

**TETRACHLOROETHYLENE DEGRADATION BY DITHIONITE WITH  
ULTRAVIOLET ACTIVATION**

A Thesis

by

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## **ABSTRACT**

Tetrachloroethylene (PCE) is a contaminant that has been frequently detected in ground water, surface water, air and soil. Advanced reduction processes (ARP) make up a set of wastewater treatment technologies that have been proposed recently. This project has conducted research on degrading PCE with an ARP that combines dithionite and ultraviolet activation. The purpose of the project is to provide knowledge for the development of potential wastewater treatment technologies.

Several control experiments (blank control, reagent control and UV control) were conducted to prove the feasibility of applying the dithionite/UV ARP to degrade PCE. ARP degradation of PCE was studied under different pH (5, 7, 8, 9) and light intensities (2, 4, 7.3 mW/cm<sup>2</sup>). The results showed that the fastest degradation was observed at pH 7 and that degradation becomes faster at higher light intensities. Combining dithionite and UV light resulted in a faster degradation of PCE than only using UV light to photolyze PCE.

## **DEDICATION**

To my family

## **ACKNOWLEDGEMENTS**

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## CHAPTER I

### INTRODUCTION

Tetrachloroethylene (PCE) is a solvent that commonly used in industries such as dry cleaning, textile processing, and metal-cleaning. It has been frequently detected in ground water, surface water, air, and soil. Exposure to PCE may cause damage to neurologic function, the kidney, liver and immune system. Also, the United States Environmental Protection Agency (EPA) classifies PCE as a contaminant that is likely to be carcinogenic to humans.<sup>1</sup> Therefore, efforts should be made to remove PCE from the environment. Several treatment methods have been investigated and developed for PCE removal including chemical oxidation-reduction and biological degradation. However, most of those conventional treatment methods have limitations when applied in the field, such as high cost and toxic byproducts.<sup>2, 3</sup>

The group of advanced reduction processes (ARPs) is a set of wastewater treatment technologies that have been proposed recently. ARPs are potential alternatives to traditional water and wastewater treatment methods. They have a similar mechanism as advanced oxidation processes (AOPs) in that they combine reagents with activation methods to produce highly reactive free radicals that can destroy target compounds. In our lab, ARPs have been shown effective in degrading contaminants such as perchlorate and vinyl chloride that are difficult for traditional treatment methods to degrade well. However, the ability of using ARP to degrade PCE has not yet been studied.

The goal of this project is to evaluate the potential of an ARP that combines sodium dithionite with ultraviolet (UV) light activation to degrade PCE. To achieve the goal of this project, the following objectives will be pursued. 1) Develop experimental and analytical procedures 2) Test effectiveness of dithionite with UV activation in PCE degradation under different pH and light intensities 3) Investigate the kinetics and determine the degradation rate of PCE degradation.

## **CHAPTER II**

### **BACKGROUND**

PCE is a colorless, nonflammable and volatile chlorinated solvent that is widely used in various industrial processes. For example, PCE is the most common dry cleaning solvent currently in use.<sup>4</sup> The EPA reported that the production of tetrachloroethylene was 184 million kilograms in 1986.<sup>1</sup> Usually PCE will not easily enter surface water due its high volatility and low aqueous solubility. Also, PCE is a liquid that does not bind well to soil, so it can easily move through the ground to groundwater. Therefore, groundwater usually has a higher concentration of PCE than surface water. However, spills, leaks or improper disposal of PCE would bring PCE into surface water, which could result in high concentrations.<sup>1</sup> Because the density of liquid PCE is larger than water, it is known as a dense non-aqueous phase liquid (DNAPL), after entering water it has the tendency to accumulate at the bottom of an aquifer. Consequently it will become a long-term source of contamination and make cleanup activities more difficult to conduct.<sup>5, 6</sup> Besides, due to its high oxidation state, PCE can only be biodegraded under anaerobic conditions.

So, PCE is one of the most diffuse pollutants in the environment and it has been detected in the air, soil, surface water as well as groundwater. One report showed PCE can be found in up to 25% of U.S. drinking water supplies.<sup>7</sup> Short exposure to PCE such as is common for dry-cleaning machine operators would have negative impacts on neurological functions and the immune system. Long exposure to PCE would damage

the liver, kidney and cause impairment to neurological functions like cognition. Also, studies have shown that exposure to PCE will cause an increased incidence of liver tumor in mice, so EPA has classified PCE as likely to be carcinogenic to humans by all routes of exposure. Based on its high frequency of occurrence at National Priorities List (NPL) sites, high toxicity and high potential for human exposure at NPL sites, PCE is ranked as number 33 on the Priority List of Hazardous Substances that has been prepared in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).<sup>8</sup> EPA set the maximum contaminant levels (MCLs) of PCE to be 5 parts per billion (ppb) in drinking water.<sup>9</sup>

Biological methods are often used to treat organic contaminants due to their low costs and environmentally friendly characteristics. However, the application of biodegradation to removing PCE is often limited due to the toxicity and high oxidation state of PCE. Only bacteria belonging to the *Dehalococcoides* genus are known have the capability to completely reduce PCE to ethane, while other microorganisms can produce byproducts of PCE degradation, such as dichloroethylenes (DCEs) and vinyl chloride (VC), which may be even more toxic than PCE.<sup>10</sup> However *Dehalococcoides* are very sensitive to oxygen and the reaction needs strictly anaerobic conditions. Furthermore, the degradation rates are slow so the time for biodegradation in situ is usually long, typically ranging from several days to months. Also, the concentration of PCE in a contaminated area is usually very high, which could inhibit microbial degradation due to toxic effects.<sup>11</sup>

Sometimes chemical methods are also used to treat contamination by chlorinated solvents. Zerovalent metals such as Fe(0) or Cu(0) have the ability to reduce organic and inorganic compounds with high oxidation state like PCE. However, the decrease in surface activity of zerovalent metals over time may inhibit the reaction and decrease the efficiency of metals in removing PCE.<sup>12</sup> Also, the additives used to enhance this reaction include trace metals like platinum, which may increase the costs.<sup>13</sup> Some laboratory studies also reported success in using permanganate as an oxidant to degrade PCE.<sup>14, 15</sup> However, manganese dioxide was produced during the reactions and it might reduce the permeability of soil and lower the rate of degradation by catalyzing the decomposition of permanganate. So, the effectiveness of this treatment method is conditional and further research is needed before it can be widely used in the field.<sup>16, 17</sup>

In addition to those traditional treatment methods, thermal decomposition of PCE has also been investigated and the technical feasibility of the process has been proven. Results showed PCE started to decompose at near 400 °C and fully decomposed at 800 °C.<sup>18</sup> However, the energy cost of thermal decomposition of PCE is much higher than that for current treatment methods, so it is not widely applied. Besides, photolysis that combines ultraviolet irradiation with ultrasonication is also proven to be a potential treatment method for PCE. The efficiencies of photolysis are larger than using ultraviolet or ultrasonication separately in most cases. However, it is a new water treatment technology so more work needs to be done before it can be applied in practice.<sup>19</sup>

A group of treatment methods called advanced oxidation processes (AOPs) has been successfully developed and applied in wastewater treatment for decades. In an AOP, the combination of an oxidant with an activating method will produce highly reactive free radicals such as the hydroxyl radical that are able to effectively destroy chlorinated organic compounds in wastewater at ambient temperature and atmospheric pressure.<sup>20, 21</sup> Common oxidants include ozone, hydrogen peroxide, as well as Fenton's reagent. Common activation methods include ultraviolet irradiation, ultrasonication and electron beam irradiation. The application of AOP to PCE treatment has been proven successful. O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/UV are two common AOPs that have been applied in the U.S. to treat PCE in groundwater for decades.<sup>21</sup> The effectiveness of these AOPs was high and no toxic byproducts were generated.<sup>22, 23</sup> However, the cost of its application is high, so more economical but effective technologies need to be developed.

ARP is a new group of treatment methods that is based on producing highly reactive free radicals to reduce contaminants. Although AOP has been proven to be a successful group of treatment methods, little research has been done on ARP development. However, recent studies showed ARP can be successfully applied to remove pharmaceutical compounds in an aquatic environment. In this research, aqueous electrons ( $e_{aq}^-$ ) were selected as the radicals to react with pharmaceutical compounds such as tetracyclines and diclofenac.<sup>24, 25</sup> ARP could also be a promising technology to degrade highly oxidized contaminants, especially when the performance of biological treatment or traditional chemical treatment is limited. The feasibility of using ARPs to degrade contaminants such as perchlorate, nitrate, vinyl chloride (VC) and 1,2-

dichloroethane (DCA) has been investigated.<sup>26, 27</sup> Several combinations of reducing agents and activation methods have been used, but most of the research has investigated the sulfite/UV-L ARP. The results of this research showed the effectiveness of ARP towards degrading those highly oxidized contaminants and also validated the theory motivating ARPs, i.e. that combining activation methods and reducing agents to produce free radicals is an effective way to degrade target contaminants.<sup>26, 27</sup>

In addition to aqueous electrons and sulfite radicals, there are also some other radicals that can be used in ARP. Dithionite ( $S_2O_4^{2-}$ ) is an effective reductant used in several studies. Because of its high reducing potential in basic solutions ( $E^0 = -1.12$  V), dithionite is able to reduce heavy metals and dechlorinate chlorinated organic pollutants. For example, it can be used to reduce Fe(III) and thus improve long term performance in zero-valent iron treatment systems, which are applied to remove chlorinated contaminants.<sup>28</sup> Reports also showed that chloroacetanilides such as propachlor can be rapidly dechlorinated in the presence of dithionite.<sup>29, 30</sup> Dithionite has been proven to generate reducing radicals and their generation can be increased by activating methods.<sup>31</sup> Also, dithionite is a cheap and commonly used bleaching agent that can be easily obtained. Dithionite contains a long but weak S-S bond that is easily decomposed to give the sulfur dioxide radical anion ( $SO_2^{\cdot-}$ ). Numerous experiments have shown that the sulfur dioxide radical anion rather than dithionite is the primary reductant in dithionite solutions, even though the amount of  $SO_2^{\cdot-}$  is relatively small.<sup>32, 33</sup> There are several potential methods that can be used to promote production of sulfur dioxide radical anions. One of them is exposing dithionite to UV light. UV irradiation has been



identified to have impacts on sulfur dioxide radical anion formation and wavelength for maximum absorption of dithionite has been reported to be 315 nm.<sup>31, 33</sup>

## **CHAPTER III**

### **METHODOLOGY**

The goal of this research is to evaluate the feasibility of applying an advanced reduction process to treat PCE. To achieve this goal, three objectives will be pursued:

- 1) Develop experimental and analytical procedures
- 2) Test effectiveness of dithionite with UV activation for PCE degradation under different pH and light intensities
- 3) Investigate the kinetics and determine the rate of degradation reactions.

#### **Experimental plan**

##### Constant conditions

Kinetic experiments were conducted in batch reactors. PCE was used as the target organic compound, dithionite was used as the reductant, and low-pressure UV light was used as an activating method. The initial concentrations of PCE and dithionite were 0.151 mM and 1 mM, respectively, and they were same for all the experiments. The concentration ratio between dithionite and PCE was 5 times the stoichiometric ratio, which provided enough dithionite to degrade all of the PCE to ethene. The low-pressure mercury lamp produced UV light primarily at one wavelength (254 nm). 254nm lamp was used because it has been widely used in industry for disinfection. A phosphate buffer was used in all experiments to maintain pH. All experiments were conducted at room temperature, i.e. approximately 23 °C.

## Variable conditions

In the first set of experiments that studied the effect of pH on PCE degradation, experiments were conducted at a fixed light intensity of  $7300 \mu\text{W}/\text{cm}^2$ , which showed the capability of degrading PCE in preliminary experiments. Experiments were conducted at 4 different pH values (5, 7, 8, 9). The second set of experiments was conducted to study the effect of light intensity on PCE degradations at pH 7, which showed the best degradation efficiency in pH-effect experiments. Experiments were conducted at 3 different light intensities ( $2000 \mu\text{W}/\text{cm}^2$ ,  $4000 \mu\text{W}/\text{cm}^2$ ,  $7300 \mu\text{W}/\text{cm}^2$ ).

## **Experimental system and procedures**

### Equipment

All major experiments were conducted in an anaerobic chamber (Coy Laboratory Products Inc). The anaerobic chamber was filled with a gas mixture containing 95% nitrogen and 5% hydrogen. Before taking samples out of chamber, the containers were sealed to prevent the evaporation of sample and leakage of air. A reaction area established in the anaerobic chamber and an UV-L lamp (254nm) was set on the top of reaction area. A lab scissor lift was used to adjust the length of light path before reaching reactors. There were two fan boxes in the corners of the chamber to maintain the gas flow and minimize dead zones. Covers that contained palladium catalysts were installed in the front of fan boxes to convert the oxygen in the chamber into water by reacting with hydrogen. The catalysts were heated once a week to reactivate them. The chamber was vacuumed and purged with mixed gases five times before every experiment in order to maintain optimal conditions. Three vials that contain different concentrations of a

colorimetric redox indicator solution (Resazurin, 89%, Aldrich) were put inside the chamber to indicate the level of oxygen. The solutions would turn pink when oxygen concentrations increase. An electric oxygen and hydrogen indicator were also put inside the chamber to give the concentrations of oxygen and hydrogen. Under normal conditions, the oxygen concentration was 0 ppm and the hydrogen concentration was around 2%.

The UV light source used in this research was a low-pressure UV lamp (Phillips, TUV PL-L36W/4P) that produces light primarily at one wavelength (254 nm). The light intensity was measured by a UV meter that was calibrated by ferrioxalate actinometer. The main instrument used in the extraction process was an orbital shaker (Thermolyne) installed with a vial rack.

#### Reagents

Tetrachloroethylene (99.9%, Fluka) was the target contaminant used in this research. Sodium dithionite (analytical standard, Fisher) was used as the reductant to degrade PCE. Methanol (HPLC grade, EMD) was used as the solvent to prepare PCE stock solution. The PCE stock solution was prepared once a week by adding 30.8  $\mu\text{L}$  pure PCE into 100 ml of methanol to achieve a concentration of 500 ppm. Hexane (98% halocarbons free grade, Acros) was used as the solvent to extract PCE from the water solution. Dibromomethane (DBM, 99%, Aldrich) was used as an internal standard in the gas chromatographic analysis of PCE. Phosphate buffer (analytical standard, Alfa Aesar) was used as a pH buffer solution. All chemicals were used as received without further purification unless otherwise noted. The deionized water (Milli-Q, Millipore) used in

experiments was deoxygenated by purging with ultra-high purity nitrogen for 4 hours, and then transferred into the chamber and further purged with the gas mixture in the chamber for 6 hours.

### **Solution preparation**

#### Dithionite solution

Sodium dithionite powder was stored inside the anaerobic chamber. Before taking it out of chamber for weighing, the powder was transferred to a 15-ml vial and sealed with cap to prevent any contact with oxygen. The weight of this vial was measured before adding dithionite. After weighing the vial containing dithionite and determining the mass of dithionite, the calculated volume of deoxygenated deionized water was added to the vial to prepare the sodium dithionite solution.

#### Sample solution

The dithionite solution was mixed in a 245-ml amber glass bottle. 12.3 ml of PCE stock solution and calculated volume of pH buffer, dithionite solution, and deoxygenated deionized water were added to this bottle to achieve an initial PCE concentration of 25.1 ppm. The total volume of solutions was approximately 245 ml, so there was no space left inside the bottle for air. Then the solution was transferred to a 200-ml glass syringe to use to fill the reactors. Each solution prepared in this way was able to fill 12 quartz cells.

### **Syringes and labware**

Due to the volatility of PCE, syringes were used as the main method to transfer PCE solution. The following syringes were used in this research: 20-ml and 10-ml

syringes with Luer-Lok (BD), 5- $\mu$ L gas tight syringes (Hamilton 7000 series) and 100-ml and 200-ml glass syringes (Tomopal Inc). Most of these syringes used disposable needles, the 5- $\mu$ L gas tight syringes did not, so they were cleaned by heating in a syringe cleaner that removed any residual chemical after each use. Inorganic solutions were prepared in 15-ml or 45-ml centrifuge tubes made of polypropylene (VWR International LLC) and organic solutions were prepared in 20-ml or 40-ml clean amber glass vials (National Scientific). Glass vials were capped with triple-layer closures (rubber, septa, lead foil and Teflon film) to prevent leakage of PCE. All UV irradiation experiments were carried out in 17-ml cylindrical quartz cells capped with Polytetrafluoroethylene (PTFE) stoppers. The volume of each cell was 17 ml, the path length was 10mm and the exterior diameter was 50 mm (Starna Cells, Inc). An oxygen meter (Extech), pH meter (Hach) and pipettes (Eppendorf) were also used in experiments.

### **Sampling**

All steps in sampling were conducted inside the anaerobic chamber. The samples were taken at 10 to 12 different times, which were chosen based on the expected reaction rate. Due to the volatility of PCE, once the cap of quartz cell was opened, the solution in the reactor cannot be used in following degradation experiment, so each quartz cell can only obtain one sample. In each sampling, 5 ml sample solution was transferred from the 17-ml quartz cell to the 20-ml extraction vial with a 10-ml syringe. Then extraction vial was placed on the orbital shaker for extraction. After extraction, the vial was directly taken for gas chromatographic (GC) analysis.

## **Analytical procedures**

PCE was extracted from samples by a liquid-liquid extraction method prior to GC analysis. Based on the results of preliminary experiment, the extraction was conducted by adding 5 ml of solution containing PCE to a 20-ml glass vial filled with 10 ml of hexane and 2 ml of dibromomethane. This vial was directly mounted on an orbital shaker that was operated at 300 rpm for 1 hour. After extraction, the vial was taken for gas chromatographic (GC) analysis.

A 2.5  $\mu\text{L}$  volume of sample solution was injected into a GC (Hewlett Packard 5890 series II) for PCE analysis. Standard curves were prepared for quantification. This GC is equipped with a DB-VRX column ( $60\text{ m} \times 0.25\text{ mm} \times 1.4\ \mu\text{m}$ ) and ECD detector. The GC inlet temperature was set at  $225\text{ }^{\circ}\text{C}$ . The carrier gas was ultra-high purity nitrogen, and its flow rate was controlled at 1.8 ml/min with a split ratio of 36:1. The oven temperature was programmed as starting at  $35\text{ }^{\circ}\text{C}$  for 5 min, and then ramped to  $200\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$ , followed by a constant temperature of  $200\text{ }^{\circ}\text{C}$  for 1 min. So, the total run time for each GC analysis was 22.5 min. A PCE calibration curve was obtained by comparing known PCE concentration with the ratio of PCE peak to DBM peak.

## **Data analysis**

A kinetic model of PCE degradation was developed based on the data collected in previous steps and research. Different reaction orders such as zero-order, pseudo-first-order were applied to fit the collected data. Those data were analyzed by non-linear regression using the Solver tool in Excel to determine the parameters in the kinetic

model that best fit the measured data. An equation to calculate the observed rate constant ( $K_{\text{obs}}$ ) was determined at the end of data analysis.



## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

#### **Control experiments**

Three control experiments were conducted before doing degradation kinetic experiments. Considering the character of volatility of PCE, a blank control was necessary to measure how much PCE will be lost during an experiment without addition of UV light or dithionite. It was also necessary to do a reagent control experiment to measure the amount of PCE that would be degraded with dithionite only. A UV control experiment was needed to measure the removal of PCE with UV light, but without dithionite.

#### **Blank control**

Methanol was added to the PCE stock solution to reduce volatilization and the loss of PCE during preparation and transfer was found to be 1%. The average measured initial concentration of PCE in the reactors was 22.3 ppm compared to the calculated concentration of 25.1 ppm during ARP experiments. Figure 1 shows the concentration of PCE at different time when stored in the quartz cells over a time period of 5 hours.

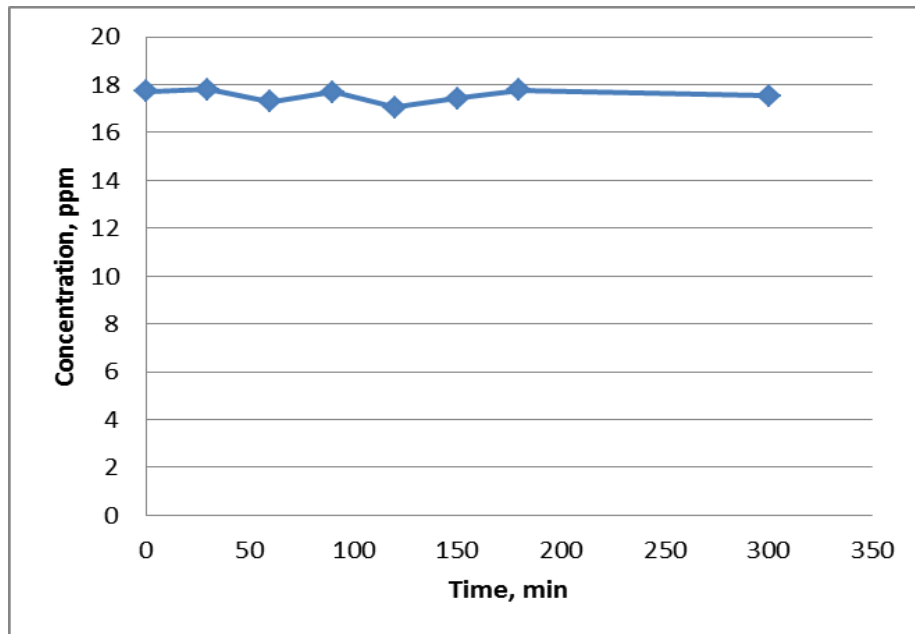


Figure 1. PCE concentration during blank control experiment

The results show that the loss of PCE was very small when compared with the concentration itself.

#### Reagent control

The reagent control experiment was conducted to measure the loss of PCE due to reaction with dithionite at pH 7 without UV light. The concentration of dithionite used was 1.01 mM, which was 5 times the stoichiometric amount required to react with PCE. Figure 2 shows that after 6 hours, the concentration of PCE in the reactor decreased to 12.9 ppm from 18.3 ppm.

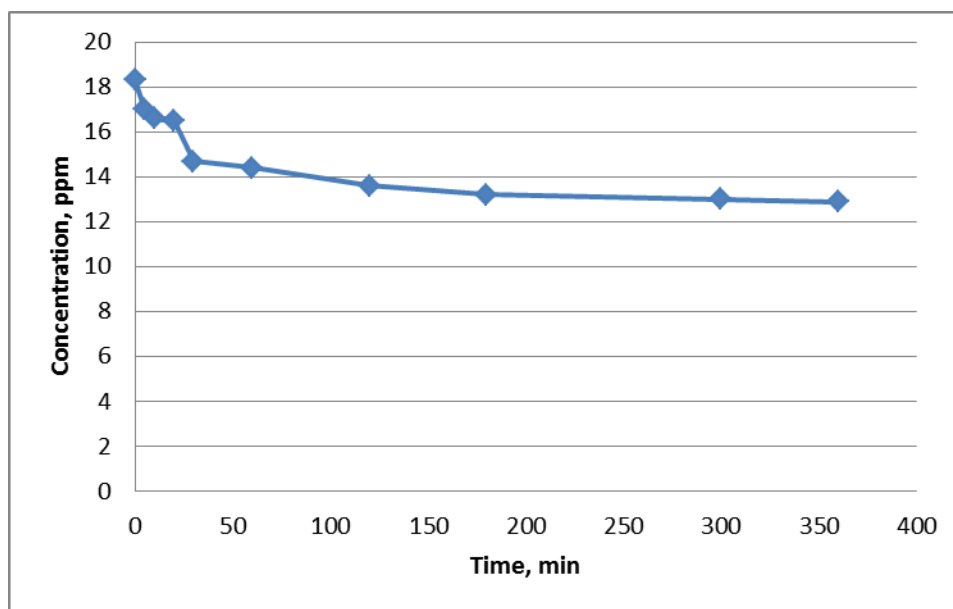


Figure 2. PCE concentration during reagent control experiment

The results show that dithionite is able to degrade a part of the PCE in the first 1 hour. After that, the degradation rate becomes much slower. A low degradation rate was also reported by Nzungu et al, who described the reaction between dithionite and PCE as lasting for several days.<sup>34</sup> But that paper did not study the change of PCE concentration during the first one hour, nor did it explain the mechanism of PCE degradation by dithionite. Although the mechanism of reaction in the first one hour is still unclear, one possible explanation for the difference between degradation rates is the hydrolysis of dithionite. Dithionite has been reported to hydrolyze at pH 7.<sup>35</sup> It is possible that most of the dithionite was consumed during the first 1 hour by hydrolysis and reaction with PCE, so that the degradation of PCE becomes much slower after about 1 hour. So, in addition to the loss of PCE during preparation, dithionite by itself will also

cause the loss of PCE. In order to compare the kinetics of this control experiment with the kinetics of ARP experiments, the initial rate and pseudo-first-order rate constant were calculated using data for the first hour and the results are listed in Table 1.

Table 1. Initial rate and pseudo-first-order rate constant for reagent control experiment

<b>Initial rate (ppm/min)</b>	<b>Initial C<sub>PCE</sub> (ppm)</b>	<b>Initial rate constant (min<sup>-1</sup>)</b>
0.0600	18.3	0.00328

If a zeroth-order model fits ARP degradation of PCE better than a pseudo-first-order model, then the initial rate of the reagent control experiment will be compared to the zeroth-order rate constant, because the rate equals the rate constant in zeroth-order reaction. If a first-order model fits better, the pseudo-first-order rate constants will be compared.

#### UV control

Figure 3 shows that 23.1 ppm of PCE was degraded to 2.20 ppm by photolysis within 7 minutes. The light intensity was controlled around 7.3 mW/cm<sup>2</sup> and pH was maintained at 7.

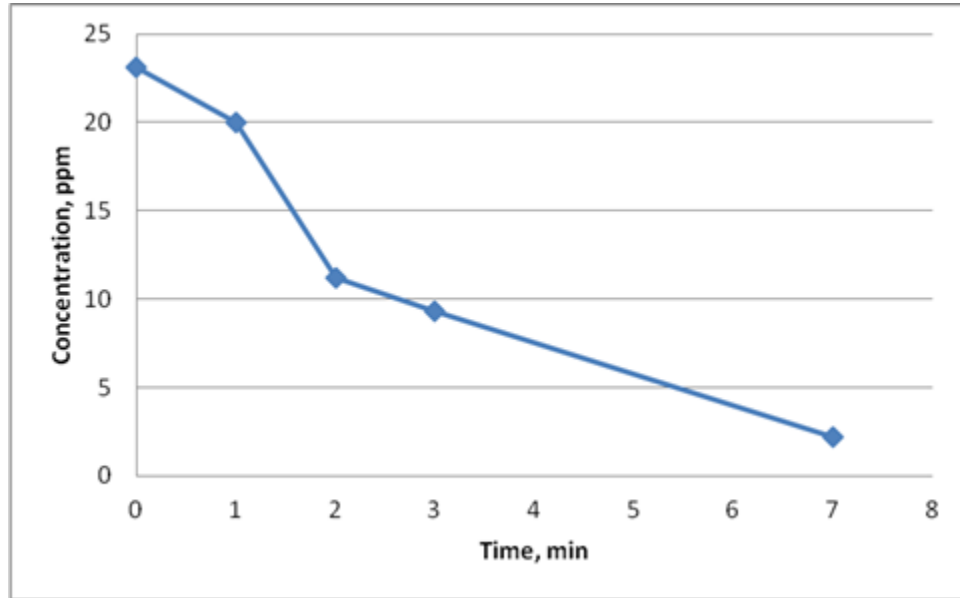


Figure 3. PCE concentration during UV control experiment

The data from the UV control experiment was fitted with first-order and zeroth-order degradation models. Non-linear regressions were conducted on the experimental data of PCE concentration and reaction time to obtain the rate constants and initial concentrations. The regressions were conducted to choose the unknown coefficients that minimized the sum of squared errors for PCE concentrations that is defined by Equation 1. Calculations were made with Solver in EXCEL. The standard error was used as measure of the goodness of fit and it is defined by Equation 2. The results of the regressions are shown in Table 2.

$$SSE_{PCE} = \sum_{i=1}^n (C_{\text{expt, PCE},i} - C_{\text{model,PCE},i})^2 \quad (1)$$

$$SE = \sqrt{\frac{SSE_{PCE}}{n - 2}} \quad (2)$$

Table 2. Results of fitting two reaction models for UV control experiment

<b>Fitting model</b>	<b>Initial C<sub>PCE</sub> (ppm)</b>	<b>Rate Constant</b>	<b>SSE<sub>PCE</sub></b>	<b>SE</b>
zeroth-order reaction	23.1	3.41 (ppm/min)	47.6	3.98
First order reaction	23.1	0.302 (min <sup>-1</sup> )	10.7	1.89

The data shows that the first-order reaction model fitted the data better than the zeroth-order model as indicated by its smaller standard error. This indicates that the photolysis of PCE is close to being a first-order reaction. In the UV control experiment, PCE is degraded by a photolysis reaction in which PCE is the only reactant. A first-order model describes a reaction that depends on the concentration of only one reactant, so the first-order reaction is expected to be able to describe the photolysis of PCE. Several reports have confirmed this result.<sup>36,37</sup>

### **Experiments on effect of pH**

#### Degradation data and curves

A series of experiments were conducted to test the effect of pH on ARP degradation of PCE. Experiments were performed at pH 5, pH 7, pH 8 and pH 9. The pH was measured before and after each experiment to make sure the pH was unchanged. Light intensity was maintained around 7.3 mW/cm<sup>2</sup>. Figure 4 shows the results of pH effect experiments and the data can be found in Appendix A.

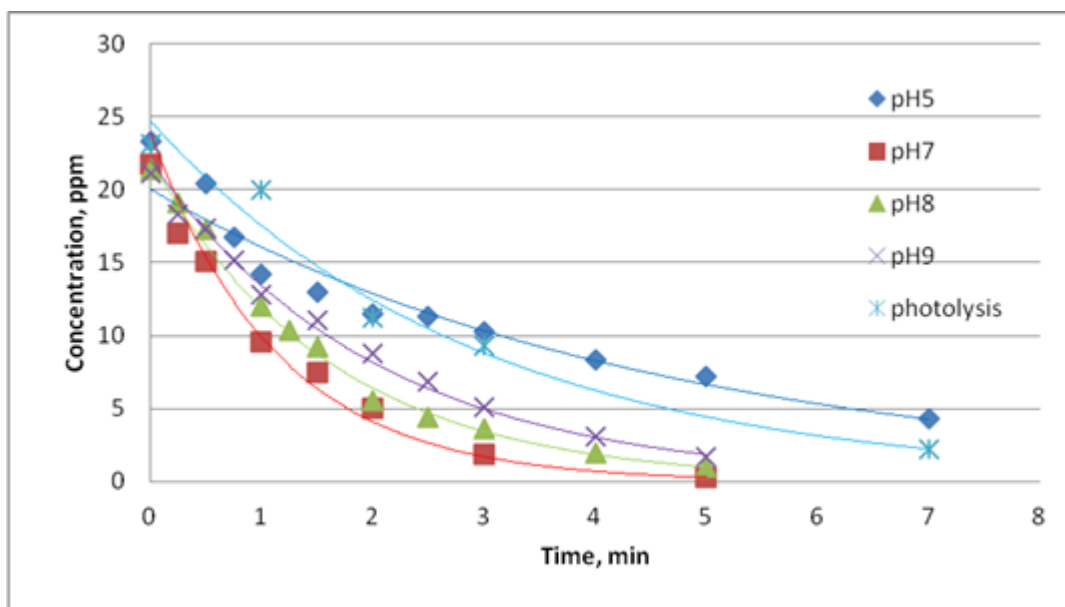
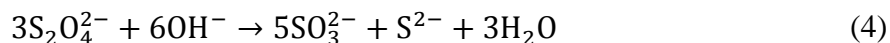


Figure 4. PCE concentrations (symbols) and predictions by a pseudo-first-order reaction model (lines) during experiments on the effect of pH and the UV control experiment (photolysis).

Figure 4 shows that using the combination of dithionite and UV results in faster PCE degradation than by direct photolysis, except at pH 5, which was faster than direct photolysis around the first two minutes, and then approached and slower than the photolysis curve. One possible explanation for the inability of dithionite to enhance degradation is that dithionite rapidly hydrolyzes at low pH. Read et al. reported that dithionite readily forms thiosulfate and hydrogen sulfite ions in acidic solutions and forms sulfite and sulfide ions somewhat more slowly in basic solutions.<sup>38</sup>



Decomposition occurs very fast at lower pH values. So, it is possible that dithionite might be converted to thiosulfate and hydrogen sulfite at pH 5, and would not be able to form radicals that could degrade PCE. It can be hypothesized that in the beginning of PCE degradation at pH 5, some of the dithionite was being converted to radicals that were reacting with PCE, while the rest was hydrolyzing, and all of the dithionite were consumed within 2 minutes. Therefore, the degradation curve was closing to the photolysis curve. The reason for the degradation at pH 5 after 2 min became slower than photolysis may because the products of dithionite hydrolysis absorbed part of light, which leads to the less light energy received by PCE when compared with UV control experiment. Or the difference may come from the error from experimental data. Besides, Figure 4 shows that the degradation rate reached a maximum at pH 7. The slower degradation rate at basic condition can be explained by higher concentration of scavengers, which is reported in the research on using an ARP to degrade vinyl chloride at pH 9 and pH 11.<sup>26</sup> High concentrations of scavengers reduces the concentration of radicals that can react with the target contaminant, thereby reducing the rate of degradation of the target. The reagent control experiment (Figure 2) showed that dithionite without UV activation could degrade PCE. However, ARP degradation of



PCE primarily happened in the first few minutes, while degradation of PCE over that time period by dithionite without UV was small compared the loss due to ARP.

Treatment of data

Table 3 and Table 4 summarize the results of fitting two reaction models to data from experiments to determine the effect of pH with regression analysis.

Table 3. Results of fitting data with different pH using a pseudo-first-order reaction model.

	<b>Initial C<sub>PCE</sub> (ppm)</b>	<b>Rate Constant (min<sup>-1</sup>)</b>	<b>SSE<sub>PCE</sub></b>	<b>SE</b>
pH 5	23.3	0.301	27.5	1.75
pH 5(before 2 min)	23.3	0.396	5.11	1.13
pH 5(after 2 min)	11.5	0.166	1.50	0.612
pH 7	21.7	0.767	1.79	0.546
pH 8	21.3	0.588	3.92	0.660
pH 9	21.1	0.459	1.67	0.431

Table 4. Results of fitting data with different pH using a zeroth-order reaction model.

	<b>Initial C<sub>PCE</sub> (ppm)</b>	<b>Rate Constant (ppm/min)</b>	<b>SSE<sub>PCE</sub></b>	<b>SE</b>
pH 5	23.3	3.51	150	4.08
pH 5(before 2 min)	23.3	6.81	11.0	1.66
pH 5(after 2 min)	11.5	1.42	0.514	0.358
pH 7	21.7	5.73	183	4.51
pH 8	21.3	5.36	141	3.96
pH 9	21.1	4.78	67.7	2.74

The results for pH 7, 8 and 9 show that the pseudo-first-order model fits the data better than the zeroth-order model as indicated by smaller standard errors. Degradation of PCE at pH 7-9 is close to being a pseudo-first-order reaction.

The data in Table 3 and Table 4 show that the pseudo-first-order reaction model fit the data for pH 5 better than the zeroth-order reaction model as indicated by a smaller standard error. But the pseudo-first-order is not a perfect fit to the data as shown in Figure 5. This can be explained by the hydrolysis of dithionite that occurred around the first 2 minutes. Based on the hypothesis, most of the dithionite was consumed after 2 minutes and then photolysis was the primary reaction degrading PCE. To examine the behavior in these two time periods, the kinetic models were fitted to data before and after 2 minutes separately. The fitting of both models were improved. The data shows the reaction in the first 2 minutes can be better described by pseudo-first-order reaction as indicated by a smaller standard error. Although the zeroth-order model provided a better fit, both models were able to describe the data well after 2 minutes, as indicated by the small standard errors. This may be because the change of concentration becomes small during the later period, which leads to a small difference between standard errors for the first-order and zeroth-order models. The rate constant in the ARP degradation at pH 5 before 2 minutes ( $0.396 \text{ min}^{-1}$ ) is larger than rate constant in direct photolysis ( $0.302 \text{ min}^{-1}$ ). The rate constant in the ARP degradation at pH 5 after 2 minutes ( $0.166 \text{ min}^{-1}$ ) is smaller than rate constant in direct photolysis ( $0.302 \text{ min}^{-1}$ ). The results confirmed that there are probably two different degradation mechanisms before and after 2 minutes.

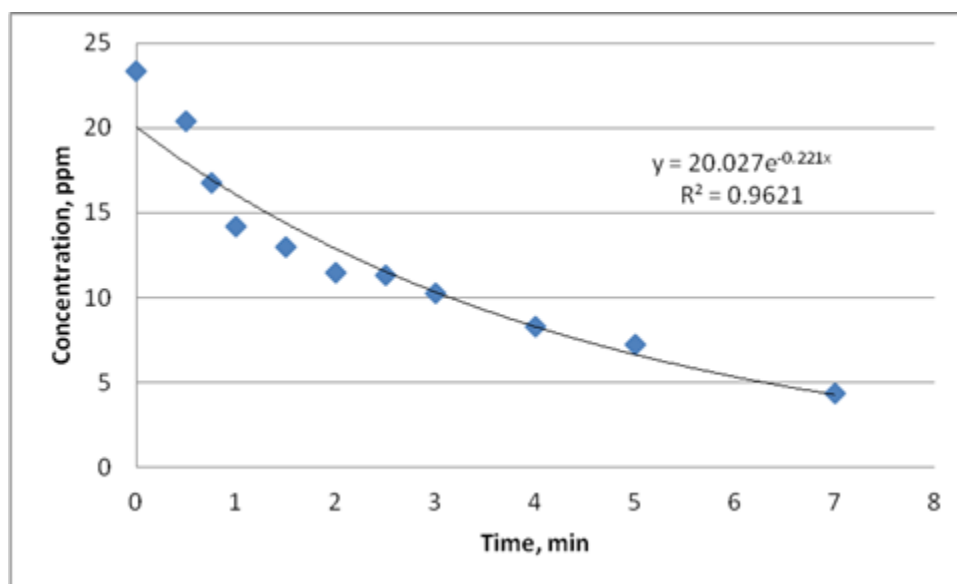


Figure 5. PCE concentrations (symbols) and predictions by a pseudo-first-order reaction model (lines) during experiments on the effect of pH at pH 5

### Experiments on effect of light intensity

#### Degradation data and curves

A series of experiments were conducted to measure the effect of light intensity degradation of PCE by the UV/dithionite ARP. Experiments were performed at 2, 4 and 7.3 mW/cm<sup>2</sup>. The pH was maintained at 7, because degradation at pH 7 showed the fastest removal rate. Data for 7.3 mW/cm<sup>2</sup> was obtained from the degradation experiment at pH 7 as described previously.

Figure 6 compares the degradation curves at different light intensities.

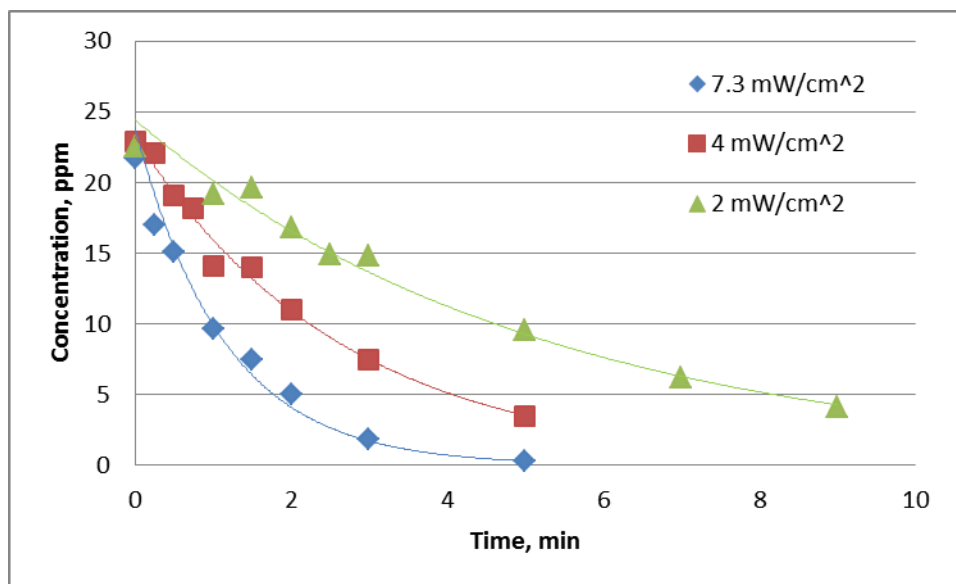


Figure 6. PCE concentrations (symbols) and predictions by a pseudo-first-order model (lines) during experiments on the effect of light intensity

The figure shows that degradation becomes faster with the increase of light intensity. This can be explained by the fact that energy will be transferred to the dithionite in reactors more rapidly at higher light intensity, which leads to a faster production of reactive radicals and thus a faster degradation rate of PCE.

#### Treatment of data

Table 5 and 6 summarize the results of fitting two reaction models to data from experiments on the effect of light intensity. The data for 7.3 mW/cm<sup>2</sup> is from the experiment conducted to evaluate the effect of pH and was conducted at pH 7.

Table 5. Results of fitting data with different light intensities using a pseudo-first-order reaction model

	<b>Initial C<sub>PCE</sub> (ppm)</b>	<b>Rate Constant (min<sup>-1</sup>)</b>	<b>SSE<sub>PCE</sub></b>	<b>SE</b>
2 mW/cm <sup>2</sup>	22.5	0.164	7.71	1.05
4 mW/cm <sup>2</sup>	22.9	0.367	5.77	0.908
7.3 mW/cm <sup>2</sup>	21.7	0.767	1.79	0.546

Table 6. Results of fitting data with different light intensities using a zeroth-order reaction model

	<b>Initial C<sub>PCE</sub> (ppm)</b>	<b>Rate Constant (ppm/min)</b>	<b>SSE<sub>PCE</sub></b>	<b>SE</b>
2 mW/cm <sup>2</sup>	22.5	2.28	14.0	1.41
4 mW/cm <sup>2</sup>	22.9	4.62	47.8	2.61
7.3 mW/cm <sup>2</sup>	21.7	5.73	183	4.51

The data shows that the pseudo-first-order model fits the data for all light intensities better than the zeroth-order model as indicated by smaller standard errors. So, the degradation of PCE at 2-7.3 mW/cm<sup>2</sup> is close to being a pseudo-first-order reaction.

Figure 7 shows the effect of light intensity on the pseudo-first-order rate constants.

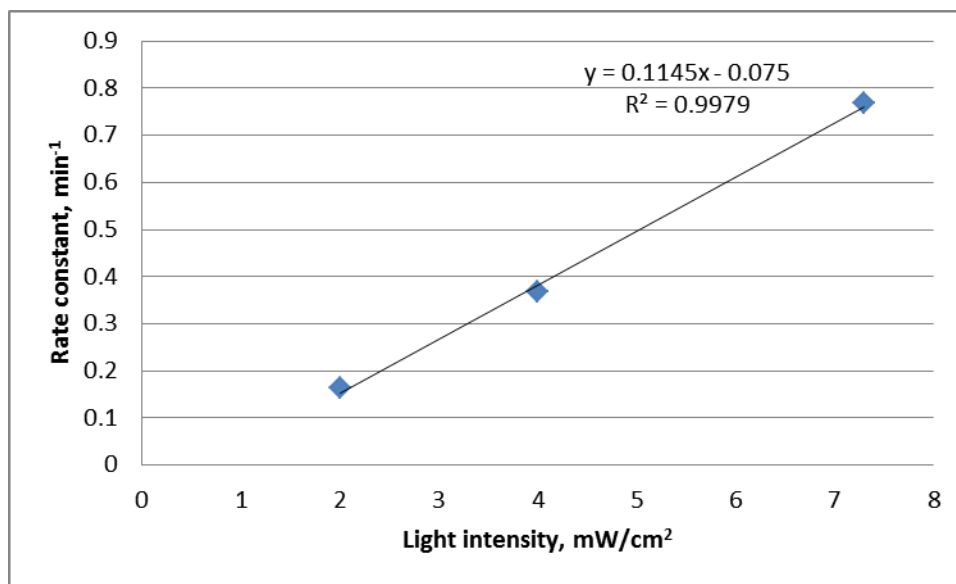


Figure 7. Effect of light intensity on pseudo-first-order rate constants

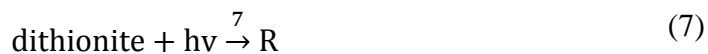
Based on the previous research of ARP degradation, important reactions in ARP degradation have been identified by previous work with other target compounds and are described in Equations 5-19 for PCE. The initial pseudo-first-order rate constant in equation 14 ( $0.00328 \text{ min}^{-1}$ ) is much smaller than rate constants discussed here and shown in figure 7 ( $0.164$ ,  $0.367$  and  $0.767 \text{ min}^{-1}$ ), so the loss of PCE due to reacting with dithionite is neglected in this model. Observed pseudo-first-order rate constant of ARP degradation of PCE is described in Equation 19.<sup>26</sup>

Table 7: Nomenclature.

$P_5, P_9, P_{11}, P_{13}$	Products of reaction (5), (9), (11) and (13), respectively
$h\nu$	UV light
$r_5, r_7, r_9, r_{11}, r_{13}$	Reaction rates of reaction (5), (7), (9), (11) and (13), respectively
$\varphi_5, \varphi_7$	quantum yield of PCE and dithionite (mol/einstein), respectively
$I_{avg}$	Average light intensity in solution ( $\mu\text{W}/\text{cm}^2$ )
$\varepsilon_{ln, \text{PCE}}, \varepsilon_{ln, \text{dithionite}}$	Molar absorptivity of PCE and dithionite ( $\text{M}^{-1}\text{cm}^{-1}$ , defined on natural logarithm basis), respectively
$C_{\text{PCE}}, C_{\text{dithionite}}, C_{\text{R}}, C_{\text{s}}$	Molar concentration of PCE, dithionite, radicals and scavenger (mol/L), respectively
$k_9, k_{11}, k_{13}$	Second-order rate constant of reaction (9), (11) ( $\text{M}^{-1}\text{min}^{-1}$ ) and pseudo-first-order rate constant of reaction (13) ( $\text{min}^{-1}$ ), respectively
$k_{obs}$	Observed pseudo-first-order rate constant in PCE degradation
$L$	Total thickness of reactor in direction of light path (cm), which is 1 cm in this research



$$r_5 = \varphi_5 I_{avg} \varepsilon_{ln, \text{PCE}} C_{\text{PCE}} \quad (6)$$



$$r_7 = \varphi_7 I_{avg} \varepsilon_{ln, \text{dithionite}} C_{\text{dithionite}} \quad (8)$$



$$r_9 = k_9 \times C_{\text{PCE}} \times C_{\text{R}} \quad (10)$$



$$r_{11} = k_{11} \times C_{\text{s}} \times C_{\text{R}} \quad (12)$$



$$r_{13} = k_{13} C_{\text{PCE}} \quad (14)$$

$$\frac{dC_{PCE}}{dt} = -r_5 - r_9 - r_{13} \quad (15)$$

The direct reaction between dithionite and PCE was much slower than ARP reactions that degrade PCE, so equation 15 can be simplified to equation 16 as shown below. The net rate of removal of PCE can be expressed by a pseudo-first-order rate equation using an observed rate constant (equation 17).

$$\frac{dC_{PCE}}{dt} = -r_5 - r_9 \quad (16)$$

$$\frac{dC_{PCE}}{dt} = -K_{obs}C_{PCE} \quad (17)$$

$$I_{avg} = \frac{I_0(1 - \exp(-(\varepsilon_{In,dithionite}C_{dithionite} + \varepsilon_{In,PCE}C_{PCE})L))}{(\varepsilon_{In,dithionite}C_{dithionite} + \varepsilon_{In,PCE}C_{PCE})L} \quad (18)$$

Combing equations 6,8,10,12,16, 17 and 18 produces the following result for the observed pseudo-first-order rate constant for PCE degradation.

$$K_{obs} = \varphi_5 I_{avg} \varepsilon_{In,PCE} + \frac{k_9 \varphi_7 I_{avg} \varepsilon_{In,dithionite} C_{dithionite}}{(k_9 C_{PCE} + k_{11} C_S)} \quad (19)$$

Equation 5 shows the photolysis reaction of PCE, which has been shown to be able to degrade a part of the PCE in the UV control experiment (Figure 3). Equations 7 and 9 describe the theory of ARP degradation, i.e. that UV light can activate dithionite so that it produces highly reactive radicals, which are able to degrade target contaminants. Equation 11 presents another possible reaction in the PCE degradation in which the radical reacts with a scavenger compound. Previous research on the ARP degradation of vinyl chloride (VC) showed that the scavenging effect is important in ARP degradation, because it affects the amount of radicals available to react with contaminants.<sup>26</sup> Equation 13 describes the reaction that occurred in the reagent control



experiment (Figure 2), i.e. the direct reaction of dithionite with PCE. But as discussed previously, the rate of degradation of PCE by dithionite without UV was small compared the rate of loss due to degradation by the ARP.

According to equation 18 and 19, pseudo-first-order rate constant for PCE degradation has a proportional relationship with light intensity. However, a linear regression on the data (Figure 7) gives an intercept of -0.075. This intercept is non-zero, probably due to errors in experimental data. The results of regression analysis are presented in table 8 and they show that zero is included within the 95% confidence interval of the intercept. The P value of intercept (0.212) is larger than 0.05. Therefore, the data does not demonstrate that light intensity has a non-proportional relationship with  $K_{obs}$  and the model described above cannot be rejected as appropriate for ARP degradation. This regression analysis was conducted with the Data Analysis tool in EXCEL.

Table 8 Regression analysis of light intensities and rate constants

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-0.0750	0.0259	-2.90	0.212	-0.404	0.254
Slope	0.1145	0.00524	21.8	0.091	0.0479	0.181

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

#### Conclusions

PCE is one of the most diffuse pollutants in the environment. The goal of this project was to evaluate the potential of an ARP that combines sodium dithionite with ultraviolet (UV) light activation to degrade PCE. The results of this research: 1) demonstrate the feasibility of applying the dithionite/UV ARP to degrade PCE, and 2) provide information on selecting pH and light intensities in degrading PCE with dithionite/UV ARP. This knowledge can be used in the developing this ARP to be an effective treatment method for chlorinated contaminants, such as PCE.

The specific conclusions from this research are:

- 1) The blank control and reagent control experiments indicate that a small part of PCE may be lost during the preparation of the solutions and by reaction with dithionite in the absence of UV activation.
- 2) The UV control experiment indicates photolysis is able to degrade PCE within a few minutes.
- 3) The first-order reaction model fits the photolysis of PCE well.
- 4) In pH control experiments, degradation at pH 7 gives the best removal rates.
- 5) The combination of dithionite and UV at pH 7, 8, 9 results in faster degradation rates than by photolysis.
- 6) Degradation of PCE at pH 5 is faster than photolysis in the first 2 minutes, then being close to photolysis.

- 7) In pH control experiments, acidic conditions increase the extent of hydrolysis of dithionite and basic conditions increase the concentration of scavengers, both of which results in lower degradation rates than degradation of PCE at pH 7.
- 8) The pseudo-first-order reaction model fits data for the degradation of PCE at pH 7, 8, and 9 well.
- 9) Degradation of PCE at pH 5 can be split into two parts. ARP reactions are the primary reactions in the first part and photolysis reactions are the primary reactions in the second part.
- 10) Increased light intensities results in a faster degradation of PCE.

## **Recommendations**

The specific recommendations for future research in similar experimental systems are:

- 1) Experiments can be conducted to test the effectiveness of dithionite with UV activation in PCE degradation with different initial concentrations of dithionite
- 2) Other potential reductants and activating methods can be tested to degrade PCE.
- 3) Lamps that emit light at wavelengths where dithionite absorb more energy than 254 nm can be tested to degrade PCE.
- 4) Experiments that test the impact of scavengers can be conducted.
- 5) Products of PCE degradation by dithionite and UV activation can be identified to study the mechanism of reactions.

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**APPENDIX A**  
**TABULATED DATA**

Table A-1. The loss of PCE during storage

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	17.7
30	17.8
60	17.3
90	17.7
120	17.0
150	17.4
180	17.8
300	17.5

Table A-2. PCE degraded by dithionite only

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	18.3
5	17.0
10	16.6
20	16.5
30	14.7
60	14.4
120	13.6
180	13.2
300	13.0
360	12.9

Table A-3. Photolysis of PCE with 254nm UV light

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	23.1
1	20.0
2	11.2
3	9.30
7	2.20
15	Not detectable
30	Not detectable

Table A-4. ARP degradation of PCE at pH 5

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	23.3
0.5	20.4
0.75	16.8
1	14.2
1.5	13.0
2	11.5
2.5	11.4
3	10.3
4	8.32
5	7.21
7	4.33

Table A-5. ARP degradation of PCE at pH 7

<b>Time (min)</b>	<b>Concentration of PCE (ppm)</b>
0	21.7
0.25	17.0
0.5	15.1
1	9.59
1.5	7.44
2	5.03
3	1.83
5	0.25

Table A-6. ARP degradation of PCE at pH 8

<b>Time(min)</b>	<b>Concentration of PCE(ppm)</b>
0	21.3
0.25	19.1
0.5	17.3
1	12.0
1.25	10.3
1.5	9.18
2	5.54
2.5	4.41
3	3.63
4	1.92
5	1.00

Table A-7. ARP degradation of PCE at pH 9

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	21.1
0.25	18.3
0.5	17.4
0.75	15.2
1	12.8
1.5	11.0
2	8.76
2.5	6.86
3	5.06
4	3.07
5	1.69

Table A-8. ARP degradation of PCE at 2 mW/cm<sup>2</sup>

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	22.5
1	19.2
1.5	19.6
2	16.8
2.5	14.9
3	14.8
5	9.50
7	6.16
9	4.12

Table A-9. ARP degradation of PCE at 4 mW/cm<sup>2</sup>

<b>Time (min)</b>	<b>Concentration of PCE(ppm)</b>
0	22.9
0.25	22.1
0.5	19.1
0.75	18.2
1	14.1
1.5	14.0
2	11.0
3	7.50
5	3.49

Table A-10. ARP degradation of PCE at 7.3 mW/cm<sup>2</sup>

<b>Time (min)</b>	<b>Concentration of PCE (ppm)</b>
0	21.7
0.25	17.0
0.5	15.1
1	9.59
1.5	7.44
2	5.03
3	1.83
5	0.25