highly sensitive chromogenic reagents, with their main absorption bands having very high extinction coefficient. They have intensive and sharp absorption

bands in the visible region. Porphyrins tend to absorb strongly near 400 nm (the Soret or B band) due to a strong transition of electrons to the second excited state ( $S_0 \rightarrow S_2$ ). The absorption spectrum of porphyrins also shows a weak transition to the first excited state ( $S_0 \rightarrow S_1$ ) at about 550 nm (the Q band). Both the B and Q bands result from  $\pi - \pi^*$  transitions. However, the Soret band is the one that has been widely used for the spectroscopic determination of metalloporphyrins. An absorption spectrum of a representative metalloporphyrin is shown in Fig 2.6.

In 1960, Martin Gouterman proposed the four orbital model to explain the absorption spectra of porphyrins (Smith, 1975). This theory stated that the absorption bands resulted from the transition of electrons between two highest occupied molecular orbitals (HOMOs) and two lowest unoccupied molecular orbitals (LUMOs). The relative energies of these transition states depend on the metal center and the substituents on the ring. The HOMOs have greater oscillator strength, giving rise to the Soret band and LUMOs have lesser oscillator strength giving rise to Q bands.

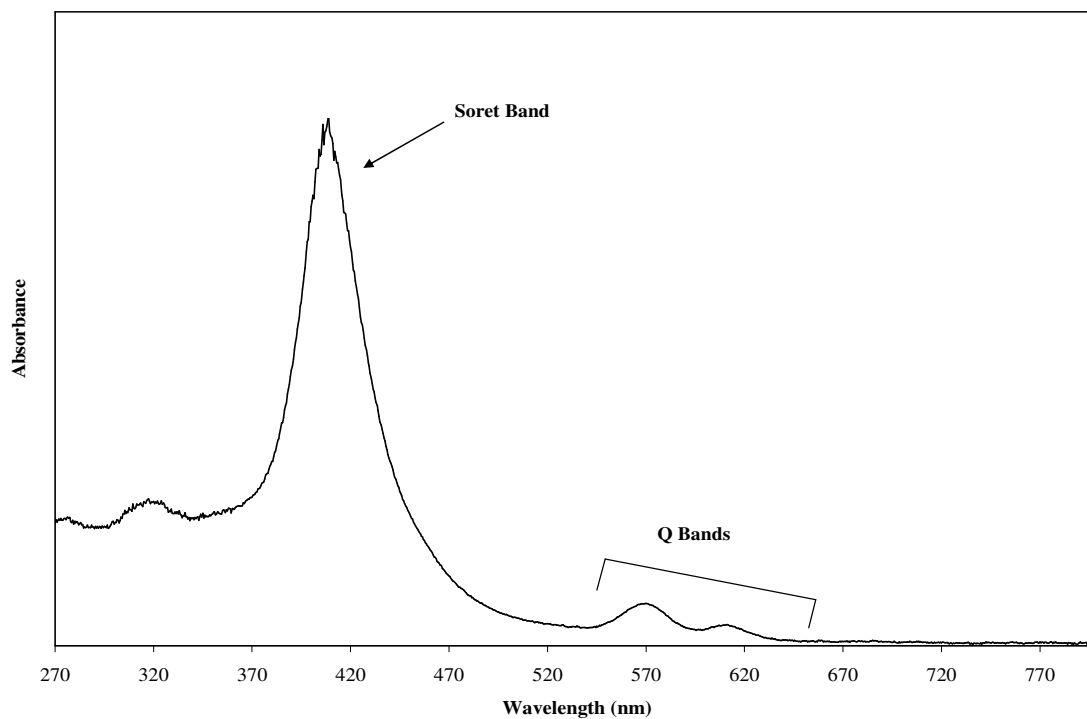


Fig 2.6: Typical absorption spectrum of a metalloporphyrin (adapted from Marsh and Mink, 1996)

Metalloporphyrins are divided into two groups, regular and hypso-porphyrins, based on their UV-Vis and fluorescence properties (Marsh and Mink, 1996). Regular porphyrins contain closed-shell metal ions ( $d_0$  or  $d_{10}$ ), in which  $d\pi$  metal based orbitals have very low energy. They have very little effect on the porphyrin  $\pi$  to  $\pi^*$  energy gap in porphyrin electronic spectra (Fig 2.7). In hypso-porphyrins the metals are of  $dm$  ( $m = 6-9$ ), having filled  $d\pi$  orbitals. There is significant metal  $d\pi$  to porphyrin  $\pi^*$  orbital interaction (Fig 2.8) causing an increased porphyrin  $\pi$  to  $\pi^*$  energy separation.

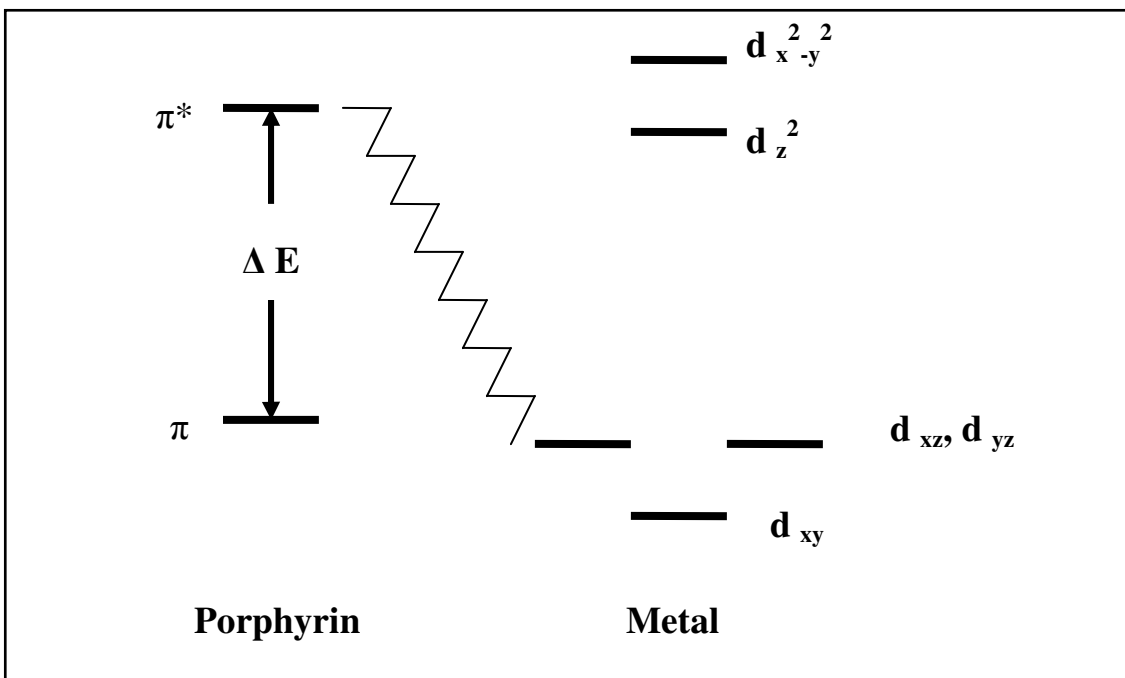


Figure 2.7: Molecular orbital diagram for metalloporphyrins (adapted from Marsh and Mink, 1996)

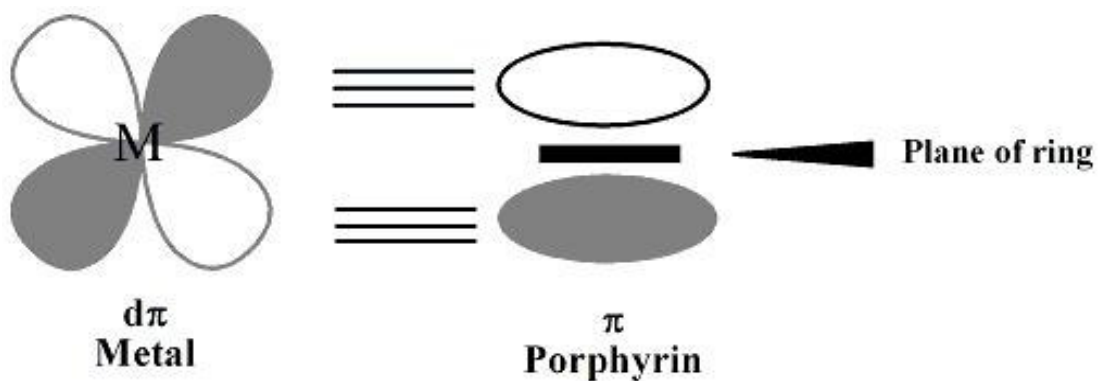


Figure 2.8: The  $d\pi$  metal orbital overlap with the  $\pi$  system of the porphyrin ring. (adapted from Marsh and Mink, 1996)

## 2.6 Immobilization of electron mediators for environmental engineering applications

Some researchers have suggested that using dissolved biomimetic macrocycles in homogenous aqueous systems would make the separation of catalysts from products and reactants and regenerating them for further use difficult (Ukrainczyk et al., 1995). Also, it is important to consider the transport (diffusion and advection) of dissolved macrocycles away from the site being treated. These problems can be overcome by immobilizing the biomimetic macrocycle onto solid supports. In the past there have been studies on heterogeneous catalysts, however, none about field applications for using immobilizing catalysts in aqueous systems (Maldotti et al., 1993). Solid supports that are particularly promising for environmental applications include natural and synthetic minerals, many of which are relatively inert and thus can be considered environmentally benign. In an experiment performed to dechlorinate PCE with titanium (III) citrate (electron donor) using Vitamin B<sub>12</sub> (electron mediator) immobilized onto Duolite S-761 (solid support), it was observed that PCE was transformed to TCE and DCE in both homogenous and heterogeneous systems (Habeck and Sublette, 1995). It was also observed that the method of immobilizing mediators onto solid support causes the contaminant to get adsorbed on the solid. However, other researchers have reported conflicting results. In a study to dechlorinate chlorinated hydrocarbons in column systems using immobilized cobalamins and porphyrins and dithiothreitol as the electron donor, it was found that lindane was efficiently dechlorinated but TCE was observed to be inactive (Marks and Maule, 1992). The advantage of using immobilized electron mediators is that they are more resistant to deactivation than the homogenous mediators and thus capable of more electron turnovers. (Chibwe and Pinnavaia, 1993).



## 2.7 Research objective

Although faster dechlorination rates have been observed in electron transfer mediated reduction reactions there has not been much explanation on why the rates are enhanced. Most of the explanations give a qualitative explanation such as the electron transfer from the bulk reductant to the final electron acceptor (i.e. the pollutant) proceeds at a slow rate, whereas the electron transfer from the bulk reductant to electron mediator and subsequently to the pollutant proceeds at a fast rate and moderate rate, respectively. Other hypotheses advanced have included the accumulation of the sparingly soluble pollutant due to the hydrophobic effect on the macrocycles or mineral surfaces or the electron mediator reduces the activation energy of the rate determining step of the reaction.

A review of the literature did not reveal other studies besides those of Dror and Schlautman (2003, 2004a, 2004b) that focused on evaluating the effects of cosolvents on the decomposition of PCE using metalloporphyrin catalysts. The overall objective of this research was to evaluate the reaction rates of metalloporphyrin mediated decomposition of PCE using different concentrations of cosolvent.



## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Materials and Equipment

5, 10, 15, 20- Tetraphenyl-21H, 23H- porphine iron(III) chloride, synthetic [Fe (III) Cl-TPP], dimethyl formamide (DMF), sodium citrate dihydrate (>99.9%, ACS reagent), trizma (99.0%, titration), sodium hydroxide (98%) pellets (NaOH), perchloroethylene, trichloroethylene, and *cis*-dichloroethylene, *trans*-dichloroethylene, 1,1-dichloroethylene, and vinyl chloride were obtained from Sigma-Aldrich (Milwaukee, WI, USA). Methanol (99.9%, HPLC grade), pentane (99.9%, GC grade) and toluene (99.9%, HPLC grade) were obtained from Burdick & Jackson. Titanium trichloride was purchased as solution from Riedel-de Haen (Seelze, Germany). All chemicals were used without further purification. Deionized water purified by a Milli-Q water system ( $\approx 18.0$  M $\Omega$ .cm) (water, hereafter) and purged with N<sub>2</sub> for at least 12 hours to remove O<sub>2</sub> was used for all experiments. For quality assurance, complete deoxygenation of water was verified by dropping a reduced redox indicator solution (resazurin) into the water in the anaerobic chamber. The solution would turn pink in the presence of oxygen. The indicator solution was kept in the anaerobic chamber at all times to monitor O<sub>2</sub> contamination. A methanolic stock solution of  $\sim 48,000$  mg/L of PCE was prepared. A stock solution of Fe (III) Cl-TPP of 2 mM was prepared in DMF and methanol.

PCE and its chlorinated degradation products were identified using an HP G1800A GCD with an electron ionization mass spectrometer detector equipped with a

DR-VRX column (60 m length, 0.25 mm diameter, 1.8  $\mu\text{m}$  film thickness). UV-Vis absorbance spectra were measured with a double-beam, double-monochromator spectrophotometer (Shimadzu UV-2501PC) using appropriate background solutions as references. Quartz cells were used to measure the absorbance of the solution. Solution pH values were measured with a model 230A pH meter (Orion) using a combination pH electrode. The pH meter was calibrated with NBS buffer solutions everyday before its use.

## 3.2 Methods

### 3.2.1 Dechlorination reaction systems

#### 3.2.1.1 Preparation of titanium (III) citrate solution

A stock solution of 250 mM Ti (III) citrate in 660 mM Tris buffer was prepared by the method described by Smith and Woods (1994). Titanium trichloride (60 mL) was added to a solution of 16.0 g Tris and 29.4 g sodium citrate in about 80 mL deoxygenated water. The pH was adjusted to 8.2 by adding 10 N NaOH. The solution was then diluted in a volumetric flask to 200 mL using water. The entire process was carried out in an anaerobic chamber to ensure that the Ti (III) citrate solution was not oxidized during preparation. This stock solution was further diluted in a 1000 mL volumetric flask to give a solution of 50 mM Ti (III) citrate in 132 mM Tris buffer. When diluting the pH was monitored to ensure the final solution pH was 8.2.

### 3.2.1.2 Batch experiments

Batch PCE dechlorination reaction experiments were carried out in 20 mL glass vials (VWR). The reactions were carried out for five different cosolvent (DMF and methanol) concentrations: 0, 1, 2, 5 and 10%. The 20 mL vials were then filled with appropriate volumes of the Ti (III) citrate stock solution, leaving a 1 mL headspace. This 1 mL headspace would result in less than 0.9% of the total mass partitioning into the headspace for PCE, with a Henry's law constant of 0.018 atm.m<sup>3</sup>/mol (Gossett, 1987), which will not significantly affect the overall results. The titanium (III) citrate concentration was 50 mM, 49.5 mM, 49 mM, 47.5 mM and 45 mM for these systems, respectively. The concentration of Fe (III) Cl-TPP was 10 μM for all reactors in consistent with previous studies (Dror and Schlautman, 2003, 2004a, 2004b). The vials were sealed with teflon-lined silicone septa (VWR). The reaction was initiated by spiking a known volume (10 μL) of methanolic stock of PCE using an air-tight syringe (Hamilton) and the vial was capped immediately. The final concentration of PCE in all vials was ~20 mg/L (0.12 mM). Table 3.1 summarizes the reactant concentrations for the different cosolvent concentrations tested. All the procedures for reactor preparation were performed in an anaerobic chamber (Coy). Four kinds of control reactors were prepared in the same way as the reactors: one without the bulk reductant [Ti (III) citrate], one without Fe (III) Cl-TPP and cosolvent, one without the cosolvent and one without Fe (III) Cl-TPP. Sealed reaction vials were mixed on a shaker table at 250 rpm at room temperature. At selected intervals, a 0.5 mL sample was withdrawn for analysis using a 1 mL gas-tight syringe (Hamilton) from the vial and the vial was sacrificed. All reactor vials were prepared with duplicates.

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

Cosolvent Concentration [% (v/v)]	0%	1%	2%	5%	10%
PCE (mg/L)	20	20	20	20	20
Fe (III)-Cl TPP ( $\mu\text{M}$ )	10	10	10	10	10
Ti (III) citrate (mM)	50	49	48	47.5	45

### 3.2.1.3 Analytical methods

The 0.5 mL aliquot withdrawn from the reactor vials was transferred to a crimp-capped 2 mL GC autosampler vial, which contained 0.5 mL pentane with 5 mg/L toluene as an internal standard. The crimp cap was replaced immediately to minimize volatilization loss during extraction. The vial was placed on a vortex mixer for 1 minute and further mixed at 250 rpm on an environmental shaker for 20 minutes. After extraction, 0.2 mL of the pentane layer was transferred to a GC autosampler vial with 0.3 mL glass insert for GC analysis. Chlorinated ethenes were identified and quantified with a GCD with an electron ionization mass spectrophotometer detector. The sample was injected in split mode. The carrier gas helium with a flow rate of 1 mL/min.

### 3.2.1.4 Kinetic modeling

A pseudo first-order kinetic model was used to fit the experimental data and to calculate apparent first-order rate constants. The data for PCE were fitted at 95% confidence interval for the removal of the parent compound. *Microsoft Excel 2003* was used to fit the experimental data to the pseudo-first order rate expressions given above and to calculate the reaction rate constants. The goodness of fitting was evaluated by the statistical parameter R-squared calculated by the software. R-squared is an indication of

magnitude of sum of squares of the differences between the observed and fitted values, and the value of 1 represents the ideal fitting.

### 3.2.2 Metalloporphyrin solubility systems

Solutions of 10  $\mu\text{M}$  Fe (III)-Cl TPP with varying cosolvent concentrations (0, 1, 2, 5 and 10%) were prepared. Fe (III)-Cl TPP was added as a concentrated stock (concentration of 2 mM) prepared by dissolving Fe (III)-Cl TPP in the appropriate cosolvent. Reference solutions contained the same amount of cosolvent as samples but did not contain the metalloporphyrin. Table 3.2 shows the preparation of the sample and the reference solutions.

The solutions were shaken by hand for about 30 seconds and were left to equilibrate for one hour. Approximately 4 mL of the sample solution and reference solution were each transferred to quartz cells with 1 cm path length. The absorbance of these solutions was measured with a double-beam, double-monochromator spectrophotometer (Shimadzu UV-2501PC).

Table 3.2 Solution preparation for the solubility systems

	Sample solutions					Reference solutions				
Cosolvent Concentration [% (v/v)]	0%	1%	2%	5%	10%	0%	1%	2%	5%	10%
Amount of Fe (III)-Cl TPP stock added (mL)	0.25*	0.25	0.25	0.25	0.25	0	0	0	0	0
Amount of pure cosolvent added (mL)	0	0	0.25	1.00	2.25	0	0.25	0.50	1.25	2.50
Amount of water added (mL)	50	49.75	49.50	48.75	47.50	50	49.75	49.50	48.75	47.50
Total solution volume (mL)	50	50	50	50	50	50	50	50	50	50
Fe (III)-Cl TPP ( $\mu\text{M}$ )	10	10	10	10	10	10	10	10	10	10

\* For 0% cosolvent concentration in the sample solutions nitrogen gas was passed through the stock solution added to the bottle and was evaporated



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Reductive dechlorination of PCE in DMF-water mixtures

Reductive dechlorination of PCE using various methodologies has been investigated (Campbell et al., 1997; Clark et al., 2003). The use of metalloporphyrins as catalysts for these reactions has received increasing attention recently (Dror and Schlautman, 2003, 2004a, 2004b; Fritsch and McNeill, 2005). The studies have used predominantly the soluble metalloporphyrins. Dror and Schlautman (2004a, 2004b) observed that the presence of cosolvent (DMF and pyridine) has an effect on the reactivity of metalloporphyrin. A cosolvent concentration of 5% (v/v) was found to activate the metalloporphyrins while they remained inactive in the absence of cosolvents. In this study the effect of cosolvent concentration on the reactivity of the metalloporphyrin was investigated. The cosolvents studied were DMF and methanol.

##### 4.1.1 Effect of DMF concentration on the reductive dechlorination of PCE catalyzed by Fe (III)-Cl TPP

The timecourses of PCE reduction for different DMF concentrations are summarized in Fig. 4.1 for average measured PCE values. The results from each individual experiment using various concentrations [0, 1, 2, 5 and 10% (v/v)] of DMF as cosolvent are shown in Fig. 4.2 a-e, respectively. The symbols in Fig. 4.2 represent actual values obtained from all duplicate samples. The reduction of PCE followed pseudo-first-order kinetics and the simple pseudo-first-order model fitting can reasonably describe

removal of parent compound PCE. The reaction rate constants are summarized in Table 4.1.

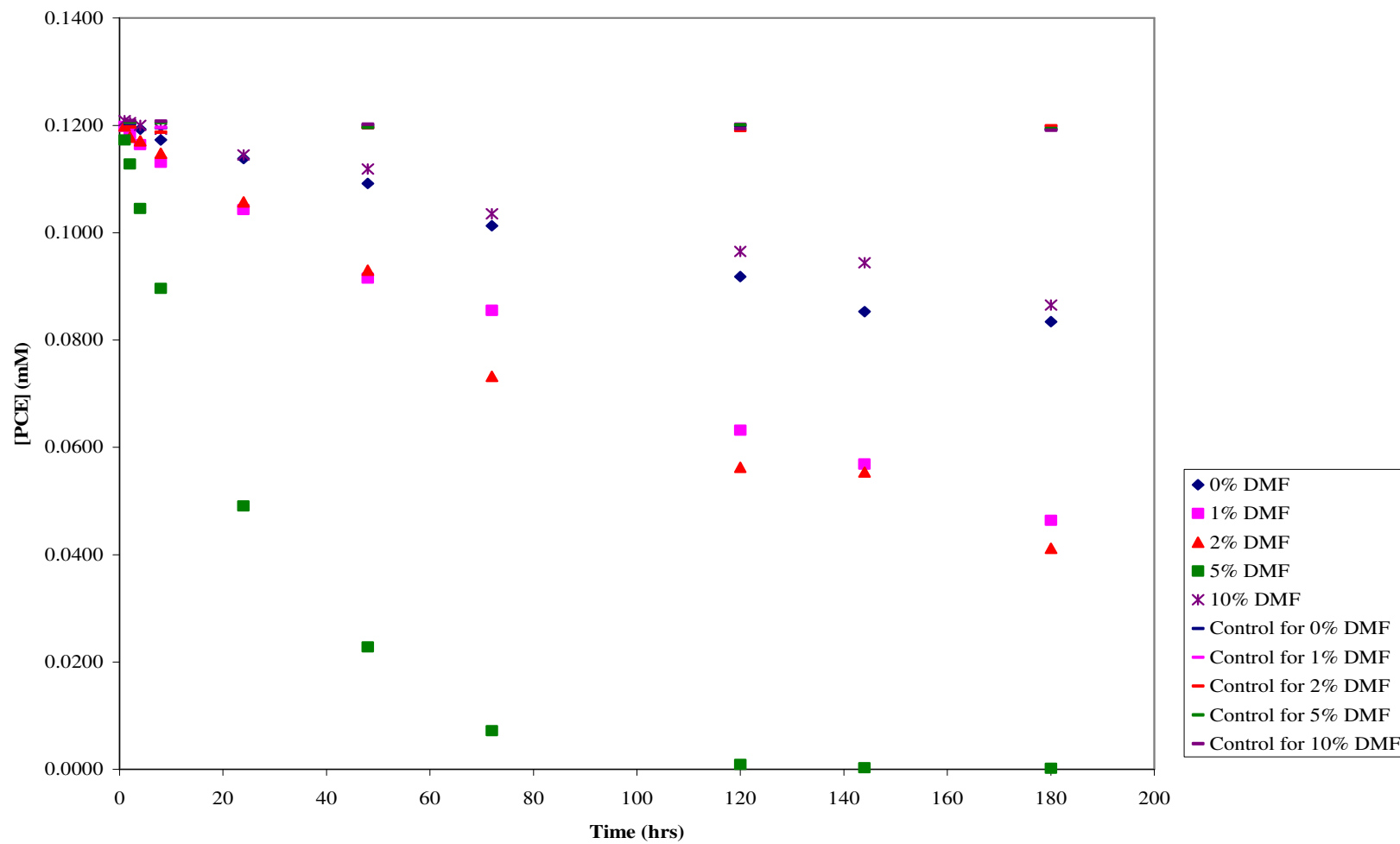


Fig 4.1 Effect of DMF concentration on PCE degradation with  $10 \mu\text{M}$  Fe (III)-Cl TPP. Data points are average values of duplicate samples. The controls do not contain Ti (III) citrate.

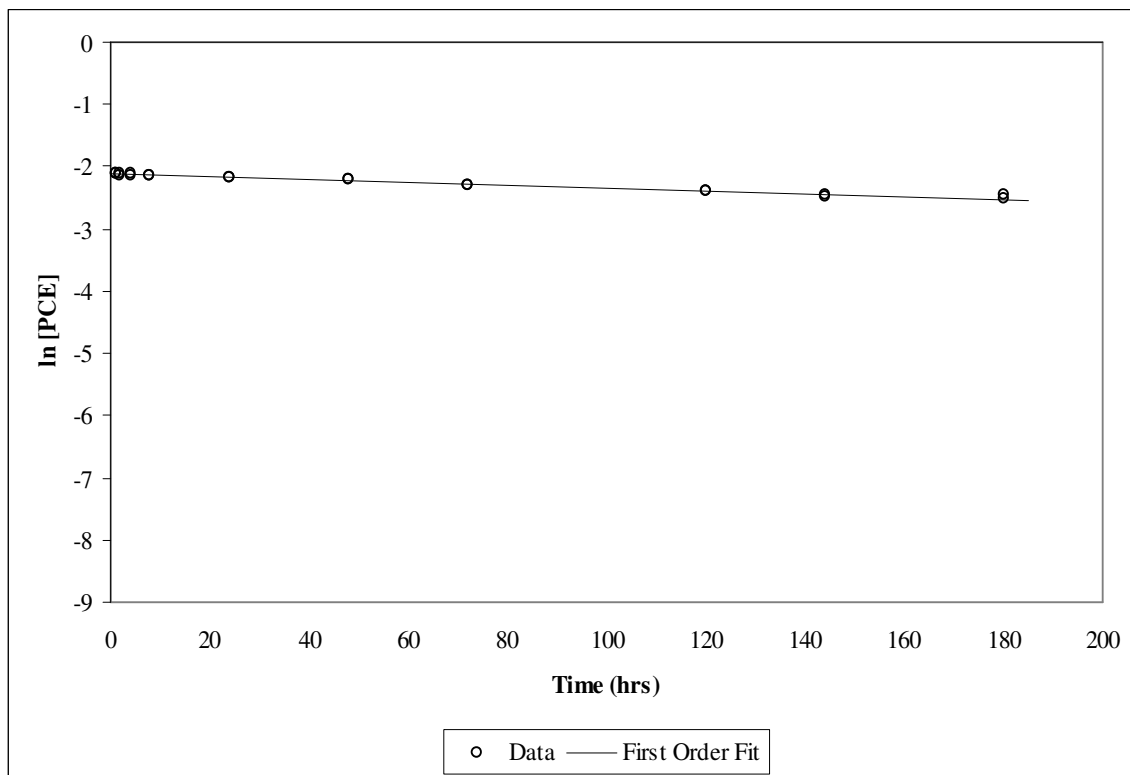


Fig 4.2a Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the absence of DMF. The line represents first order fitting of data points.

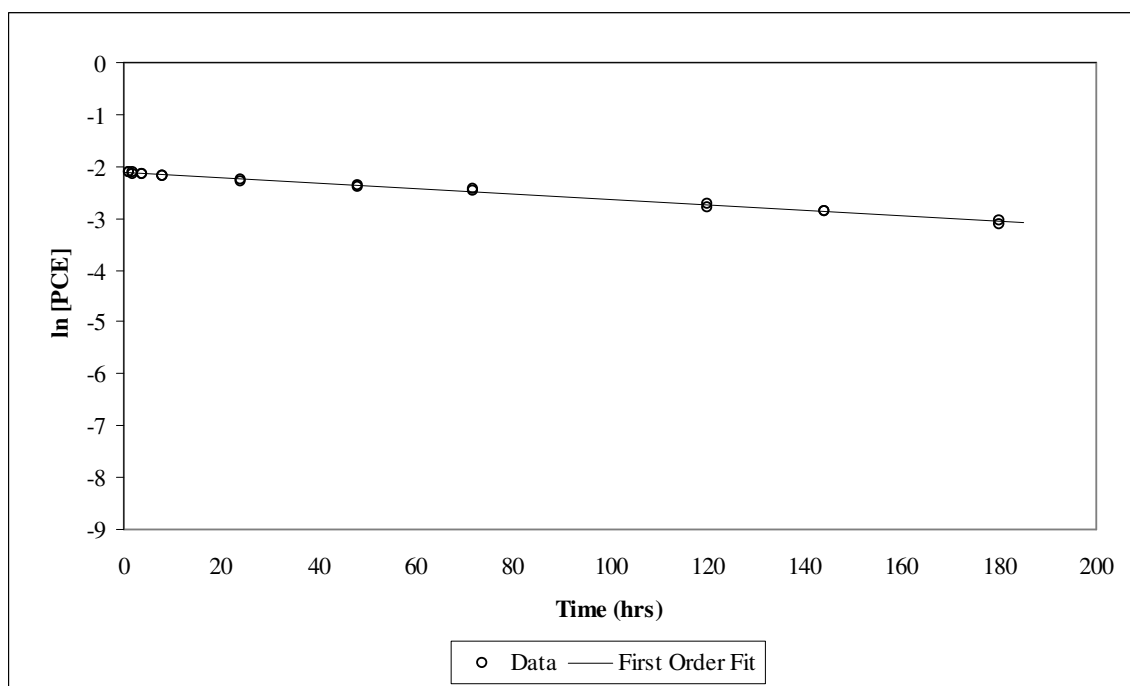


Fig 4.2b Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the presence of 1% (v/v) DMF. The line represents first order fitting of data points.

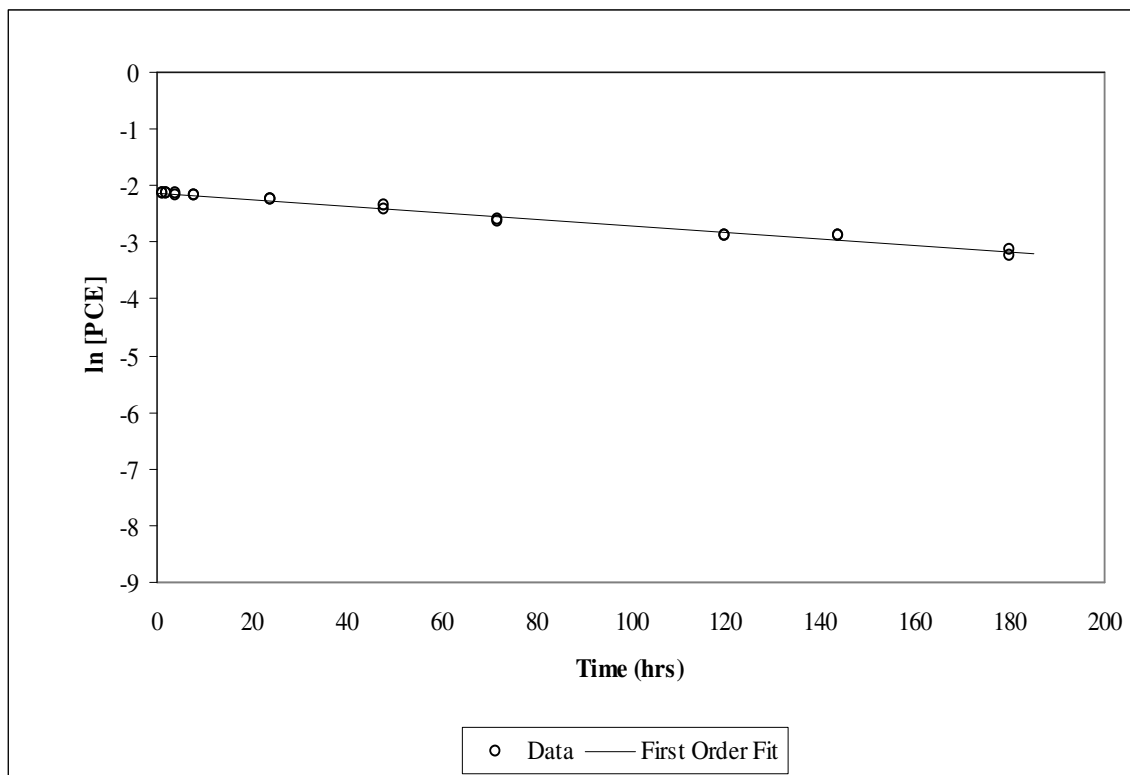


Fig 4.2c Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the presence of 2% (v/v) DMF. The line represents first order fitting of data points.

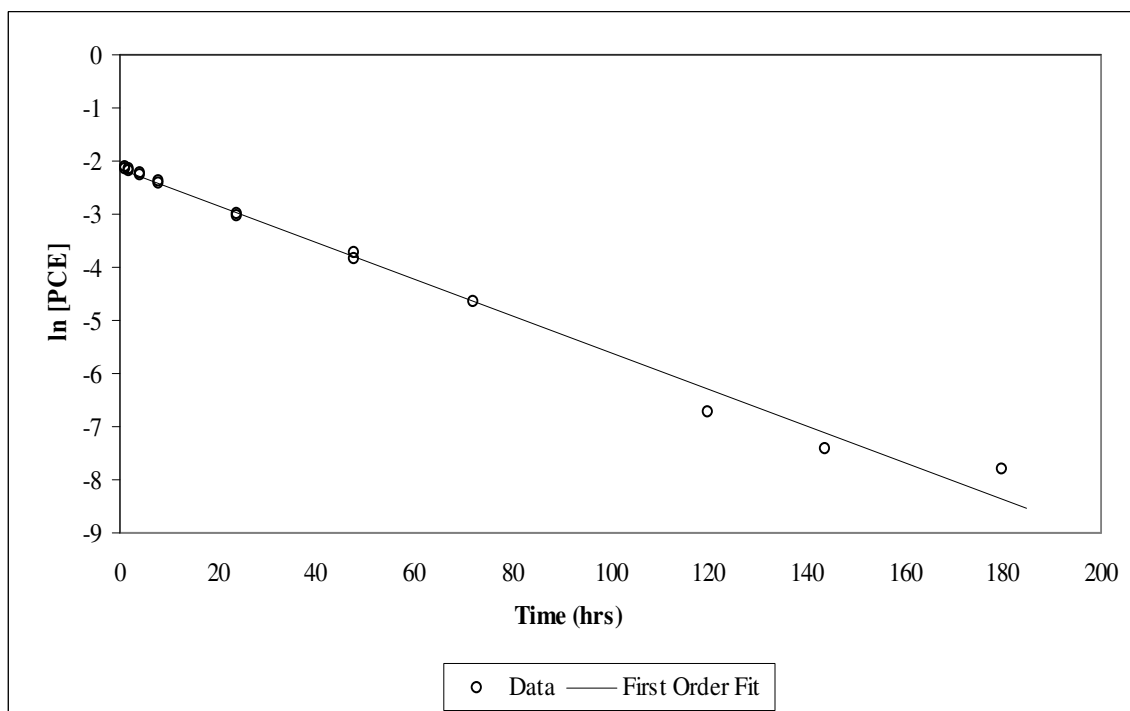


Fig 4.2d Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the presence of 5% (v/v) DMF. The line represents first order fitting of data points.

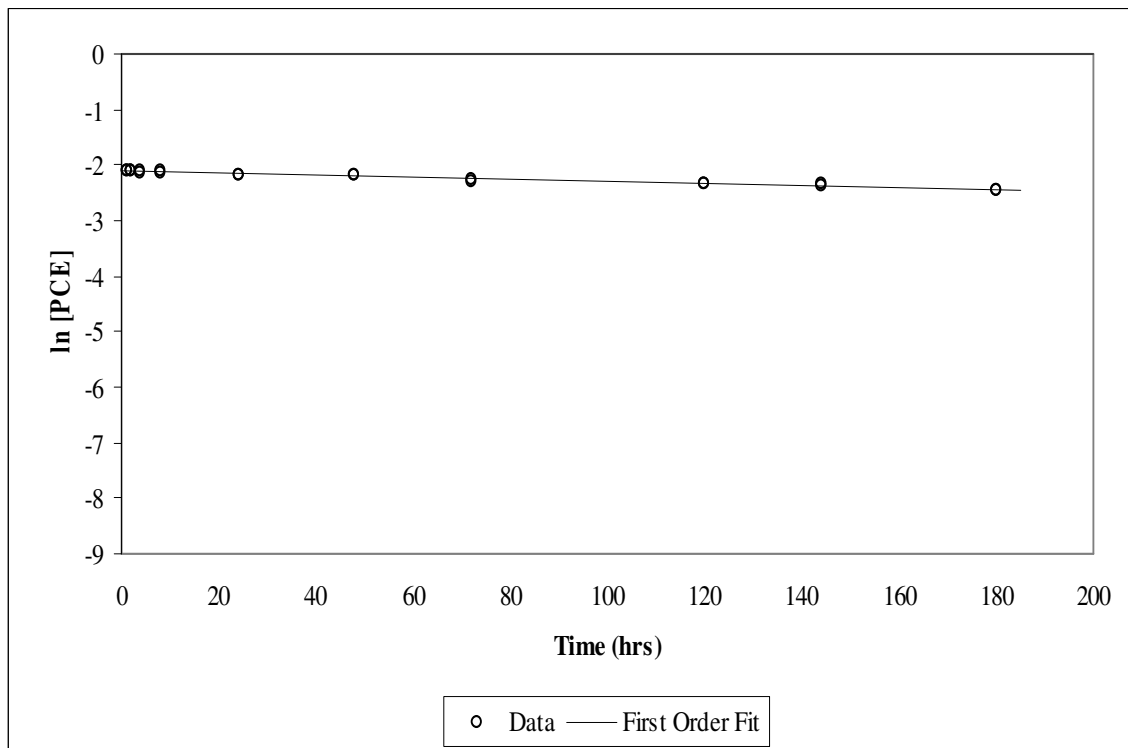


Fig 4.2e Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the presence of 10% (v/v) DMF. The line represents first order fitting of data points.

Table 4.1 Observed rate constants ( $k_{\text{obs}}$ ) for PCE reduction using 50 mM Ti (III) citrate as reductant and catalyzed by 10  $\mu\text{M}$  Fe (III)-Cl TPP with different amounts of DMF present

Amount of cosolvent (% v/v)	$k_{\text{obs}}$ ( $\text{hr}^{-1}$ ) <sup>a</sup>	$R^2$	$n$ <sup>b</sup>
0%	$(220 \pm 4) \times 10^{-5}$	0.9942	19
1%	$(510 \pm 9) \times 10^{-5}$	0.9946	20
2%	$(580 \pm 16) \times 10^{-5}$	0.9868	20
5%	$(3440 \pm 93) \times 10^{-5}$	0.9899	16
10%	$(180 \pm 4) \times 10^{-5}$	0.9928	18

<sup>a</sup>reported uncertainties represent 95% confidence limits

<sup>b</sup>number of data points used to determine the rate constants ( $k_{\text{obs}}$ )

From Table 4.1 it can be observed that the rate of the dechlorination reaction increases with increase in cosolvent concentration up to 5%. This is in accordance with the effects seen by previous researchers (Dror and Schlautman, 2003, 2004a, 2004b) that a 5% (v/v) cosolvent activates metalloporphyrin that are otherwise inactive in the absence of cosolvent. This led to the conclusion that the cosolvent enhances the solubility of the metalloporphyrin and thus there is an increase in the rate of reaction at higher cosolvent concentrations. However, there has been no experiment to test the hypothesis that the cosolvent enhances the solubility of the metalloporphyrin. Moreover, from Table 4.1 it can be observed that at 10% concentration there is a considerable decrease in the reaction rate. This result is in contradiction to the hypothesis that the rate of reaction is attributed to solubility of metalloporphyrins if reaction involves electron mediation of electron carriers. This seemingly contradictory result was further investigated with the study of solubility of metalloporphyrins which is discussed in Section 4.2.

There has also been work done to show that the addition of cosolvent increases the rate of reduction by the dissolution of the target compound in the absence of metalloporphyrin (Li and Andren, 1994; Li et al., 1996). Thus before testing the effect of cosolvents on the solubility of metalloporphyrins, which might be a reason for the trend seen in the rate of reduction of PCE shown in Table 4.1, it is important to test if the trend in the rate of the reduction is due to solubility of PCE by the addition of cosolvents.

#### 4.1.2 Effect of DMF concentration on reductive dechlorination of PCE in the absence of Fe (III) – Cl TPP

Cosolvents have the ability to increase the solvation properties of organic compounds. This property of the cosolvent can be utilized to enhance the rate of



reductive dechlorination reactions by either increasing the solubility of the organic pollutant or the metalloporphyrin added to catalyze the reductive dechlorination reaction. To determine whether direct enhancement of PCE dechlorination by DMF contributed to the results in the previous section, the rate of dechlorination was monitored at varying cosolvent concentration in the absence of Fe (III) – Cl TPP. The timecourses of PCE reduction at different DMF concentrations were plotted together in Fig. 4.3 for average measured PCE values. Figures 4.4 a-e show the results from PCE reduction at varying concentration of DMF in the absence of Fe (III) – Cl TPP. Symbols in Fig. 4.4 represent the actual values obtained from all duplicate samples. The reduction of PCE followed pseudo-first-order kinetics as pseudo-first-order model fitting can reasonably describe removal of parent compound PCE. The reaction rate constants are summarized in Table 4.2.

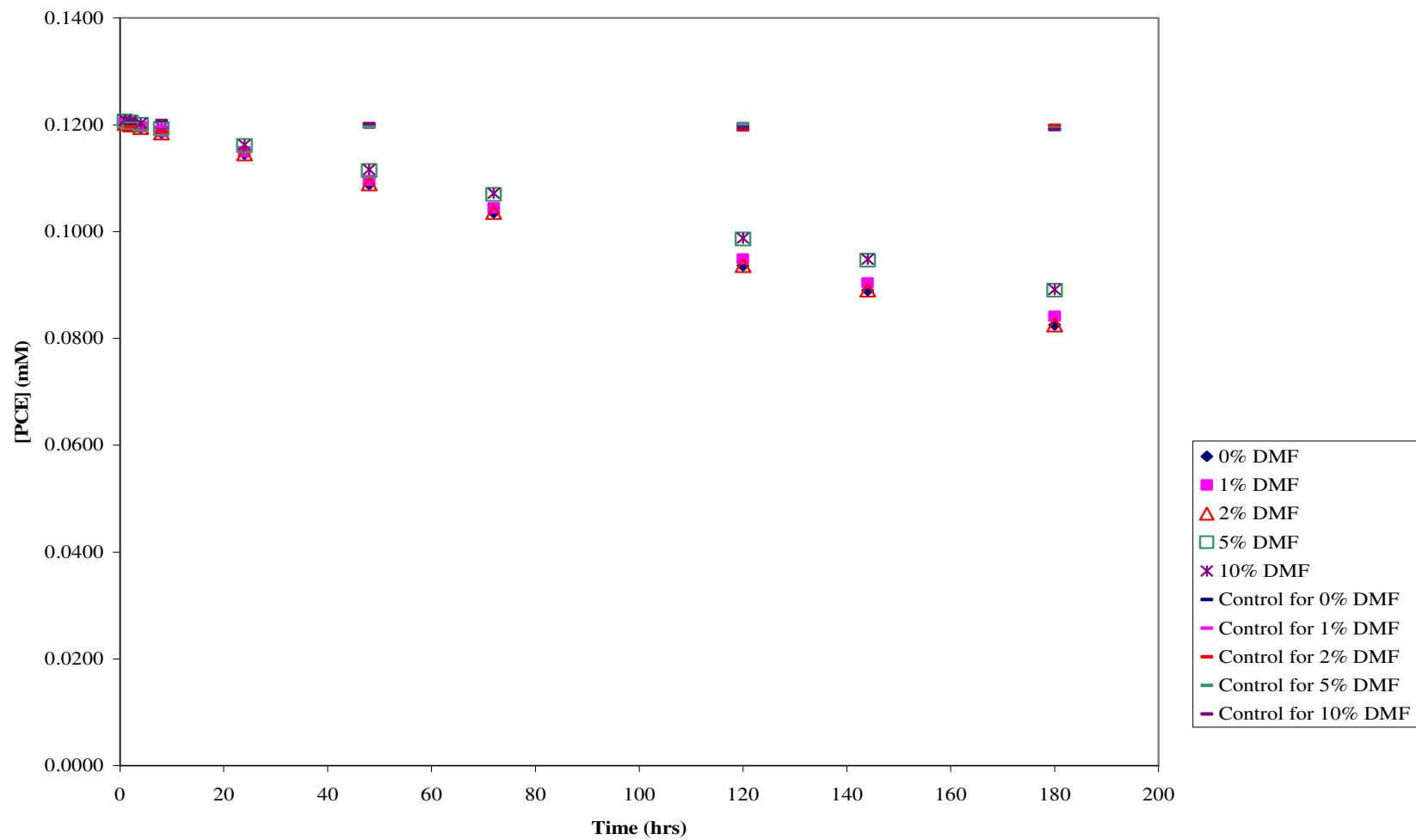


Fig 4.3 Effect of DMF concentration on PCE reduction in the absence of Fe (III) – Cl TPP. Data points are average values of duplicate samples. The controls do not contain Ti (III) citrate.

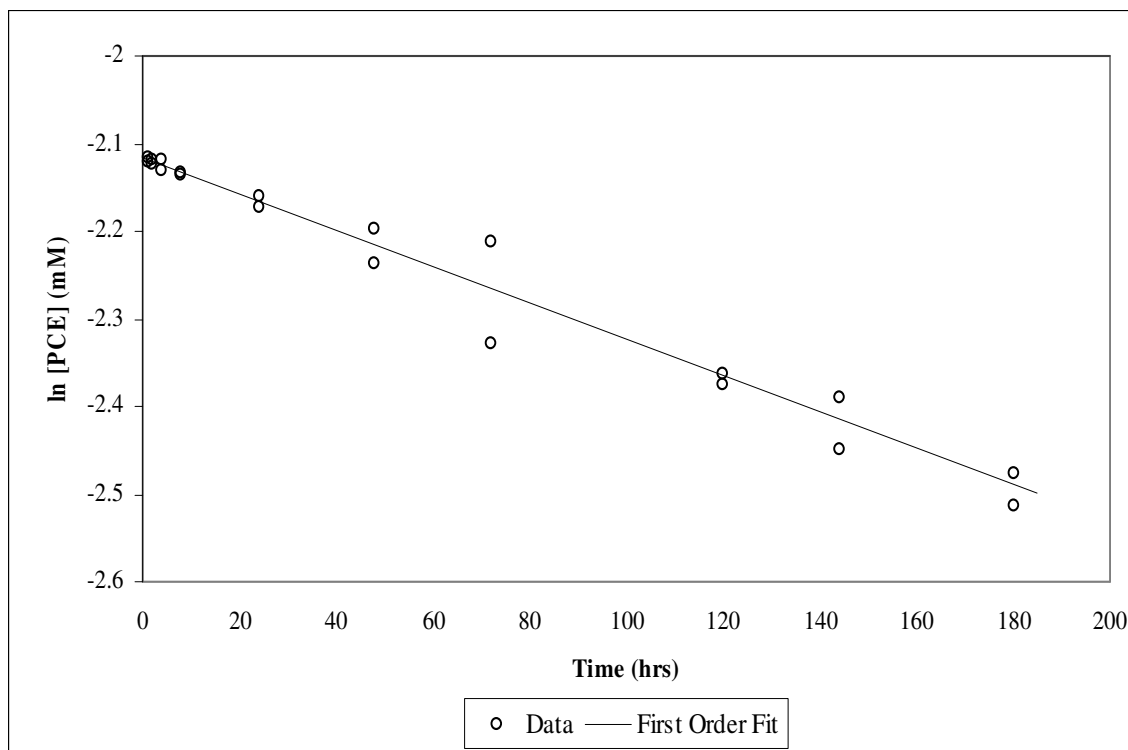


Fig 4.4a Reduction of PCE in the absence of cosolvent. The line represents first order fitting of data points.

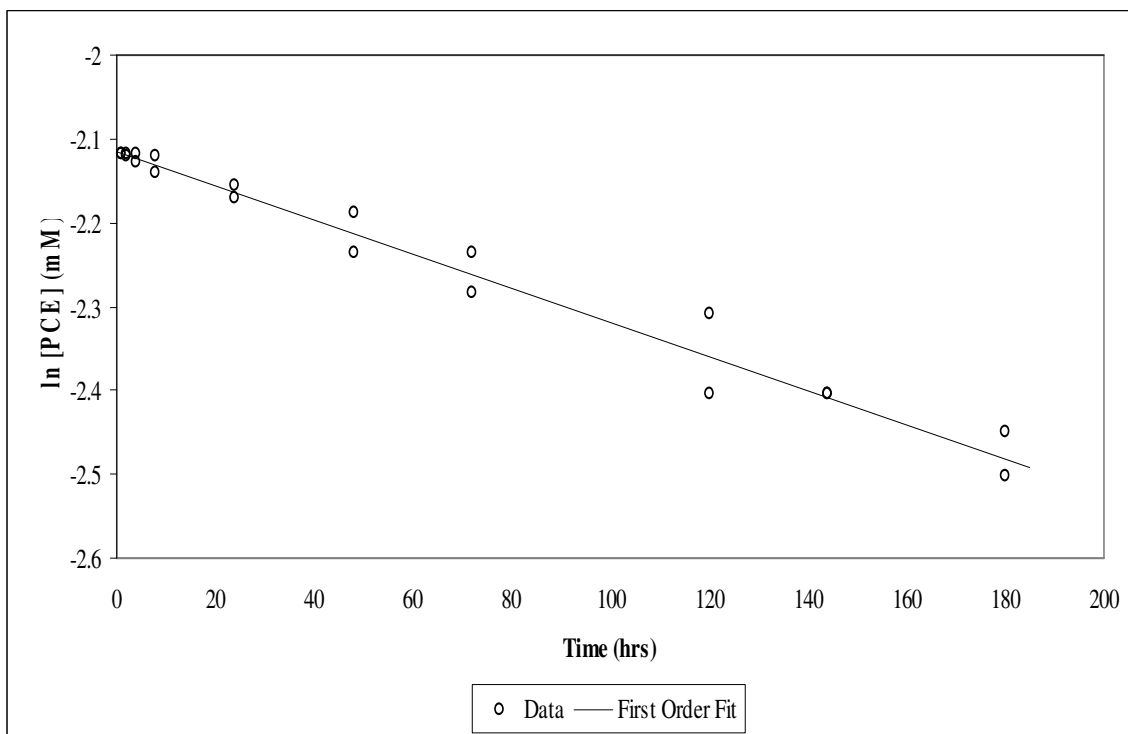


Fig 4.4b Reduction of PCE in the presence of 1% (v/v) DMF. The line represents first order fitting of data points.

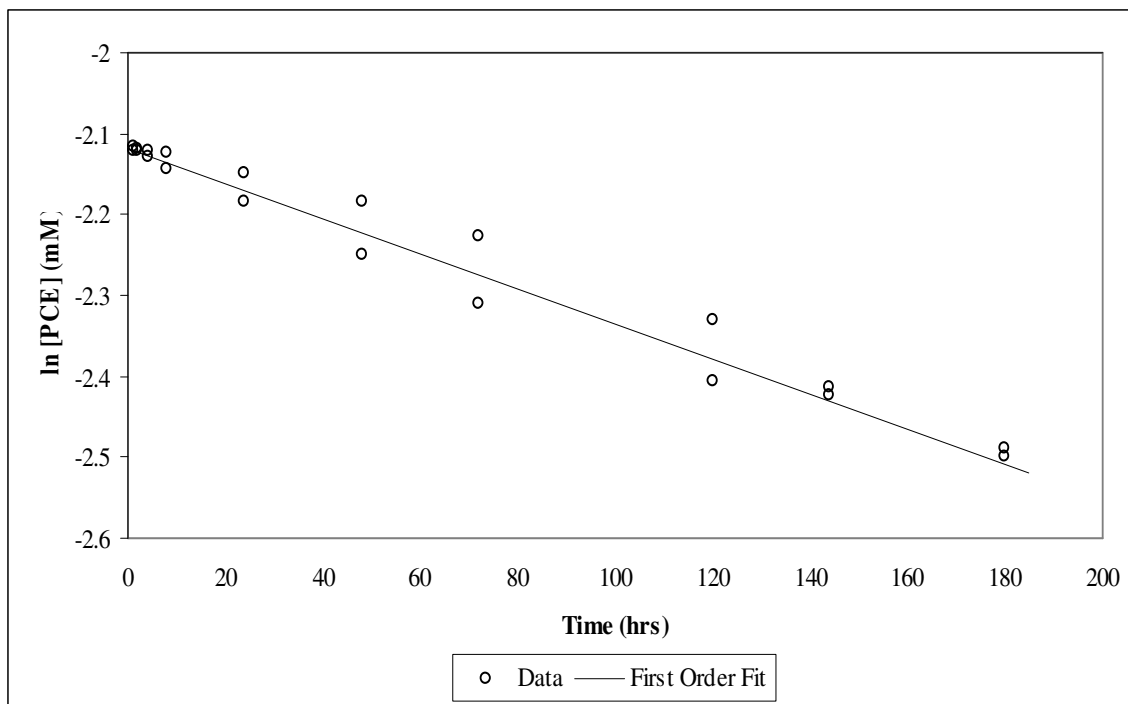


Fig 4.4c Reduction of PCE in the presence of 2% (v/v) DMF. The line represents first order fitting of data points.

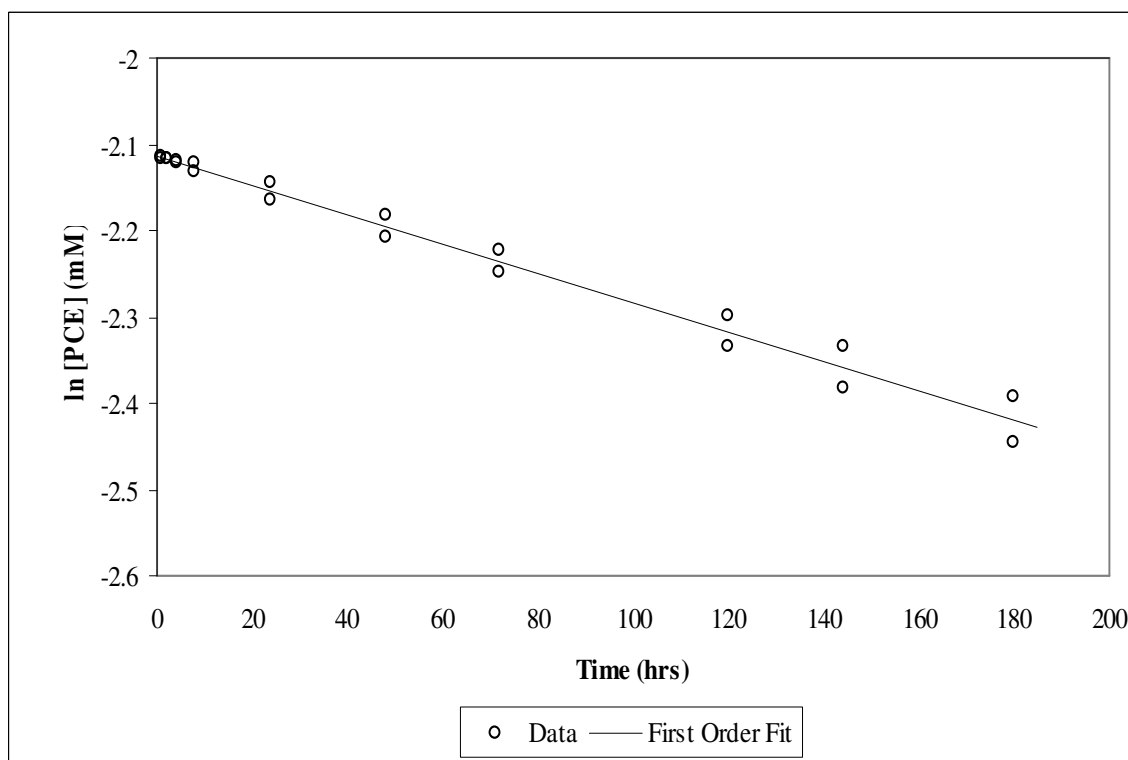


Fig 4.4d Reduction of PCE in the presence of 5% (v/v) DMF. The line represents first order fitting of data points.

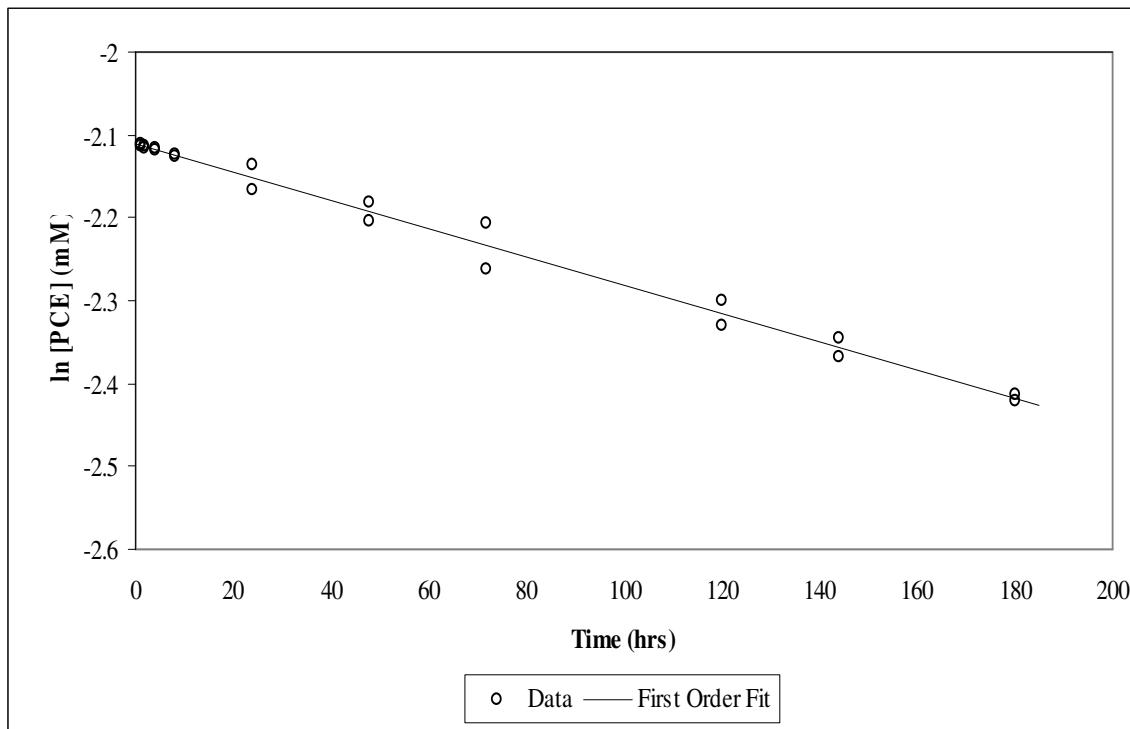


Fig 4.4e Reduction of PCE in the presence of 10% (v/v) DMF. The line represents first order fitting of data points.

Table 4.2 Observed rate constants ( $k_{\text{obs}}$ ) for PCE dechlorination with 50 mM Ti (III) citrate in the presence of different amounts of DMF (no Fe (III) – Cl TPP added)

Amount of cosolvent (% v/v)	$k_{\text{obs}}$ ( $\text{hr}^{-1}$ ) <sup>a</sup>	$R^2$	$n$ <sup>b</sup>
0%	$(210 \pm 5) \times 10^{-5}$	0.9921	17
1%	$(200 \pm 7) \times 10^{-5}$	0.9794	18
2%	$(220 \pm 11) \times 10^{-5}$	0.9591	18
5%	$(170 \pm 5) \times 10^{-5}$	0.9827	20
10%	$(170 \pm 5) \times 10^{-5}$	0.9968	20

<sup>a</sup>reported uncertainties represent 95% confidence limits

<sup>b</sup>number of data points used to determine the rate constants ( $k_{\text{obs}}$ )

From Table 4.2 it can be observed that there is no major change in PCE reduction rate with DMF concentration in the absence of Fe (III) – Cl TPP. Hence it can be concluded that DMF alone is not directly responsible for the trends observed in Section 4.1 for the rate of PCE reduction.

#### 4.2 Absorbance of Fe (III) – Cl TPP in DMF – water mixtures

Absorption spectroscopy is a commonly used technique to quantify the concentration of dissolved constituents in ideal solutions. Metalloporphyrin solutions are colored solutions and absorb light. According to the Beer-Lambert law (Eqn 2.2), an increase in absorbance implies that there is an increase in concentration. Since evidence in the literature has suggested soluble metalloporphyrins are much more effective in mediating contaminant reduction (Schwarzenbach et al., 1990; Lewis et al., 1995; Glod et al., 1997; Burris et al., 1998) it is expected that the rate of dechlorination reaction will be proportional to the concentration of metalloporphyrins. For example, Fritsch and McNeill (2005) reported that PCE and TCE degradation was first order with respect to metalloporphyrin catalyst concentration. If the increase in rate of reaction here is due to the increase in concentration of metalloporphyrin, then the rate constant and the absorbance would have a linear relationship as shown in Figure 4.5.

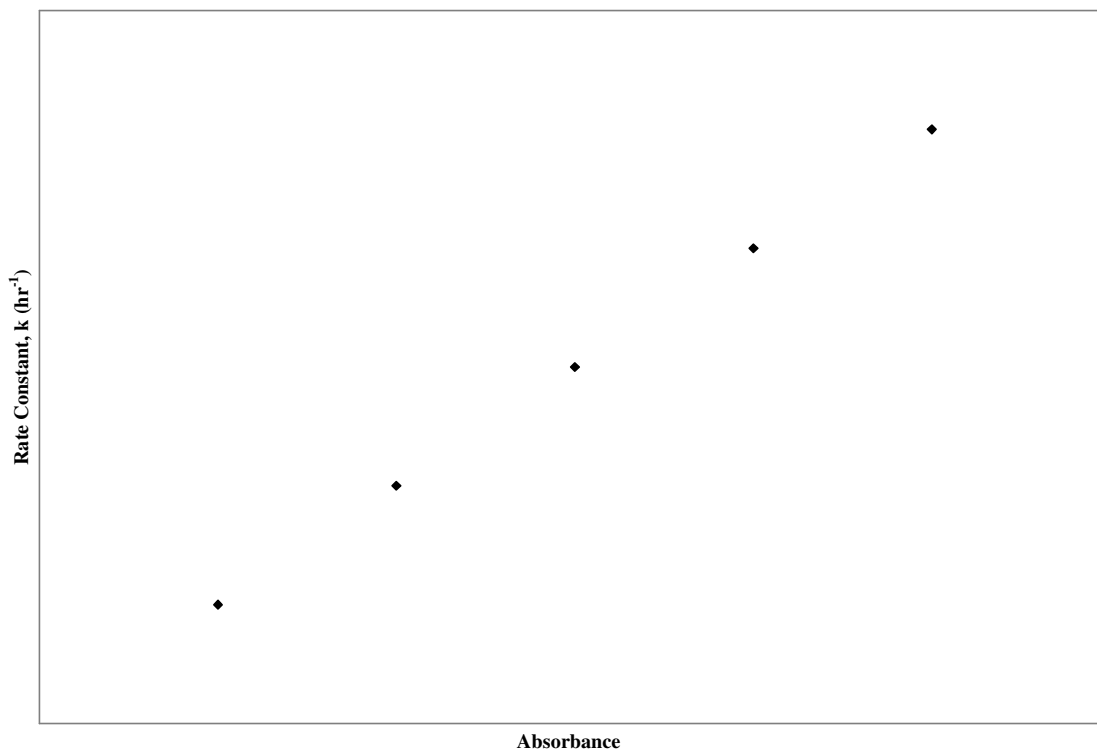


Figure 4.5 Expected relationship between rate constant and absorbance

To test the effect of cosolvent concentration on metalloporphyrin absorbance, UV-vis spectra of Fe (III)-Cl TPP were measured in the presence of varying DMF amount. A concentrated stock of Fe (III)-Cl TPP in DMF was added to premixed cosolvent and water mixtures to give a final metalloporphyrin concentration of 10  $\mu$ M. The DMF concentrations were 1, 2, 5 and 10% (v/v) to be consistent with the PCE degradation studies. The absorption spectra of Fe (III)-Cl TPP at varying DMF concentration are shown in Fig. 4.6. The peak absorbance of Fe (III)-Cl TPP followed the order of 1 $\approx$ 2 > 10 > 5% DMF, indicating that peak absorbance was not correlated with the PCE degradation rate constant as had been expected as shown in Fig. 4.5.



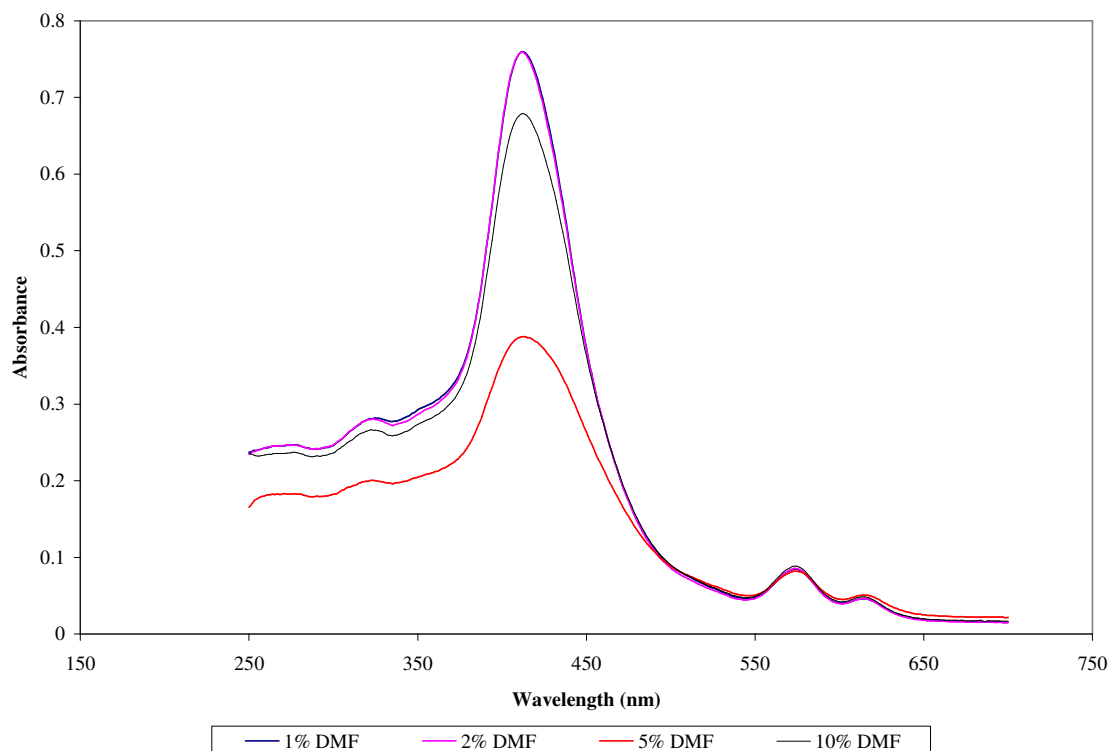


Figure 4.6 Absorption spectrum of 10  $\mu\text{M}$  Fe (III)-Cl TPP in water/DMF mixtures

The failure to see the expected relationship shown in Fig. 4.5 may be due, in part, to floc formation that was observed in all of the samples containing cosolvent. It has been reported that organic solvents containing a high concentration of oxidized iron (i.e., Fe (III)) porphyrin results in the formation of  $\mu$ -oxo dimers (Cheng et al., 1995; Kasuno et al., 2005). In the presence of water, these complexes may precipitate out of solution and result in decreasing absorbance. The formation of  $\mu$ -oxo dimers is also favored at alkaline conditions with a  $\text{pK}_d$  for dimerization around 7.8 (Yushmanov et al., 2001). Furthermore, it has been reported that formation of dimers shift the Soret band of Fe (III)-Cl TPP from 394 nm (monomeric) to a higher region (Ren et al., 1999; Kawasaki et al.,

2003). The absorption spectrum shown in Fig. 4.6 shows the Soret band at 412-413nm range, consistent with such a band shift due to dimer formation.

From the studies performed here it can be concluded that the effect of DMF on PCE degradation (Table 4.1) is not merely to increase the concentration of Fe (III)-Cl TPP. A different study noted that the dimers show higher catalytic properties than the corresponding monomers (Ren et al., 2001). Thus, one possibility for the increase in reaction rate at reduced amount of solubilized Fe (III)-Cl TPP could be due to more dimers formed at corresponding cosolvent concentration. Following this logic, then the order of reactivity should have been  $10 > 5 > 2 > 1$  % DMF solutions. However, the reaction rate at 10% DMF was the slowest rate of all.

The decrease in reaction rate at 10% DMF concentration was hypothesized to be attributed to the effect of the presence of nitrogen in DMF. Although, there is no specific mention of catalyst poisoning of metalloporphyrins in the literature, nitrogen containing compounds have been shown previously to deactivate catalysts (Kogan et al., 2003). N-containing compounds are adsorbed on both Lewis and Bronsted acidic sites due to their basicity (Furimsky and Massoth, 1999). Therefore, I hypothesized that the N-containing compound DMF was complexed to the iron core metal of Fe (III)-Cl TPP. This potential poisoning effect by DMF was tested by using a different cosolvent (methanol) which does not contain nitrogen.

### 4.3 Reductive dechlorination of PCE in methanol-water mixtures

#### 4.3.1 Effect of methanol concentration on the reductive dechlorination of PCE catalyzed by Fe (III)-Cl TPP

The timecourses of PCE reduction for different methanol concentrations are summarized in Fig. 4.7 for average measured PCE values. The results from each individual experiment using various concentrations [0, 1, 2, 5 and 10% (v/v)] of methanol as cosolvent are shown in Fig. 4.8 a-e, respectively. The symbols in Fig. 4.8 represent actual values obtained from all duplicate samples. The reduction of PCE followed pseudo-first-order kinetics and the simple pseudo-first-order model fitting can reasonably describe removal of parent compound PCE. The reaction rate constants are summarized in Table 4.3.

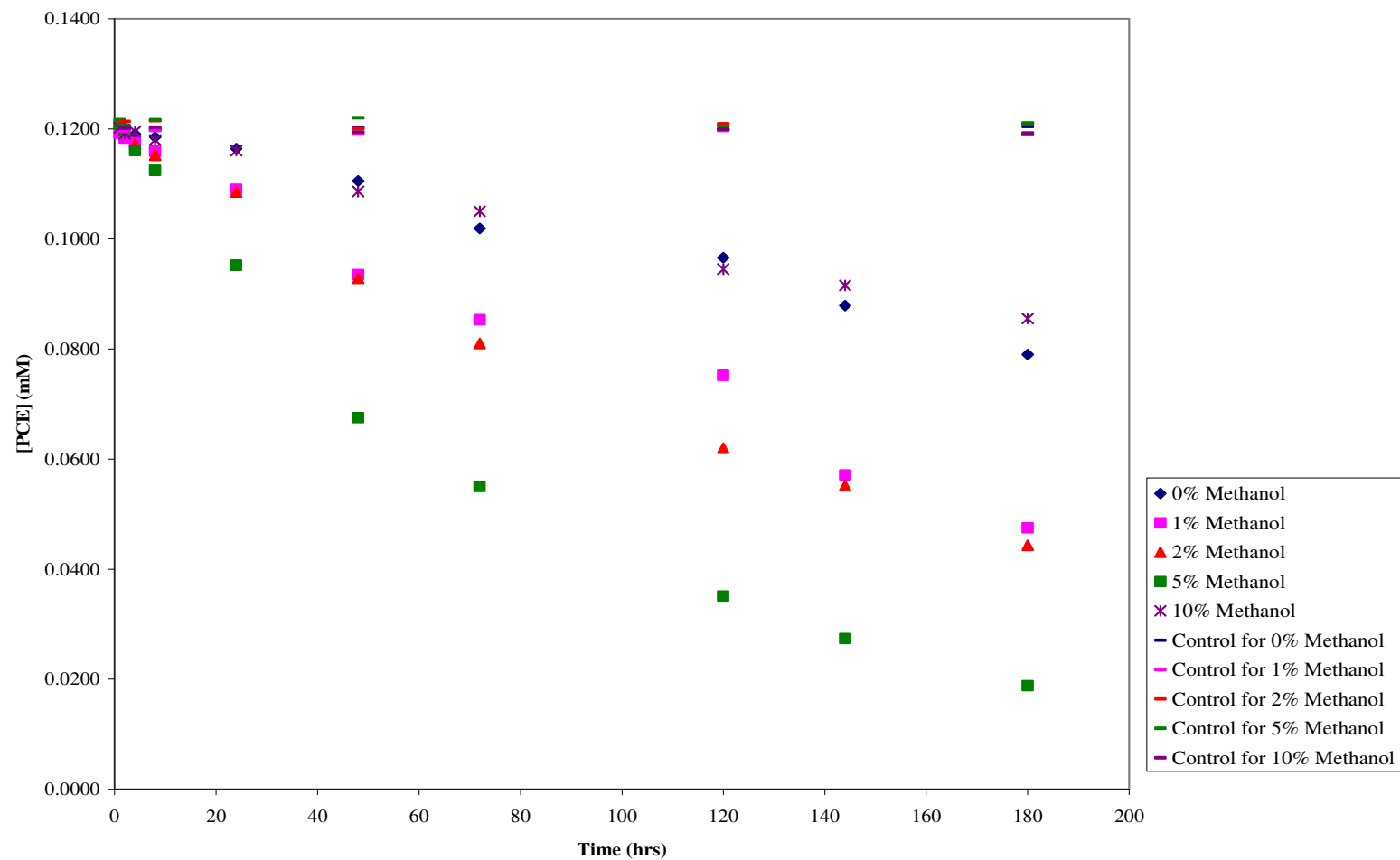


Fig 4.7 Effect of methanol concentration on PCE degradation with  $10 \mu\text{M}$  Fe (III)-Cl TPP. Data points are average values of duplicate samples. The controls do not contain Ti (III) citrate.

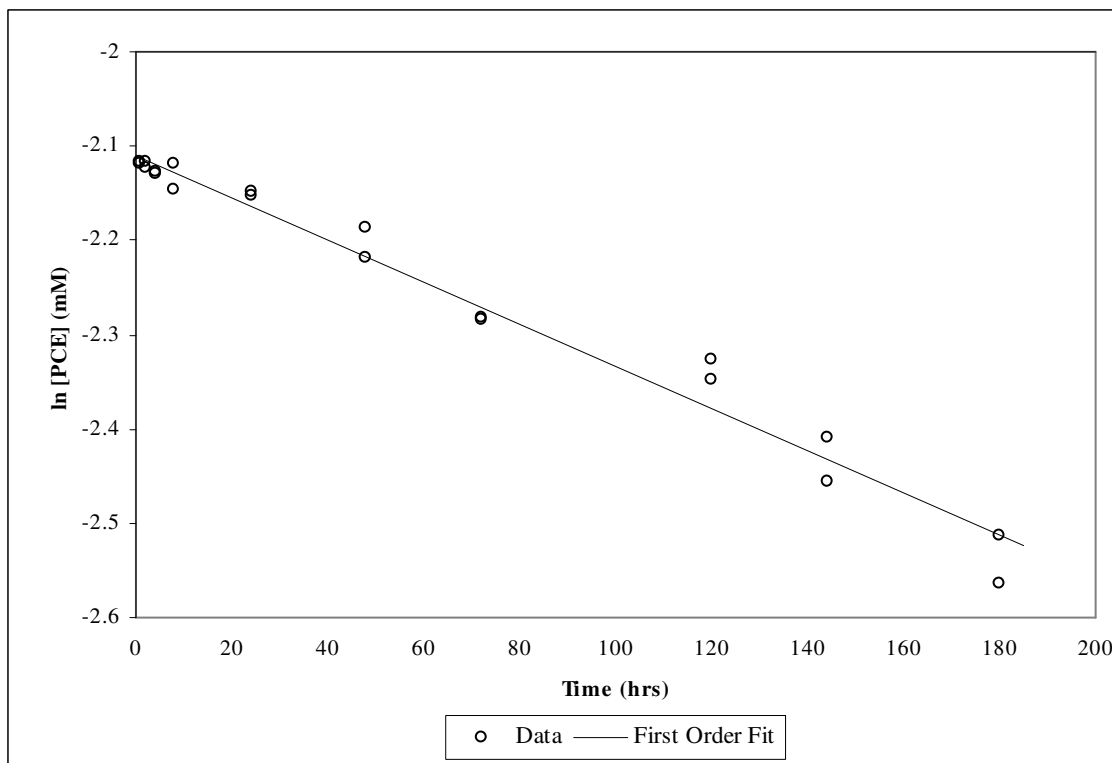


Fig 4.8a Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the absence of methanol. The line represents first order fitting of data points.

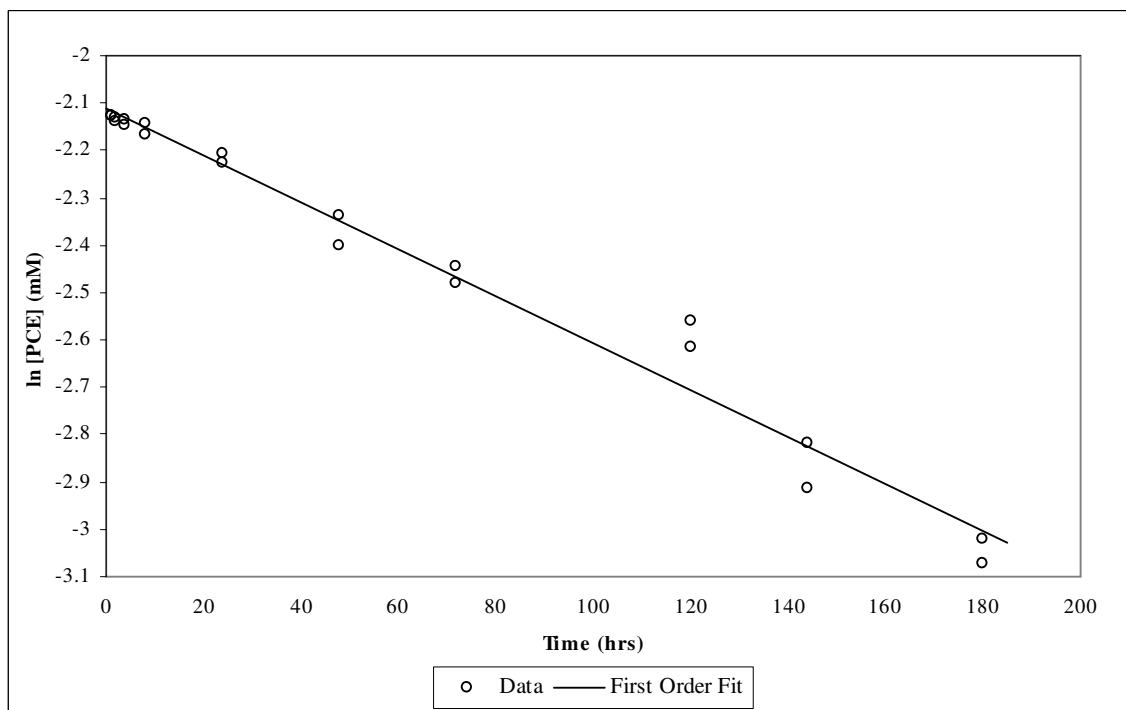


Fig 4.8b Reduction of PCE with 10  $\mu$ M Fe (III)-Cl TPP in the presence of 1% (v/v) methanol. The line represents first order fitting of data points.

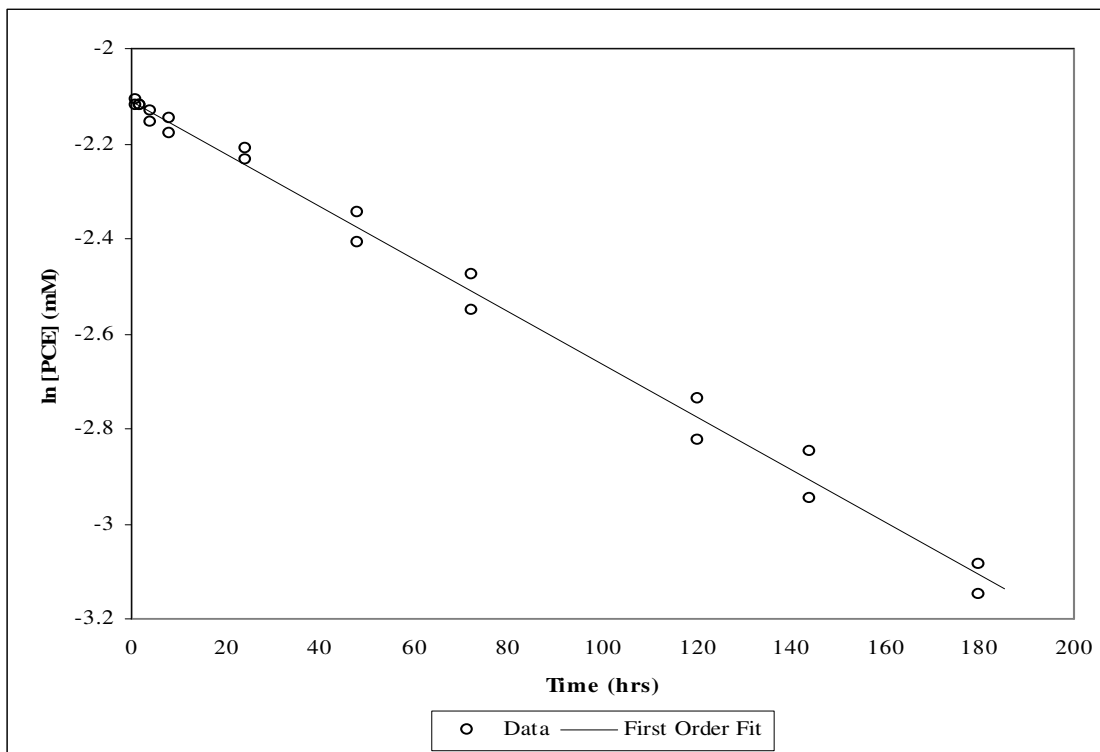


Fig 4.8c Reduction of PCE with 10  $\mu\text{M}$  Fe (III)-Cl TPP in the presence of 2% (v/v) methanol. The line represents first order fitting of data points.

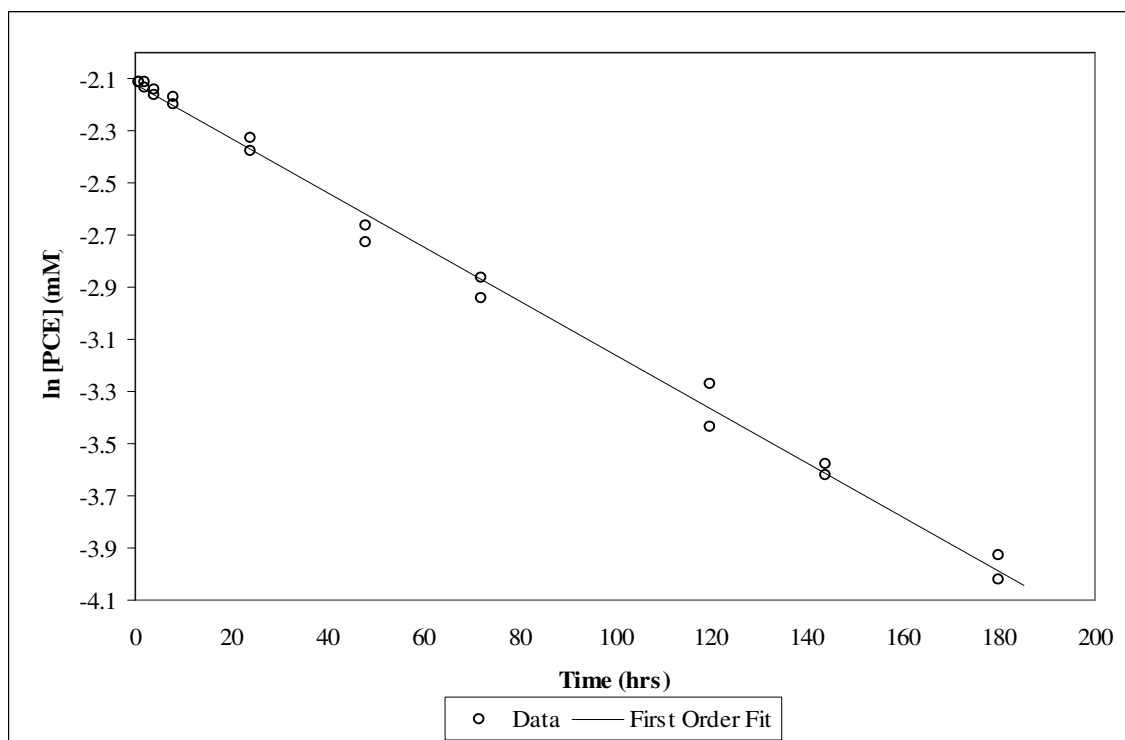


Fig 4.8d Reduction of PCE with 10  $\mu\text{M}$  Fe (III)-Cl TPP in the presence of 5% (v/v) methanol. The line represents first order fitting of data points.

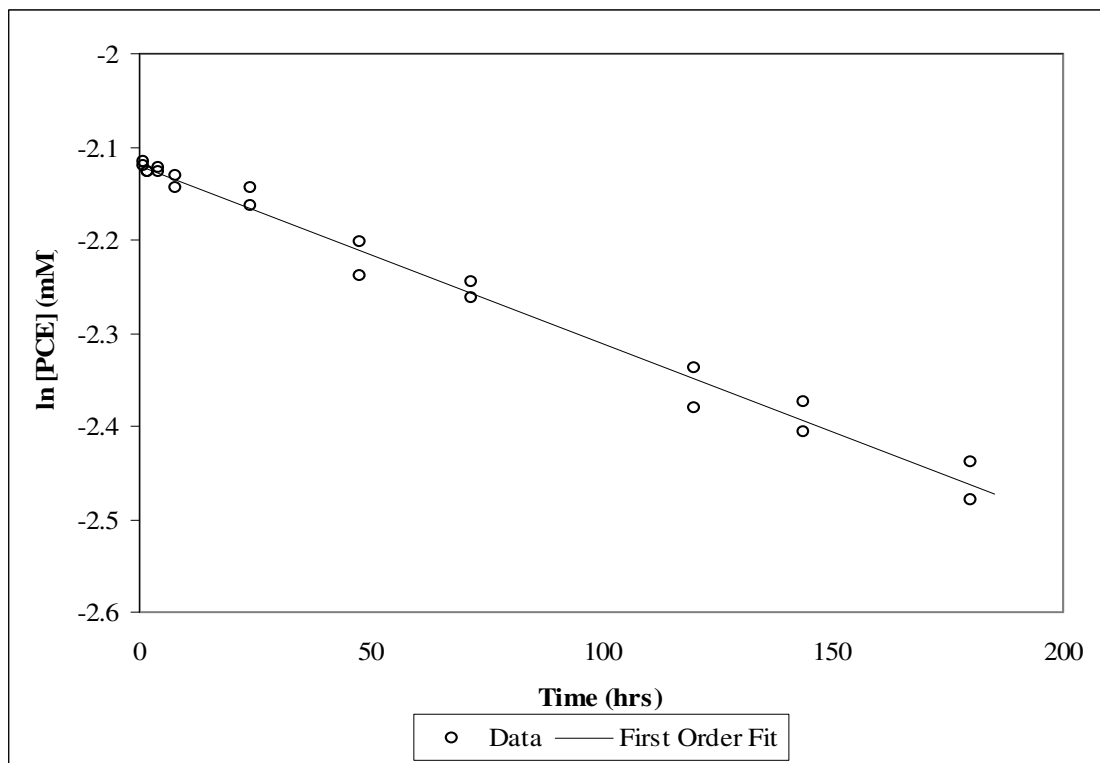


Fig 4.8e Reduction of PCE with 10  $\mu\text{M}$  Fe (III)-Cl TPP in the presence of 10% (v/v) methanol. The line represents first order fitting of data points.

Table 4.3 Observed rate constants ( $k_{\text{obs}}$ ) for PCE reduction using 50 mM Ti (III) citrate as reductant and catalyzed by 10  $\mu\text{M}$  Fe (III)-Cl TPP with different amounts of methanol present

Amount of methanol (% v/v)	$k_{\text{obs}}$ ( $\text{hr}^{-1}$ ) <sup>a</sup>	$R^2$	$n^b$
0%	$(220 \pm 9) \times 10^{-5}$	0.9752	19
1%	$(490 \pm 18) \times 10^{-5}$	0.9758	20
2%	$(550 \pm 11) \times 10^{-5}$	0.9933	18
5%	$(1030 \pm 17) \times 10^{-5}$	0.9948	20
10%	$(190 \pm 5) \times 10^{-5}$	0.9857	20

<sup>a</sup>reported uncertainties represent 95% confidence limits

<sup>b</sup>number of data points used to determine the rate constants ( $k_{\text{obs}}$ )



The rates of reaction using methanol as a cosolvent are shown in Table 4.3. A trend similar to that observed with DMF was also observed with methanol, namely a reaction rate increasing up to 5% cosolvent concentration and then decreasing at 10% cosolvent concentration. This appears to rule out the possibility of DMF poisoning the catalyst as proposed in the previous section. The values of the reaction rates were lower than that seen with DMF as cosolvent. This is because methanol has a smaller impact on the activity coefficient of an organic solute when compared to DMF. Thus DMF is a better cosolvent than methanol. Fig 4.9 shows a comparison of the dechlorination rate constants with DMF and methanol as cosolvents.

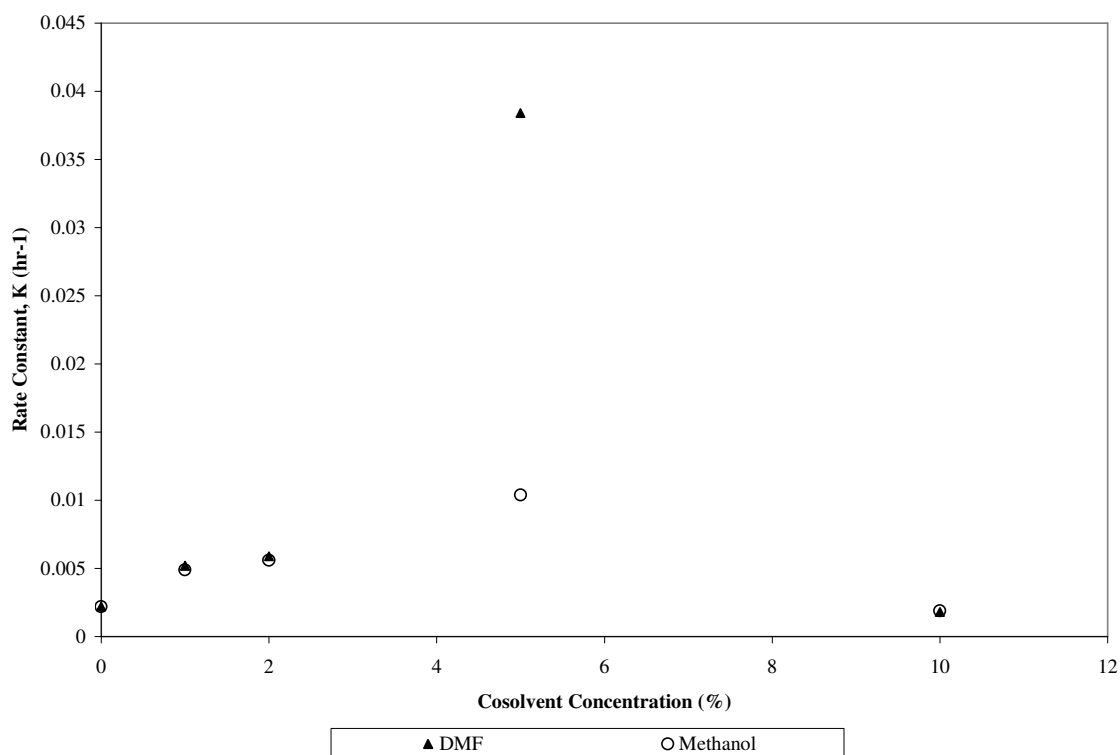


Fig 4.9 Comparison of rate constants of PCE dechlorination catalyzed by Fe (III)-Cl TPP with DMF and methanol as cosolvents

#### 4.3.2 Effect of methanol concentration on reductive dechlorination of PCE in the absence of Fe (III) – Cl TPP

The effect of methanol on the rate of dechlorination of PCE in the absence of Fe (III) – Cl TPP was tested. The timecourses of PCE reduction at different methanol concentrations were plotted together in Fig. 4.10 for average measured PCE values. Figures 4.11 a-e show the results from PCE reduction at varying concentration of methanol in the absence of Fe (III) – Cl TPP. Symbols in Fig. 4.11 represent the actual values obtained from all duplicate samples. The reduction of PCE followed pseudo-first-order kinetics as pseudo-first-order model fitting can reasonably describe removal of parent compound PCE. The reaction rate constants are summarized in Table 4.4.

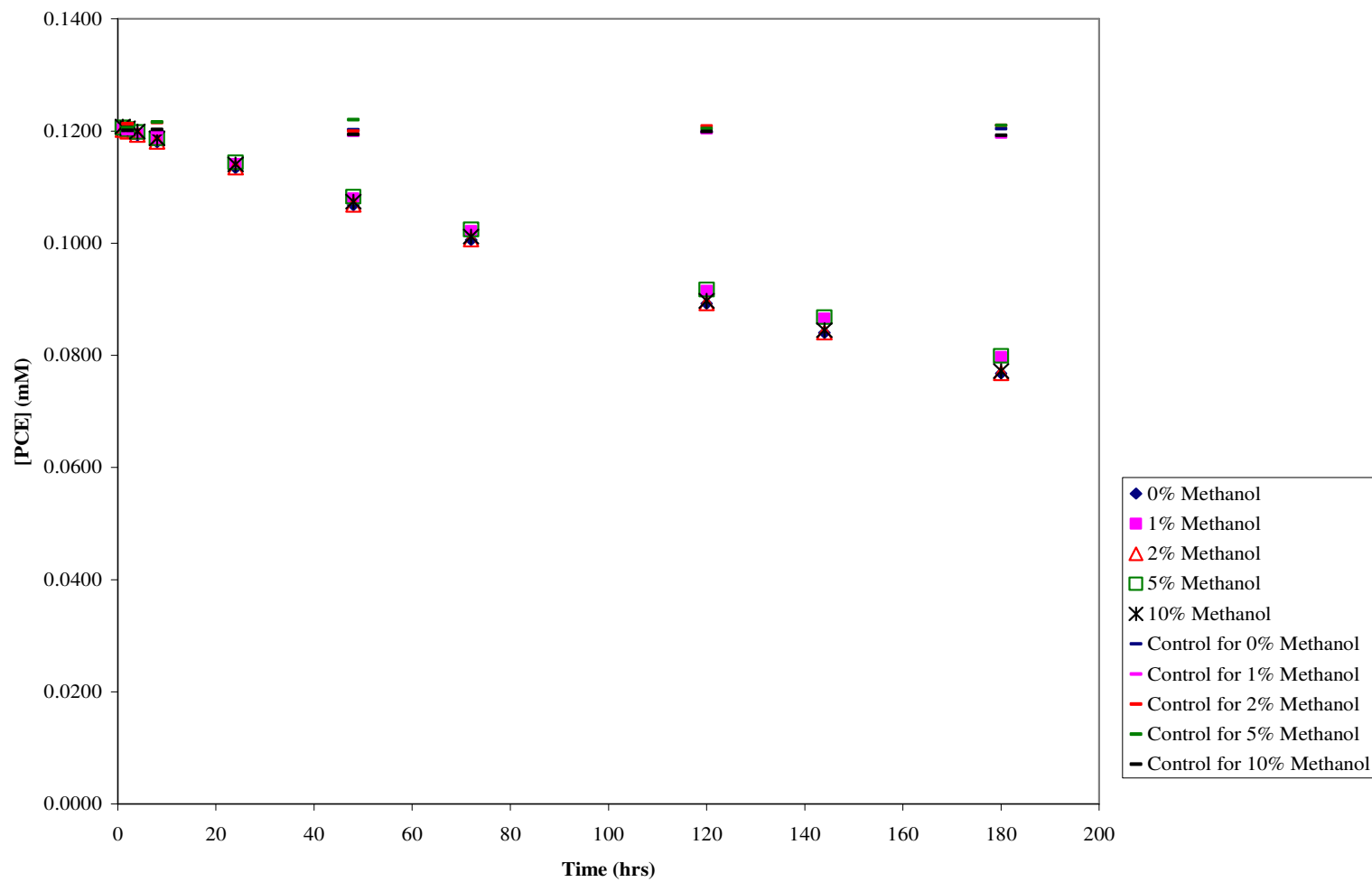


Fig 4.10 Effect of methanol concentration on PCE reduction in the absence of Fe (III) – Cl TPP. Data points are average values of duplicate samples. The controls do not contain Ti (III) citrate.

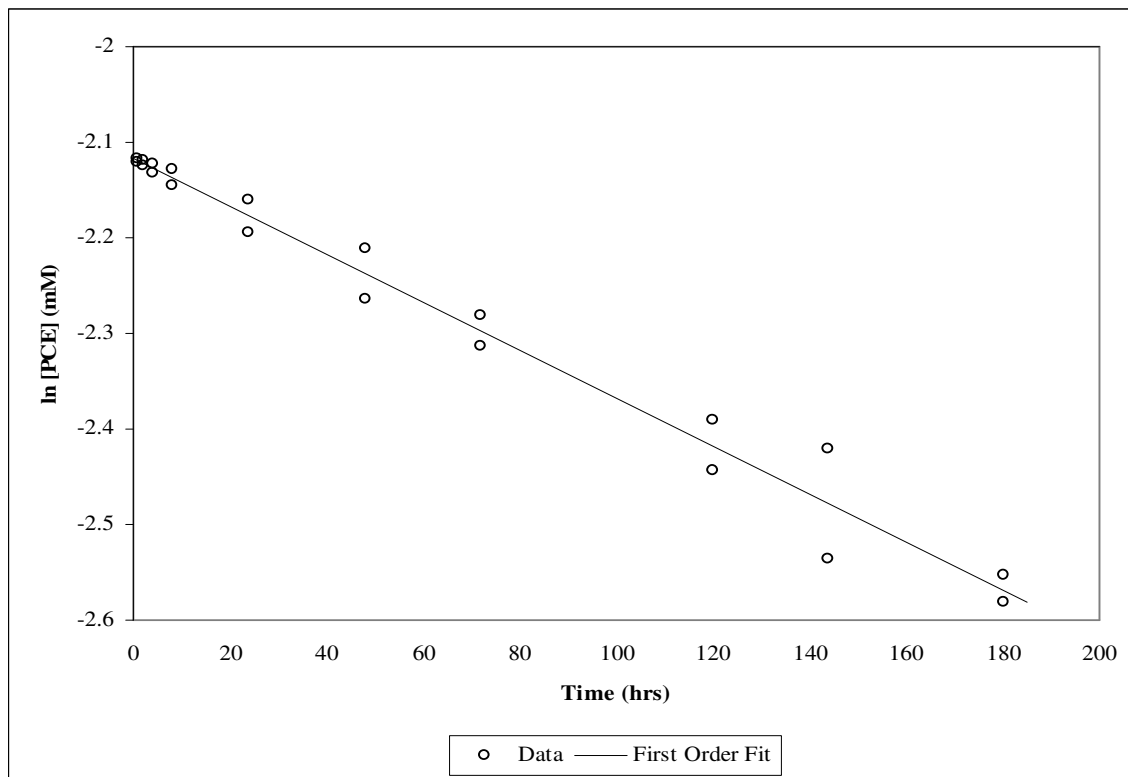


Fig 4.11a Reduction of PCE in the absence of cosolvent.  
The line represents first order fitting of data points.

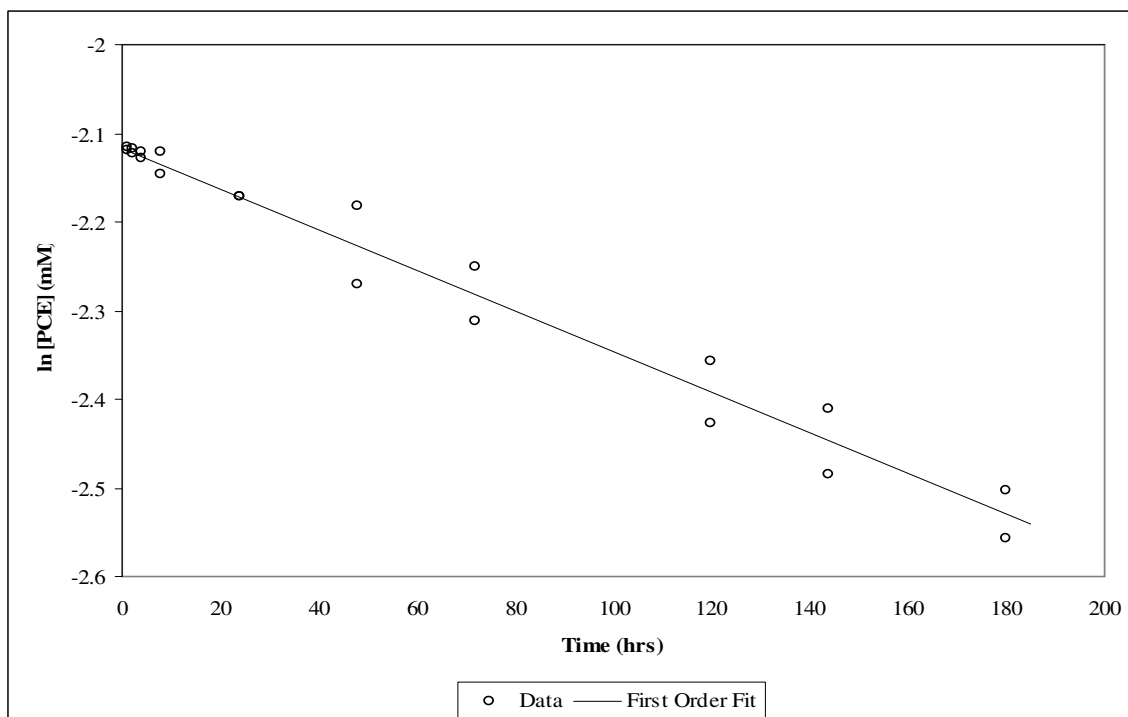


Fig 4.11b Reduction of PCE in the presence of 1% (v/v) methanol.  
The line represents first order fitting of data points.

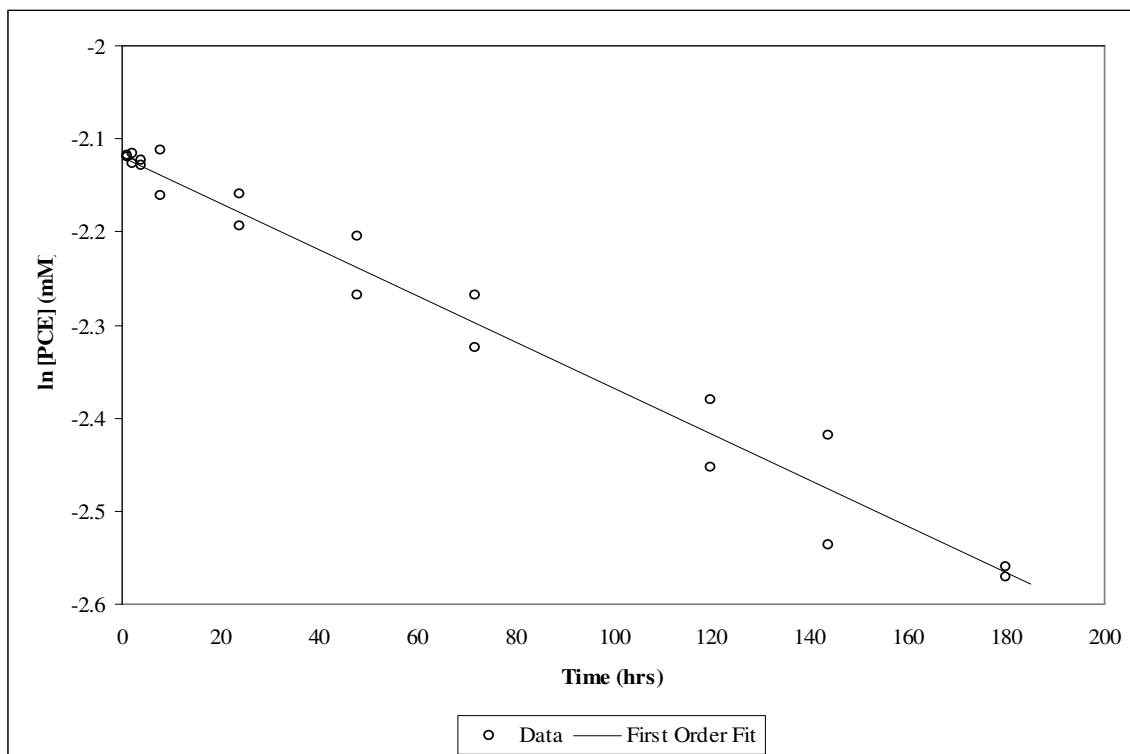


Fig 4.11c Reduction of PCE in the presence of 2% (v/v) methanol.  
The line represents first order fitting of data points.

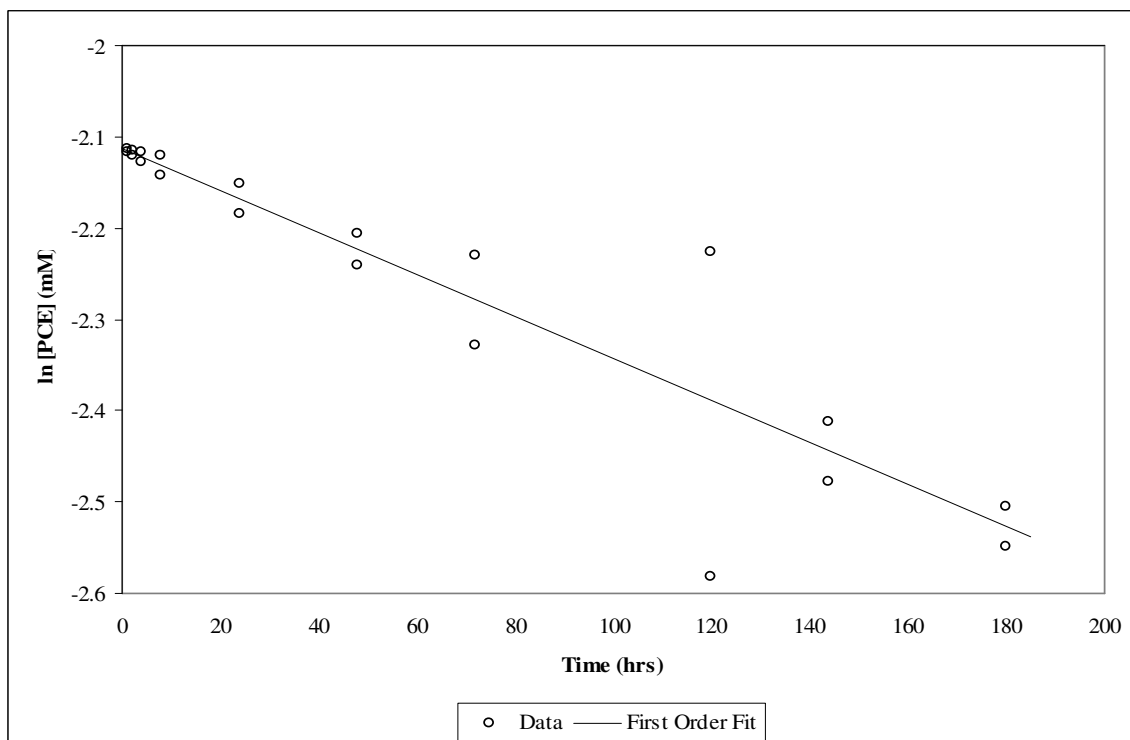


Fig 4.11d Reduction of PCE in the presence of 5% (v/v) methanol.  
The line represents first order fitting of data points.

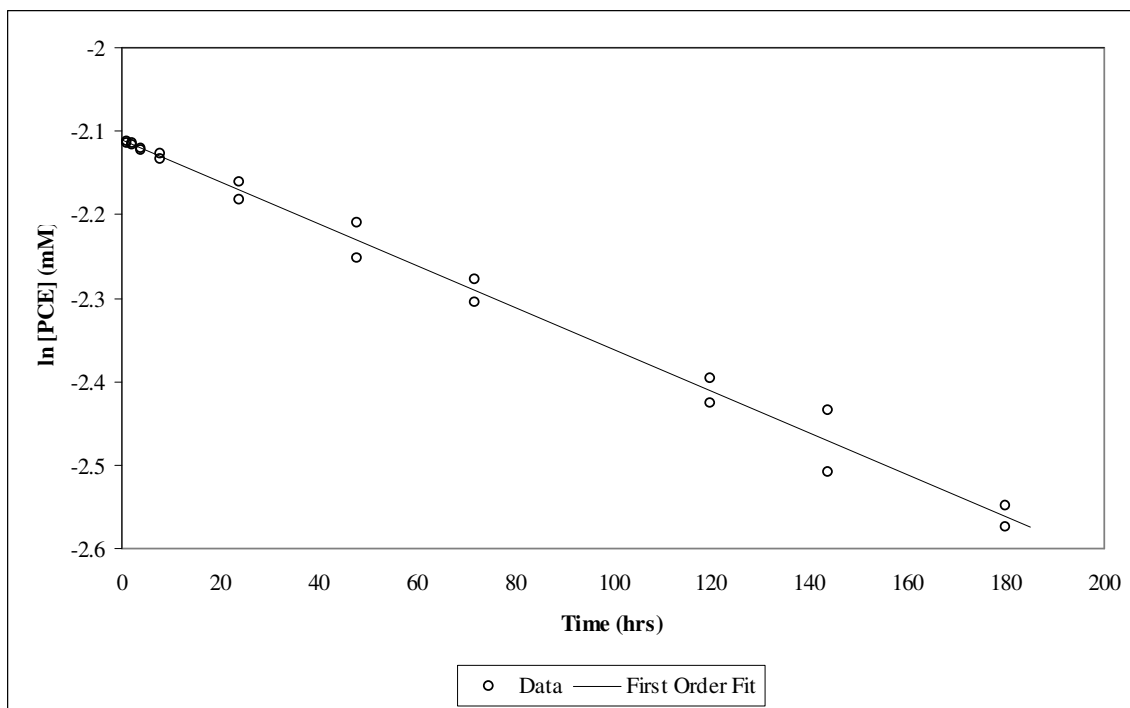


Fig 4.11e Reduction of PCE in the presence of 10% (v/v) methanol.  
The line represents first order fitting of data points.

Table 4.4 Observed rate constants ( $k_{\text{obs}}$ ) for PCE reduction with 50 mM Ti (III) citrate in the presence of different amounts of methanol (no Fe (III) – Cl TPP added)

Amount of cosolvent (% v/v)	$k_{\text{obs}}$ ( $\text{hr}^{-1}$ ) <sup>a</sup>	$R^2$	$n^b$
0%	$(250 \pm 9) \times 10^{-5}$	0.9773	19
1%	$(230 \pm 10) \times 10^{-5}$	0.9688	19
2%	$(250 \pm 11) \times 10^{-5}$	0.9686	18
5%	$(230 \pm 10) \times 10^{-5}$	0.9747	17
10%	$(250 \pm 6) \times 10^{-5}$	0.9895	20

<sup>a</sup>reported uncertainties represent 95% confidence limits

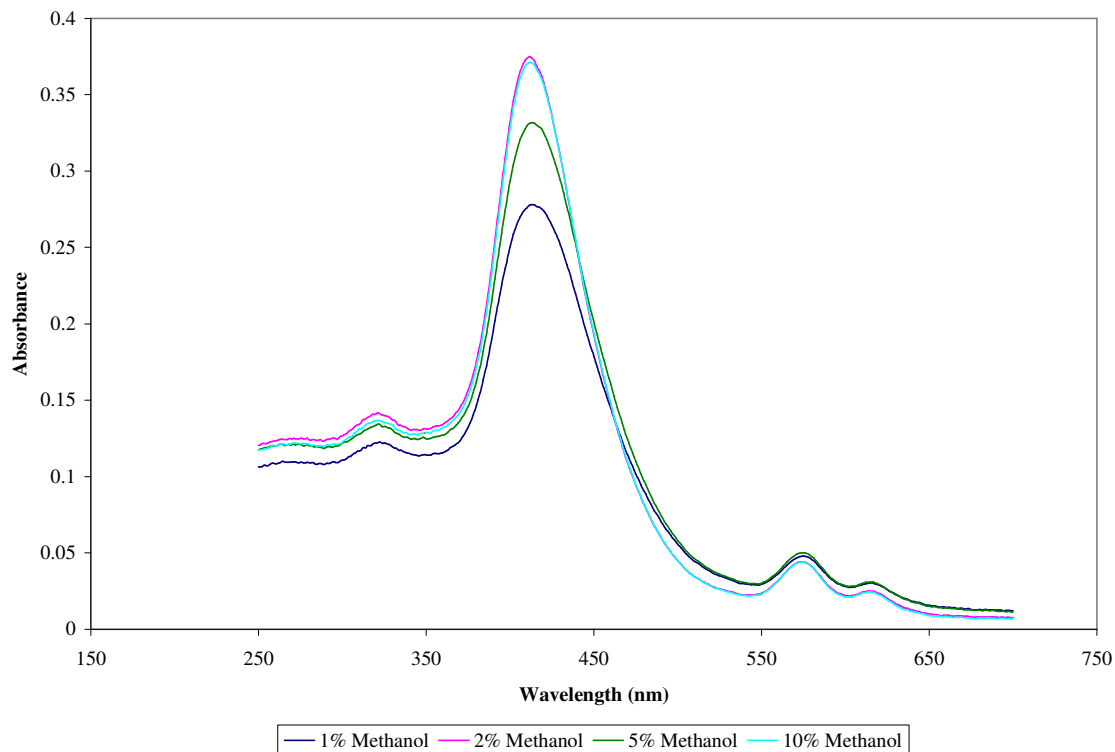
<sup>b</sup>number of data points used to determine the rate constants ( $k_{\text{obs}}$ )

There is no major change in the reaction rates with increase in methanol concentration in the absence of Fe (III) – Cl TPP (Table 4.4). Hence methanol alone is not directly responsible for the trends observed in Section 4.3.2 for the rate of PCE reduction.

#### 4.4. Absorbance of Fe (III)-Cl TPP in methanol – water mixtures

The effect of methanol concentration on metalloporphyrin absorbance was tested by measuring UV-vis spectra of Fe (III)-Cl TPP in the presence of varying amounts of methanol. The methodology used was exactly the same as with DMF. A concentrated stock of Fe (III)-Cl TPP in methanol was added to premixed methanol and water mixtures to give a final metalloporphyrin concentration of 10  $\mu\text{M}$ . The methanol concentrations were 1, 2, 5 and 10% (v/v). The absorption spectra of Fe (III)-Cl TPP at varying methanol concentration are shown in Fig. 4.12.





Concentration of methanol (v/v)	1%	2%	5%	10%
Peak	0.2779	0.3748	0.3317	0.3713
Wavelength (nm)	414	412	413	412

Figure 4.12 Absorption spectrum of 10  $\mu\text{M}$  Fe (III)-Cl TPP in water/methanol mixtures

The peak absorbance of Fe (III)-Cl TPP followed the order of 2 $\approx$ 10 > 5 > 1% methanol. Again, this indicates that peak absorbance is not proportional to the PCE degradation rate constant. The formation of flocs was noticed in these samples too, which complicated the interpretation of the absorbance spectra.

#### 4.5 Product Analysis

Product analysis from PCE reduction in reaction systems containing 50 mM titanium (III) citrate, 10  $\mu$ M Fe (III)-Cl TPP and varying amounts of DMF was performed. In the analysis, only chlorinated reaction products (TCE, DCEs, and VC) were monitored. The results are presented in Figures 4.13a-e.

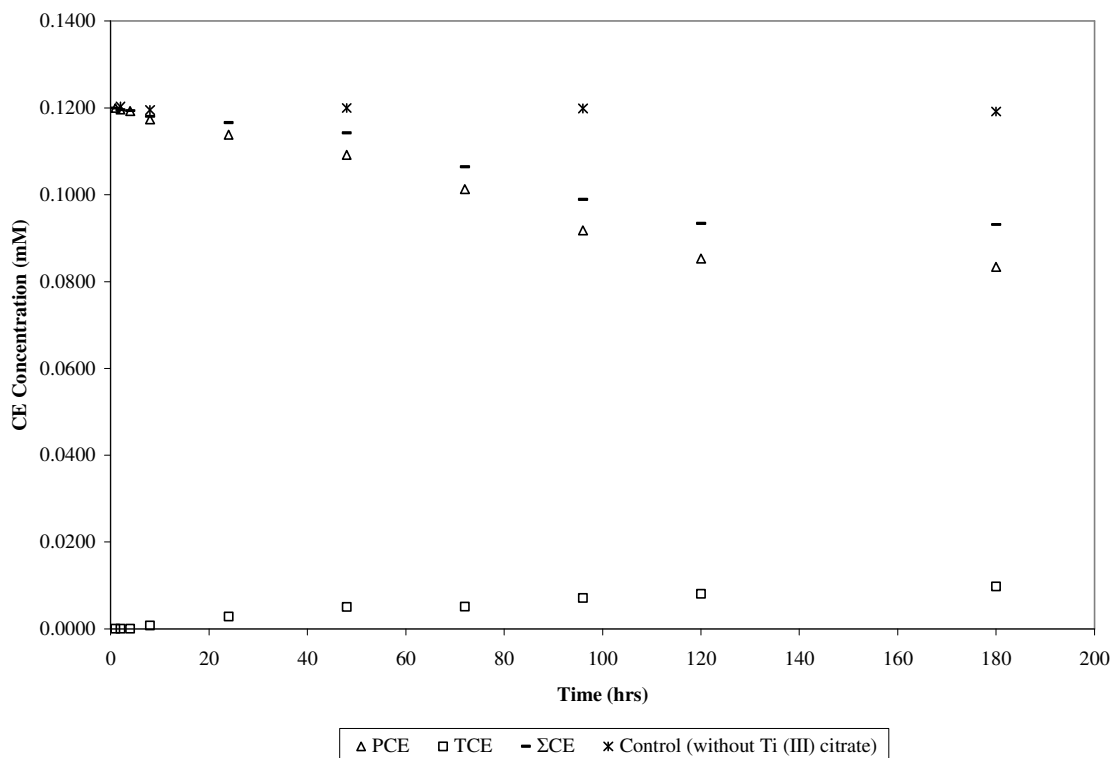


Fig 4.13a Reduction of PCE and chlorinated ethene (CE) product evolution in the absence of DMF.

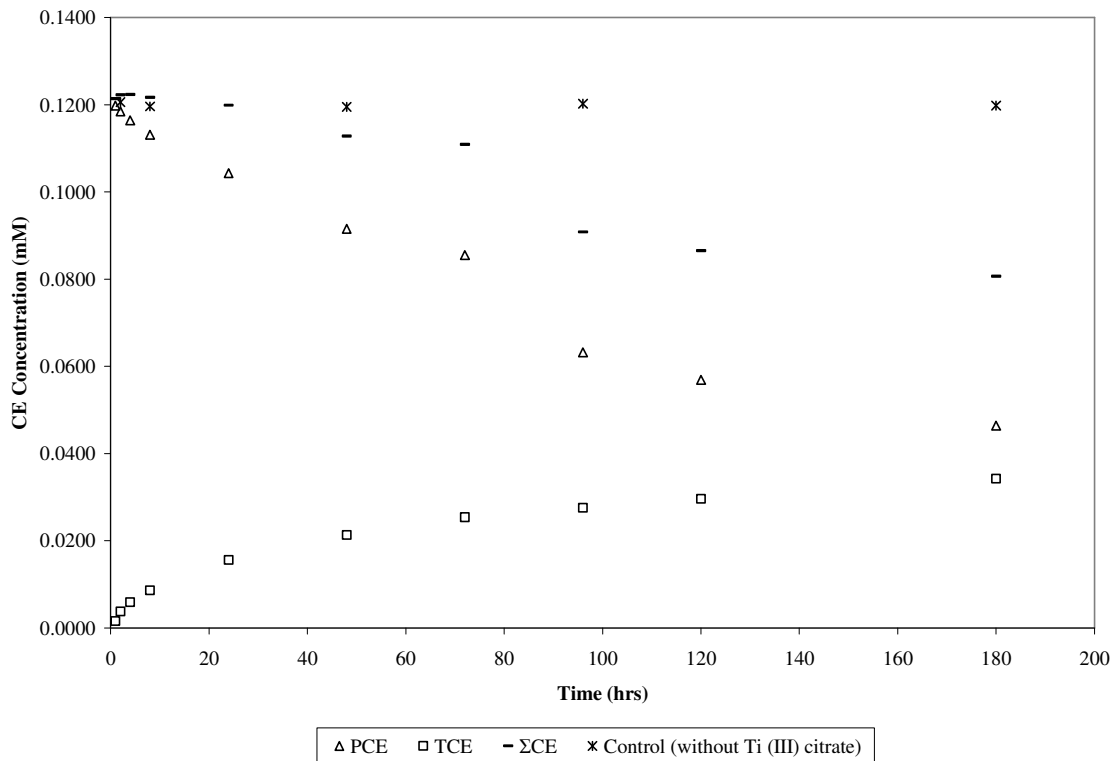


Fig 4.13b Reduction of PCE and CE product evolution in the in presence of 1% (v/v) DMF.

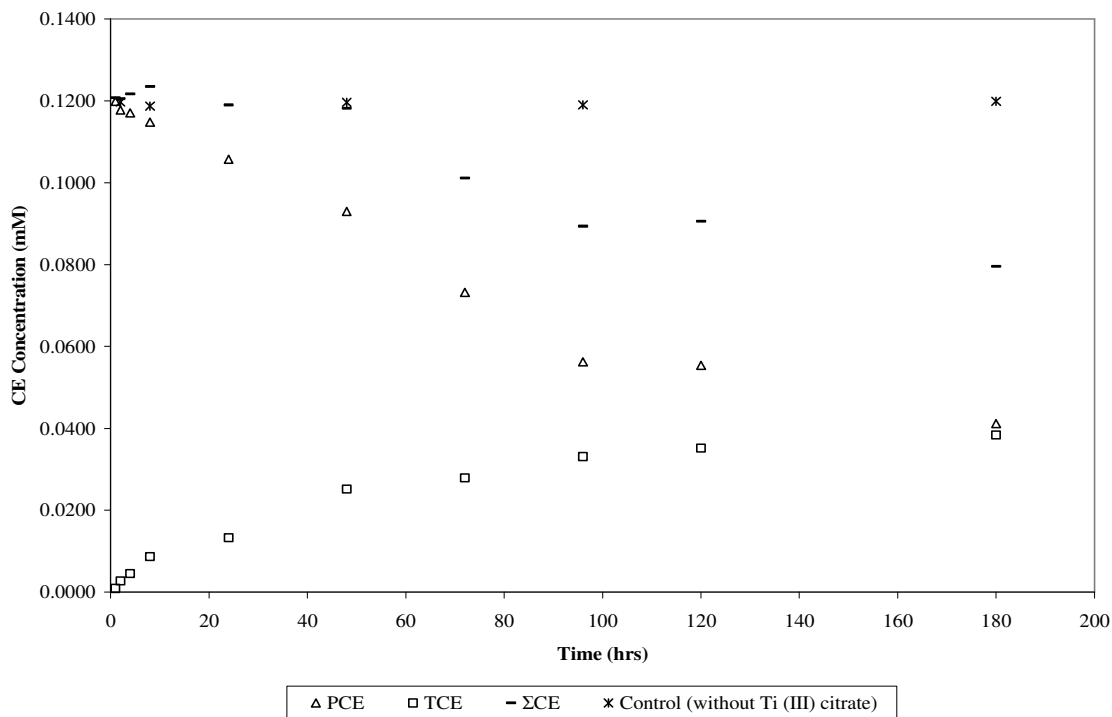


Fig 4.13c Reduction of PCE and CE product evolution in the in presence of 2% (v/v) DMF.

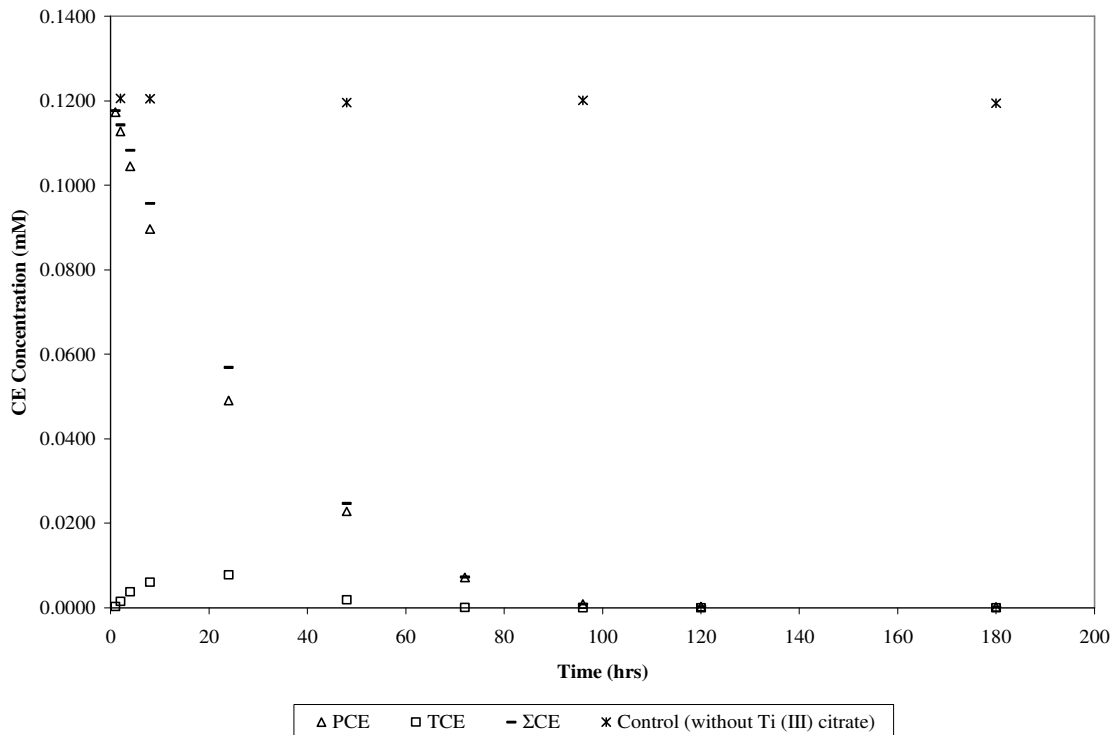


Fig 4.13d Reduction of PCE and CE product evolution in the in presence of 5% (v/v) DMF.

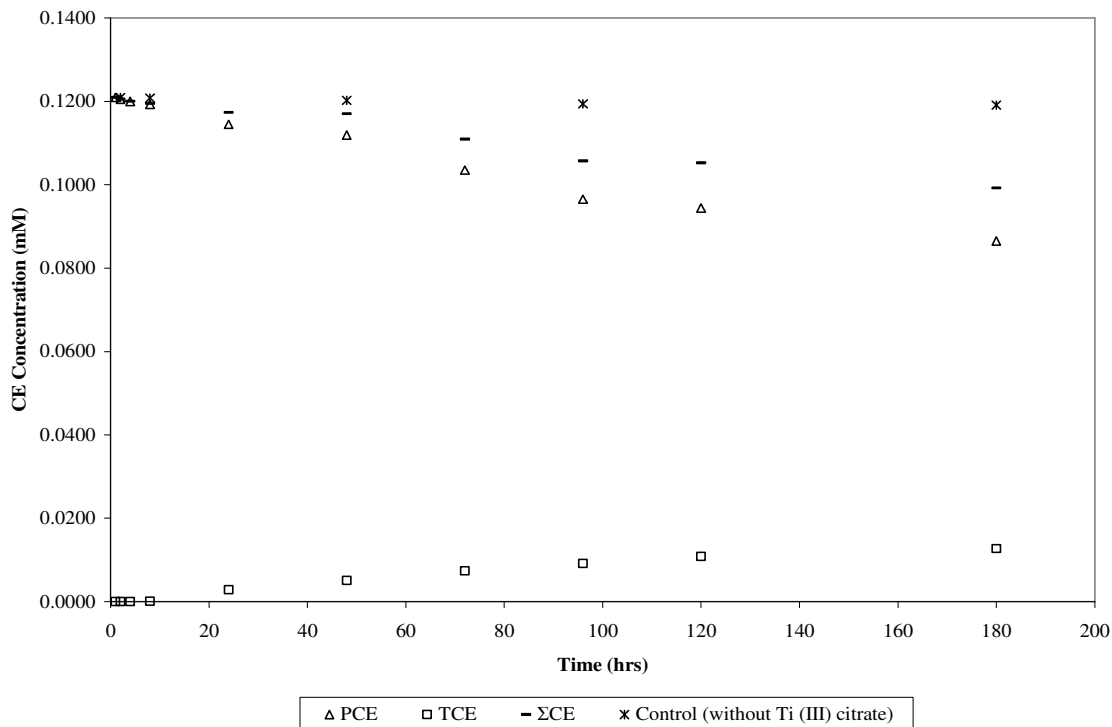


Fig 4.13e Reduction of PCE and chlorinated ethene (CE) product evolution in the in presence of 10% (v/v) DMF.

In all cases, the sole chlorinated product detected was TCE. The  $\Sigma$ CCE presented in the figures are the sums of the PCE and TCE concentrations at each sampling time. Because,  $\Sigma$ CCE decreases with time, this suggests that the reaction does not stop with the production of TCE and that other nonchlorinated products are being formed. In other words, because the DCE isomers and VC were not detected, the lack of mass balance closure suggests fully dechlorinated gaseous products (e.g., ethene, acetylene, ethane) were produced. Complete decomposition of TCE occurred only when 5% DMF (v/v) was present. In all other cases, there was residual TCE present at the end of the experiments. A previous study showed that with 10 mM Ti (III) citrate, 10  $\mu$ M Fe (III)-Cl TPP in 5% (v/v) DMF, 50 ppm PCE was directly converted to acetylene without the production of any intermediate products (Dror and Schlautman, 2004b). Also, PCE was only 30% reduced after 168 h whereas in the current study complete degradation of PCE was seen after 96 h.



## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

The overall objective of this project was to examine the effect of cosolvent concentration on the rate of reductive dechlorination of PCE catalyzed by one metalloporphyrin, Fe (III)-Cl TPP. A secondary objective was to test the hypothesis that metalloporphyrin concentration is linked to the rate of degradation of PCE. The concentration of Fe (III)-Cl TPP using cosolvents was investigated using UV-vis absorbance spectroscopy and the Beer-Lambert law.

The rate of PCE degradation generally increased up to 5% cosolvent concentration for both DMF and methanol and then dropped considerably at 10% cosolvent concentration. Although the increase up to 5% cosolvent concentration is consistent with the assumption that cosolvent increases the concentration of otherwise non-soluble metalloporphyrins, the drop at 10% cosolvent concentration is not consistent with this simple idea. Absorbance tests using UV-vis spectroscopy produced inconclusive results. Measured peak absorbance values did not increase in the expected order of  $0 < 1\% < 2\% < 5\% < 10\%$  cosolvent concentration. Formation of flocs, which was noticed in all absorbance samples, likely had an adverse effect on the spectroscopic measurements.

The use of methanol as cosolvent ruled out the possibility of catalyst poisoning by DMF. Chlorinated ethene product analysis revealed only the presence of TCE. Only at 5% DMF concentration were PCE and TCE completely degraded whereas at other DMF

concentrations residual PCE and TCE were present at the end of each experiment. The DCE isomers and VC were not detected. However, the mass balance was not complete, suggesting that other non-chlorinated products like ethylene, ethene and ethane were formed. The conclusions of this study are:

1. An increase in the concentration of cosolvent does not consistently increase the rate of dechlorination of PCE.
2. DMF enhances the rate of dechlorination more than methanol at 5% cosolvent concentration, while the PCE dechlorination rates were similar for methanol and DMF at 1%, 2% and 10%.

### 5.2 Recommendations

1. As discussed earlier, the increase in reaction rate up to 5% cosolvent concentration was believed to be due to the catalytic activity of the dimers which however needs further investigation. The reason for decrease in reaction rate at 10% cosolvent concentration was not known. Further investigation needs to be done on the catalytic activity of dimers.
2. A better knowledge of the interaction between the metalloporphyrin and cosolvent will help in understanding the results seen in this work. There could be a possibility of the cosolvent interacting with the metalloporphyrin thus transforming them from tetradentate to hexagonal forms making it catalytically active which are otherwise inactive. Also, it could be that the cosolvent forces/allows the metalloporphyrin molecule to a symmetry that promotes the catalytic activity.



3. It is also essential to understand the solubility behavior of metalloporphyrin. The use of cosolvents did not affect the solubility of the metalloporphyrin. However it would be good to study the effect of metalloporphyrin solubility on the reductive dechlorination reactions using an alternate method to dissolve the metalloporphyrin.
4. A better understanding about the nature of flocs formed and quantification the flocs formed with increasing cosolvent concentration would be something good to know. Also, it will help to investigate the effect of cosolvent concentration on the rate of dechlorination of PCE and solubility of metalloporphyrins by controlling the aggregation that takes place in the solutions.



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