Removal of Diazinon from Water
by Potassium Ferrate (VI) Oxidation

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Abstract

Diazinon, used as a pesticide, poses great threats to ecosystem and human health. This project sought to study the kinetics of the potassium ferrate (VI) oxidation of diazinon and to investigate the effects of pH, time, temperature, and ferrate (VI) dosage on the reaction using gas chromatography (GC). The reaction was found to be second-order with activation energy of 98.7 KJ/mol. The reaction was effective at higher temperature, higher pH, and larger dosage of ferrate (VI) in a basic condition.

Acknowledgements

We would like to thank our project advisor John A. Bergendahl for his advice and guidance. We also would like to thank the lab manager Donald J. Pellegrino for his assistance. Without their extensive support, we would not have been able to accomplish as much as we did throughout our project.

Executive summary

Introduction

Using pesticides is an effective way to improve and maintain crop production. However, pesticides can pose great threats to ecosystems and human health. For example, pesticides can kill various organisms, which may cause an imbalance in the ecosystem. In addition, pesticides may health effects in people. One of the most widely used pesticides was diazinon (O,O-diethyl-O-(6-methyl-2-(1-methylethyl)-4-pyrimidinyl) phosophorothioate). Although it was banned in 2004 for residential usage in the United States (U.S.), it is still used for agricultural and industrial purposes (Howard, 2013). A study conducted by the U.S. Geological Survey showed that diazinon was detected in almost 25.9% of the water samples collected from a network of 139 streams across 30 states in the U.S., which poses great potential threats (Kolpin et al., 2002).

Previous research demonstrated that ferrate (VI) has remarkably high treatment efficiency, especially towards organic compounds (Basu et al., 1987). The purpose of this research was to study the kinetics of potassium ferrate (VI) oxidation of diazinon and to investigate how the reaction was effected by pH, temperature, ferrate (VI) dosage, and reaction time.

Methodology

In order to achieve the objectives, laboratory experiments were performed. The procedures were discussed in the methodology section.

Stock solutions of 20 mg/L diazinon were prepared by dissolving diazinon in purified water from a Thermo Scientific E-Pure unit in a period of 24 hours and used no later than seven days. Ferrate solutions were prepared by adding solid potassium ferrate (VI) directly to 10 mg/L diazinon solution. Methanol was used to quench the ferrate (VI) oxidation reaction. Sodium chloride (NaCl) was added into the gas chromatography vials to produce greater contaminant signals during the GC analysis. Chlorobenzene was used as internal standard for diazinon samples and its stock solution was also prepared and diluted for use. All the samples were analyzed by Headspace Solid Phase Microextraction (HS-SPME) throughout the project.

A calibration curve was created by preparing diazinon solutions at 1.25, 2.5, 5, 10, 20, and 40 mg/L in water. The concentration of chlorobenzene was controlled at 7.5 mg/L in the GC analysis, because it gave the area of peak ratio (diazinon to chlorobenzene) close to one when diazinon was saturated, which would provide a more accurate calibration curve.

To study the degradation of diazinon with different amount of ferrate (VI), 10 mg/L diazinon was mixed continuously with different molar ratios of potassium ferrate (VI) varying from 1:1 to 20:1 (potassium ferrate (VI) to diazinon) over 24 hours at room temperature.

To study the kinetics of the potassium ferrate (VI) oxidation of diazinon and to investigate how the reaction was affected by pH, temperature, and reaction time, 10 mg/L diazinon was used and the molar ratio of potassium ferrate (IV) to diazinon was controlled at eight to one.

To study the effect of pH on the ferrate (VI) oxidation of diazinon, hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust the solution pH. The pH of solution was adjusted to 2.1, 3.6, 6.3, 8.1, 9.6, and 11.8 at room temperature. The reaction was conducted for 24 hours.

To study the kinetics of ferrate (VI) oxidation of diazinon, the ferrate (VI) oxidation reaction to degrade diazinon was conducted for one hour and the samples were collected and quenched shortly after each time step at 0, 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, 50, and 60 minutes reaction times at room temperature.

To study the effect of temperature on ferrate (VI) oxidation of diazinon, the ferrate (VI) oxidation reactions were conducted for one hour and the samples were collected and quenched shortly after each time step at 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 40, 60 minutes reaction times at 31±1°C without pH adjustment.

Methanol was used to quench the ferrate (VI) oxidation reactions. However, methanol had effects on the HS-SPME analysis of diazinon. An experiment was performed to investigate this effect. In the experiment, diazinon solution was prepared at 20 mg/L. The amount of methanol added was controlled so the concentration of methanol in the vials was 0, 500, 750, and 1000 mg/L.

Results and discussion

The results of the experiments were analyzed and discussed in this section.

A calibration curve was created to determine the concentration of diazinon in later experiments. A best fit straight line was applied to the graph of peak area ratio (diazinon to chlorobenzene) against diazinon concentration using Microsoft Excel. The R-squared value was found to be 0.983, indicating a good linear fit to the data.

In the study of the degradation of diazinon with different amount of ferrate (VI), it was found that with the same initial concentration of diazinon at 10 mg/L, increasing the amount of potassium ferrate (VI) decreased the final concentration of diazinon in the water at room temperature without pH adjustment. The greatest removal of diazinon reached 93%, which showed that potassium ferrate (VI) can effectively remove diazinon from water.

In the study of the effect of pH on the ferrate (VI) oxidation to diazinon, the experimental results showed a general trend that with same initial concentration of diazinon at 10 mg/L, increasing pH from 2 to 12 decreased the final concentration of diazinon in the water at room temperature. The concentration of diazinon reached the lowest point at pH 9.6, which was the initial pH of the ferrate solution.

In the study of the effect of temperature on the ferrate (VI) oxidation of diazinon, it was found that with same initial concentration of diazinon at 10 mg/L and same molar ratio at 8 to 1 of ferrate (VI) to diazinon, increasing the reaction temperature accelerated the rate of reaction, which means that at higher temperature, the reactions took less time to reach equilibrium and the final concentration of diazinon in water was lower.

In the study of the kinetics of ferrate (VI) oxidation of diazinon, it was found that with same initial concentration of diazinon at 10 mg/L, increasing the reaction time decreased the final concentration of diazinon in the water without pH adjustment. At both 20°C and 31°C, the pseudo second order fit the best to the experimental results. Therefore, the ferrate (VI) oxidation reaction of diazinon was determined to be second order. Using the Arrhenius equation, the activation energy of the reaction was calculated to be around 98.7 KJ/mol.

An error analysis was conducted to determine the validity of the experimental results. It was found that the use of methanol to quench the ferrate (VI) oxidation reaction of diazinon negatively affected the accuracy of the HS-SPME analysis for the concentration of diazinon. In addition, it was found that the volatilization of diazinon decreased the concentration of diazinon in the solutions.

Conclusions and recommendations

In this project, it was found that ferrate (VI) was very effective in mineralizing diazinon in a short period of time. The removal of diazinon from water using ferrate (VI) oxidation works more effective at high temperature, long reaction time, and large ferrate (VI) dosages in a basic condition.

Several recommendations were made for further studies regarding the ferrate (VI) oxidation reaction of diazinon. First, it was recommended to search for a better reaction quenching method. Adding excess amount of methanol in the samples was not adequate to quench the ferrate (VI) oxidation reaction, since presence of methanol has negatively effect on the accuracy of HS-SPME analysis of diazinon concentration. One of the recommended methods to improve the accuracy was to include methanol in the sample while creating the calibration curve. Second, it is recommended to prepare a stock solution of diazinon concentration of less than 10 mg/L to shorten the stock solution preparation time, which will reduce the chance of volatilization of diazinon. Lastly, it was recommended to repeat the procedures of experiment of *Temperature effect on diazinon degradation* at 40°C or higher temperature. It may be helpful to provide more evidence on the conclusion of the temperature effect on the reaction. Also, it may improve the accuracy of the calculation of the activation energy.

Authorship

Our team took a collaborative approach towards writing this report. We both took on the roles of drafting, writing, editing, and formatting.

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Chapter 1: Introduction

The world crop production capacity is facing several challenges due to the ever-growing world population and the falling ratio of arable land to population. In fact, the world population is expected to reach nine billion by 2045 and approximately 30 percent of the world's potential crop production is lost annually because of the pests and other environmental factors (Hofstrand, 2014). The most effective way to improve and maintain the crop production is using pesticides. According to the Environmental Protection Agency (EPA), pesticides are chemicals used in agriculture to control weeds, pests, and disease carriers, such as mosquitoes, ticks, rats, and mice (EPA, 2015). Even after harvest, crops are subject to attack by pests. Hence, pesticides are used to prevent pre and post-harvest losses from pests and diseases. If existing pesticides are banned for agricultural uses, the amount of the crop production would reduce by half (Hofstrand, 2014).

Although using pesticides benefits the agricultural industry significantly, there are many negative consequences of using them extensively. When exposed to a certain type of pesticides for a long period of time, pests tend to develop resistance through the process of genetic selection. A recent study reported that there are more than 500 species of pests that have developed some level of pesticide resistance (Gut et al., 2014). Consequently, stronger and higher dosages of pesticides are applied to control pests each year, causing complex environmental problems. Due to their chemical make-up, pesticides are prone to microbial degradation, hydrolysis, photolysis, and other means of degradation. However, these degradation processes are relatively slow that pesticides tend to remain in the environment for a considerable amount of time. Since pesticides can kill various organisms present in the nature rather than just targeted organisms, they may lead to the imbalances of ecosystem if certain species are wiped out.

Moreover, pesticides can pose a great threat to humans when they enter human body through inhalation, and oral and dermal contact. For example, as one of the most widely used pesticides after Dichlorodiphenyltrichloroethane (DDT) prohibition, diazinon was applied extensively for residential uses, increasing probability for direct contract with it. Diazinon was eventually banned in the U.S. in 2004 for residential uses when epidemiologic studies showed that diazinon and other insecticides may cause miscarriage as well as leukemia in children (Howard, 2013). Chronic exposure to pesticides may happen when they enter into the water supplies through ground and surface water system. Since treatment facilities with conventional water and wastewater treatment process are not designed to remove specific pesticides, it is hard to remove pesticides from the water supplies although most of them have moderate to low water solubility. According to a study conducted by EPA, the maximum removal efficiency of the pesticide was from 47% to 72% depending on the types of pesticides. Removal efficiency of pesticides, however, was increased dramatically to 97% when oxidation process was implemented (Yarkin, 2008).

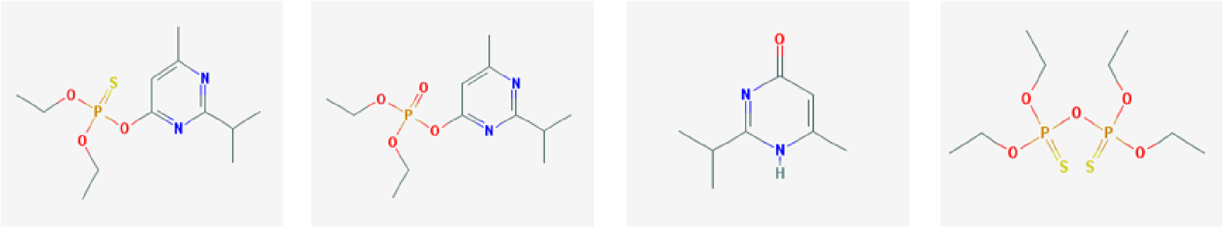
The purpose of this research was to study the potassium ferrate (VI) oxidation reaction and to understand how each parameter, including temperature, pH, ferrate (VI) dosage, and reaction time, affects the removal of diazinon in test samples. Diazinon was selected as a target compound because it was still used for agricultural and industrial purposes. Furthermore, its reaction kinetics under different conditions was studied to determine the order of the reaction as well as the reaction rate constant. The goal of the project was to investigate the ferrate (VI) oxidation reaction under varying conditions. Recommendations for further studies were suggested at the end of the report.

Chapter 2: Background

The goal of this section is to provide background information on diazinon, ferrate (VI), and the reaction quenching process. Characteristics and environmental impacts of diazinon will be discussed to explain the importance of removing diazinon and other pesticides from the environment. To understand the kinetics and mechanisms of the ferrate (VI) oxidation reactions, the characteristics of ferrate (VI) as well as its behavior in different conditions and reaction by-products were studied. In addition, the process to quench the chemical reactions using an excess amount of methanol was explained.

Diazinon

Diazinon (O,O-diethyl-O-(6-methyl-2-(1-methylethyl)-4-pyrimidinyl) phosophorothioate) was first registered in the U.S. in 1956. Prior to the prohibition of all indoor and outdoor residential uses in 2004, diazinon was one of the most widely used organophosphorous insecticides for landscape maintenance, structural pest control, and agricultural and livestock pest management. Diazinon was sold in forms of liquids, powders, granules, and microencapsulations under a variety of names such as Nucidol, Alfatox, and Gardentox (Aggarwal et al., 2012). The amount of diazinon used annually before 2004 was estimated to be greater than 6 million pounds, 69% of which was used around residential areas (Turner, 2002). Diazinon is toxic to living organisms, but it does not exhibit extreme toxicity that would have an instant, lethal effect on the organisms. The primary factor that led to the prohibition of diazinon was its extremely toxic by-products such as diazoxon and sulfotepp whose lethal concentrations to kill half of the target population (LC50) are significantly lower than that of diazinon. In fact, sulfotepp and diazoxon are proven to be at least 75 and 20 times more toxic to fish and other aquatic organisms than diazinon, respectively (Turner, 2002). The chemical structures of diazinon and its by-products are shown in Figure 1.



Diazinon, $C_{12}H_{21}N_2O_3PS$ Diazoxon, $C_{12}H_{21}N_2O_4P$ Oxypyrimidine, $C_8H_{12}N_2O$ Sulfotepp, $C_8H_{20}O_5P_2S_2$

Figure 1: Chemical structures of diazinon and its by-products (“Diazinon”, n.d.)

Although more stringent regulations are currently applied to the application of diazinon, it is still found in many of the water bodies across the U.S. According to a study conducted by the U.S. Geological Survey, diazinon was detected in almost 25.9% of the water samples collected from a network of 139 streams across 30 states (Kolpin et al., 2002). In California, diazinon is still widely used for construction maintenance and agricultural purposes. Table 1 showed the distribution of urban and agricultural uses of diazinon in ten California counties between 2000 and 2009 (Aggarwal et al., 2012).

Table 1: Amount of diazinon used in California from 2000 to 2009 (Aggarwal et al. 2012)

County	Urban (kg)	Agricultural (kg)	Total (kg)
Monterey	4,735	614,339	619,074
Los Angeles	216,426	28,131	244,557
Fresno	20,978	195,169	216,146
Imperial	883	146,630	147.513
Stanislaus	58,258	41,469	99,727
Kern	5,713	86,038	91,751
Sutter	967	87,040	88,007
Tulare	34,144	43,746	77,890
Santa Clara	30,130	46,761	76,890
San Benito	920	68,727	69,648

To study the occurrence and concentration of diazinon in California, samples from major water bodies in nine California regions, including Sacramento Valley Region, San Joaquin Valley Region, Pajaro Region, Salinas Valley Region, Tulare Region, Santa Maria Valley Region, Antelop Region, Ventura Region, and Imperial Valley Region, were collected and analyzed for diazinon. The samples from most of the regions exceeded diazinon concentration of 100 ng/L, with highest detection frequency of 66.7% in the Santa Maria Valley. The highest concentration was reported in the Salinas Valley with a concentration of 24 µg/L found (Zhang, 2011). Unlike in California, diazinon is not as great a concern in Massachusetts. A recent study reported that only one sample out of 78 samples collected from Aberjona River in Boston, MA contained diazinon, albeit at low concentration (Wijnja et al., 2013). In fact, diazinon is still prevalent in nature and poses a potential threat to some living organisms in the environment.

Diazinon is a non-systemic contact insecticide which kills target organisms by altering their nervous system. Diazinon is known to inhibit the enzyme acetylcholinesterase (AChE), which removes the neurotransmitter called acetylcholine (ACh) (NPIC, 2009). When diazinon enters the body, it oxidizes to diazoxon which is a more potent AChE inhibitor than diazinon. Abnormal accumulation of ACh in the nervous system leads to abnormal behavior of the target organism which makes it more vulnerable to its predators. Although slow, mammalian species degenerate diazinon and diazoxon within its body through hydrolyses in the liver. Insects and invertebrates lack this degenerating ability and die due to high concentration of ACh and diazinon in their system (NPIC, 2009). Since it is a neurotoxic chemical, any form of physical contact such as inhalation, and oral and dermal contact is less likely to cause systemic impairment. However, exposure can occasionally lead to an intermediate impact with symptoms that may include anorexia, generalized weakness, muscle tremors, abnormal posturing and behavior, depression, and in worst case, death (Satcher, 1996). In long term exposure, diazinon can damage the liver and pancreas due to high oxidative stress, but no significant body impairment may be observed. Diazinon is not a carcinogen and does not have developmental and reproductive effects on living organisms. Moreover, it has rapid adsorption and excretion when contacted orally. When applied dermally, only a small fraction of diazinon enters the body system while most of it remains on the skin (Satcher, 1996).

Diazinon released into the environment is moderately mobile and persistent. If diazinon is released to soil, it is not expected to strongly adsorb to the soil, but stays mobile. One study found that diazinon leached through more than 80% of soil tested and had a half-life of 21 days to 103 days depending on the temperature, pH, and type of soil (NPIC, 2009). The type of soil is based on partition coefficient, Koc, which was shown in Table 2. In fact, under certain conditions, diazinon can reach and contaminate aquifers before it is degenerated through natural processes. Biodegradation is the major fate process in soils with a reported half-life of one to five weeks in non-sterile soils and six to twelve weeks in sterile soils (NPIC, 2009). Diazinon is also degraded in the nature through hydrolysis. Hydrolysis under room temperature and acidic conditions reduces the half-life of diazinon from 43 days (~pH 7) to possibly 12 days (~pH 5). Photolysis was found to be significant on the surface of soil with diazinon half-life of 17.3 to 37.4 hours when exposed to the sun light (Howard, 1993).

In water, diazinon is highly mobile and highly persistent. It is reported to persist in water for as long as 6 months. Hydrolysis is the major degradation process of diazinon in water with a reported half-life of 185 days in neutral water. The hydrolysis of diazinon favors acidic pH and high temperatures in which, the half-life of diazinon reduces to two to three weeks. Further, diazinon degradation is fastest in natural water than in saline water. Major by-products of diazinon in the hydrolysis process are diazoxon, sulfotepp, and oxypyrimidine (Turner, 2002). Evaporation of diazinon from water is not probable based on its low Henry’s Law constant as listed in Table 2 (Garber et al., 2007). However, recent studies revealed that about 46% of diazinon applied in rice field volatilized within 10 days. In fact, volatilization of diazinon from water could be one of its major transport pathways in nature (Howard, 1993).

If diazinon is released to the atmosphere, it readily volatilizes into air at room temperature and exists in both vapor and particulate phases. Since diazinon absorbs sun light above 290 nm wavelength, it may be subject to direct photolysis. The half-life for the vapor-phase reaction of diazinon with photochemically produced hydroxyl radicals was determined to be approximately four hours in the atmosphere containing 5 x 10^5 hydroxyl radicals/m^3 at room temperature (Howard, 1993).

Table 2: General chemical properties and environment fate of diazinon (Garber et al., 2007)

Chemical/Fate Parameter	Value	Source
Molecular mass	304.3	Product chemistry
Vapor pressure (20°C)	1.40 x 10^{-4} torr	U.S. EPA, 1988
Henry's Law Constant (20°C)	1.40 x 10^{-6} atm m^3/mol	U.S. EPA, 1988
Water Solubility (20°C)	40 mg/L	U.S. EPA, 1988
Octanol-to-water partition coefficient (K_{OW})	2.5 x 10^4	U.S. EPA, 1988
Freundlish soil-to-water partition coefficients (K_f) for adsorption (soil type)	5.6 (1/n = 0.63) (sand) 113.5 (1/n = 0.70) (unclassified) 11.7 (1/n = 0.77) (loam) 3.7 (1/n = 0.60) (sand) 4.5 (1/n = 0.55) (loamy sand) 23.4 (1/n = 0.93) (sandy clay loam)	MRID 00118032
Organic carbon normalized partition coefficients (K_{OC})[2]	439, 485, 560, 638, 720, 854 L/kg_{OC}	MRID 00118032
Hydrolysis half-life	12 d (pH 5) 138 d (pH 7) 77d (pH 9)	MRID 40931101
Aqueous photolysis half-life	37 days	MRID 40863401
Soil Photolysis half-life	17.3 hrs 37.4 hrs	MRID 00153229 MRID 00153229
Aerobic soil metabolism half-lives	37.4 days 38.0 days	MRID 40028701 MRID 44746001
Fish bioconcentration	542 x (edible) 583 x (viscera) 542 x (whole fish)	MRID 40660808

[1] Some chemical properties of the stabilized technical diazinon used in product formulations differ from those of unstable technical diazinon

[2] K_{OC} values were calculated based on K_f values for adsorption (e.g. K_{OC} = K_f (adsorption) / % organic carbon)

Ferrate oxidation

As one of the most abundant elements on earth, iron is present in many different oxidation states. Elemental iron, ferrous (Fe (II)) and ferric (Fe (III)) ions are mainly found in nature while higher oxidation states of iron, also commonly known as ferrate, are less likely to be found due to their high reactivity. Table 3 lists names and chemical formulas of the iron oxide compounds at different oxidation states (Tiwari, 2011). Among the higher states of iron, ferrate (VI) is relatively stable compared to ferrate (IV) and ferrate (V) and thus used for many different applications, one being water treatment.

Table 3: Iron oxide compounds at different oxidation states of iron (Tiwari, 2011)

Compound	Name	Mineral/Salt
FeO	Ferrous Oxide	Wuestite
Fe_2O_3	Ferric Oxide	Hematite
Fe_3O_4	Ferrosoferric Oxide	Magnetite
FeO_2^{2-}	Hypoferrite	Na_2FeO_2
FeO^{2-}	Ferrite	$NaFeO_2$, $KFeO_2$
FeO_3^{2-}	Ferrate (IV)	Na_2FeO_3
FeO_4^{4-}	Ferrate (IV)	Na_4FeO_4
FeO_4^{3-}	Ferrate (V)	K_3FeO_4
FeO_4^{2-}	Ferrate (VI)	Na_2FeO_4, K_2FeO_4
FeO_5^{2-}	Ferrate (VIII)	Na_2FeO_5

Ferrate (VI) is known to treat a variety of compounds in water that are classified as hazardous to the environment and dangerous to human health. These compounds include, but are not limited to, endocrine disrupting chemicals, pharmaceuticals, pesticides, metals, and hydrocarbons. Moreover, ferrate (VI) is capable of disinfecting bacteria and other micro-organisms by inactivating them. It is reported that the oxidation of E. coli DNA polymerase I by ferrate (VI) results in loss of polymerization and 3-5 exonuclease activity, causing irreversible inactivation of the enzyme. At pH 8.2 and a dose of 6 mg/L, ferrate (VI) is reported to inactivate and kill 99.9% of E. coli in 7 minutes (Jiang, 2007). For virus inactivation, ferrate (VI) oxidation is favored at slightly acidic condition. At pH 7.8, 6.9, and 5.9, ferrate (VI) is reported to achieve 99% inactivation of the f2 virus within 22 minutes, 5.7 minutes, and 0.77 minutes (Basu et al., 1987).

Ferrate (VI) has remarkably high treatment efficiency, especially towards organic compounds, with the greatest potential among all the commonly used oxidants such as ozone and hydrogen peroxide. Table 4 lists commonly used oxidants and their oxidation potentials.

Table 4: Redox potential for various oxidants (Tiwari, 2011)

Oxidant	Reaction	E^0,V
Chlorine	$\mathrm{Cl}_{2(g)} + 2e^2 \leftrightarrow 2Cl^-$ $\mathrm{ClO}^- + H^+ + 2e^- \leftrightarrow Cl^- + 2OH^-$	1.358 0.841
Hypochlorite	$\mathrm{HClO} + \mathrm{H}^+ + 2e^- \leftrightarrow Cl^- + H_2O$	1.482
Chlorine Dioxide	$\mathrm{ClO}_{2(aq)} + e^- \leftrightarrow ClO_2^-$	0.954
Perchlorate	$\mathrm{ClO}_4^- + 8 + 8e^- \leftrightarrow Cl^- + 4H_2O$	1.389
Ozone	$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + 2H_2O$	2.076
Hydrogen Peroxide	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.776
Dissolved Oxygen	$O_2 + 4H^+ + 4e^- \leftrightarrow 2\mathrm{H}_2O$	1.229
Permanganate	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$ $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$	1.679 1.507
Chromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2\mathrm{Cr}^{3+} + 7H_2O$	1.33
Ferrate (VI)	$\mathrm{FeO}_4^{2-} + 8H^+ + 3e^- \leftrightarrow \mathrm{Fe}^{3+} + 4H_2O$ $FeO_4^{2-} + 8H_2O + 3e^- \leftrightarrow Fe(OH)_3 + 8H_2O$	2.20 0.70

The reaction mechanism of ferrate (VI) is electron transfer in which ferrate (VI) is converted into lower oxidation state of iron such as ferrate (V) through reduction. Ferrate (V) and ferrate (IV) are order of magnitude more reactive than ferrate (VI) and they have the potential to oxidize the target compounds more rapidly (Barisci et al., 2014). If ferrate (VI) is reduced further to Fe (III), it acts as a coagulant which aggregates colloidal contaminants such as metals and facilitates their removal through sedimentation and filtration. Fe (III) is non-toxic chemical and thus ferrate (VI) treatment is free from toxic by-products (Tiwari, 2011). In fact, at relatively low costs, ferrate (VI) can serve as a strong oxidant and coagulant which effectively disinfects water without causing further complications. The stability of ferrate (VI) is affected by several factors, including ferrate concentration, ion content, temperature, and pH of the solution. In high concentration, ferrate (VI) tends to degrade faster than diluted ferrate (VI). One study demonstrated that a solution of 0.01 M ferrate (VI) decomposed to 79.5% within 2.5 hours while a solution of 0.0019 M ferrate (VI) decomposed to 37.4% after four hours in room temperature (Lloyd, 2001). The stability of ferrate (VI) increases significantly when the solution does not contain ions such as Ni^{2+} and Co^{2+}. Also, the stability of ferrate (VI) is increased when phosphate is introduced to the solution. When KCl and KNO_3 are present, ferrate (VI) is stabilized without further decomposition at relatively low concentration (Bouzek et al., 1999). However, nitrate salts of Cu^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, and other salts have no effect or minimum effect on the stability of ferrate (VI) (Sharma, 2002). Ferrate (VI) is hydrophilic in that it rapidly dissolves into an aqueous solution and decomposes. Ferrate (VI) also decomposes in alcohol that contains water and forms ketones and aldehydes. Unlike in the aqueous solution, it remains undissolved when introduced to commonly used organic solvents such as benzene, ether, and chloroform (Tiwari, 2011).

The decomposition of ferrate (VI) depends heavily on temperature and pH of the solution. Ferrate (VI) is unstable when stored at elevated temperature. At a constant temperature of 50°C, ferrate (VI) concentration was reduced by 35.3% while at 4°C, its concentration remains unchanged for one hour period (Barisci et al., 2014). Like in elevated temperature, ferrate (VI) is unstable in aqueous solution with low pH. At pH 5, ferrate (VI) solution decomposes completely within 7 minutes while at pH 9, it remains stable even after 20 minutes (Tiwari, 2011). It can be seen that under acidic conditions, ferrate (VI) has a high oxidation potential that it goes through a rapid redox reaction. At low pH, the disinfecting ability of potassium ferrate (VI), H_2FeO_4, is observe to increase, however, steady and effective removal of target compounds is achieved at pH values higher than 8 (Basu et al., 1987). The decomposition ferrate (VI) at different pH values is represented in Figure 2.

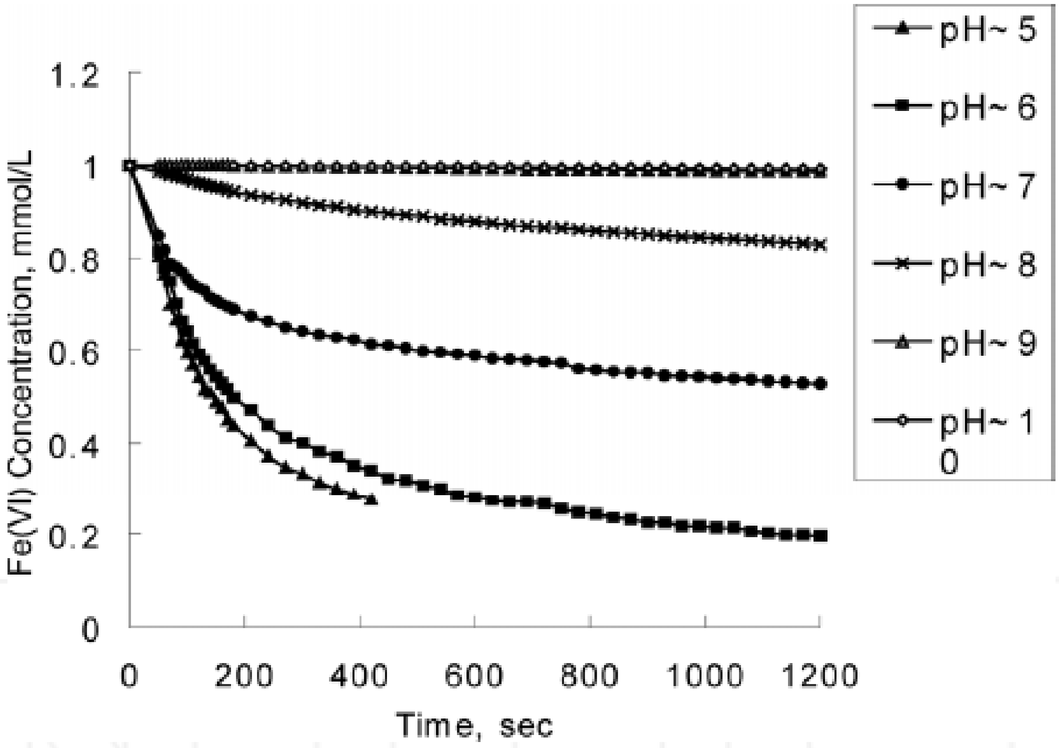


Figure 2: Decomposition of ferrate (VI) with respect to time at various pH (Tiwari, 2011)

Ferrate (VI) in aqueous solution occurs in four forms, including three protonated forms, which depend on pH as shown below (Sharma, 2012).

$$H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \quad pKa = 1.6 \pm 0.2$$

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \quad pKa = 3.5$$

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \quad pKa = 7.3 \pm 0.1$$

Based on the pKa values, it is apparent that H_2FeO_4, HFe_4^-, and FeO_4^{2-} are predominant in acidic, mildly acidic to neutral, and alkaline region, respectively. The reaction kinetics of ferrate (VI) at wide range of pH and low concentration of phosphate followed second-order with no catalytic effect of phosphate ion (Sharma, 2012). Assuming no self-decomposition occurs, the second-order reaction with a number of target compounds [C] can be expressed as following (Noorhasan et al., 2009).

$$-\frac{d[Fe(VI)]}{dt} = k_{app}[Fe(VI)]_{tot}[C]_{tot} \qquad \text{(Equation 1)}$$

The values of k_{app} can be determined by conducting kinetic runs under pseudo-order conditions with varied pH. The pseudo-order rate constant, k', can be obtained by setting the decay of ferrate (VI) at wavelength of 510 nm with time for each kinetic run. Variation of k' as a function of [C] yields k_{app} (Noorhasan et al., 2009). Since ferrate (VI) is more reactive at low pH, k_{app} is higher for a reaction that takes place in acidic conditions.

Ferrate (VI) oxidation of different contaminants

Researchers have done investigations on ferrate (VI) oxidation of several different contaminants. The kinetics of the reactions have been studied and some of the information was summarized in Table 5. In the table, it showed that most of the ferrate (VI) oxidation reactions were found to be first-order with respect to each reactant. Half-order and second-order were also found. Effects of temperature and pH on ferrate (VI) oxidation were also studied. In these studies, the pH was controlled between 6 and 12, and the temperature was controlled between 15°C and 45°C. It was found that rate of the reaction decreased with an increase in pH. Rate of the reaction increased with an increase in temperature.

Table 5. Kinetic information of ferrate (VI) oxidation of different contaminants

Contaminants	**Reaction order**
Zinc-cyanide	Half (Yngard et al., 2007)
Aqueous cyanide	First (Sharma et al., 1998b)
Hydrogen sulfide	First (Sharma et al., 1997)
Sulfamethoxazole	First (Sharma et al., 2006)
Thioacetamide	First (Sharma et al., 2000)
Ammonia	Second (Sharma et al., 1998a)
Thiourea	Second (Sharma et al., 1999)

Reaction quenching process

Quenching a reaction is extremely important when measuring the extent of reaction. If a reaction is left unquenched, the reaction proceeds until the limiting reagent is depleted. In fact, without proper quenching process, obtaining reliable data from a time trial could be very difficult. More importantly, all reactive substances need to be quenched before disposing of into a hazardous waste container in order to prevent any unsafe release of heat or gas. Table 6 lists quenching processes for various reactive substances (Vtech, 2006).

Table 6. Quenching Reactive Substances (Vtech, 2006)

Types of Reactive Substances	Quenching Process
Highly Reactive Hydrides and Metals (sodium hydride, potassium metal, sodium-potassium alloy)	1. Quench with isopropanol or ethanol and dilute with water. 2. Add diluted sulfuric or hydrochloric acid until a neutral or slightly acidic pH is achieved 3. Allow hydrogen gas to be vented.
Less Reactive Hydrides and Metals (lithium metal, calcium hydride, sodium borohydride)	1. Quench directly with water. 2. Use argon instead of nitrogen when working with lithium.
Acid Chlorides and Anhydrides (phosphorus pentoxide, thionyl chloride, boron trichloride, trifluoroacetic anhydride)	1. Quench with water under a nitrogen or argon counter stream. 2. Allow HCl, HBr, and other acidic fumes to be vented. 3. After quenching, neutralize the solution with sodium hydroxide, potassium hydroxide, or sodium bicarbonate. 4. Neutralize with sulfuric or hydrochloric acid if sodium bicarbonate is used.
Organometallic Reagents	1. If Sure-Seal bottles are used to contain organometallic reagents, no further treatment is required. 2. If the bottles contain small amounts of residue from butyllithium, methyllithium, Grignard reagents, or alkylaluminum halides, create a counterstream of nitrogen in the bottles and add acetone and water to quench.
Inorganic Carbonates	1. Neutralize with hydrochloric or sulfuric acid until no carbon dioxide is formed

Chapter 3: Methodology

In this section, experimental procedures to carry out the ferrate (VI) oxidation of diazinon are discussed in succinct manner. Sample preparation, materials and tools used to obtain and analyze data, and methods to explore the effects of different parameters are briefed to give an overview of the experiment and its approaches.

Stock solution preparation

Due to the low water solubility of diazinon, stock solutions of 20 mg/L diazinon were prepared by dissolving diazinon in purified water from a Thermo Scientific E-Pure unit in a period of 24 hours and used no later than seven days. Ferrate solutions were prepared by adding solid potassium ferrate (VI) directly to 10 mg/L diazinon solution. Methanol was used to quench the ferrate (VI) oxidation reaction. In experiment, 6 μl of pure methanol was added into the ferrate solution such that the solution in the vial contained 500 mg/L methanol. The vial was then placed at room temperature for approximately five minutes to let methanol fully quench the potassium ferrate (VI). After that, four grams of sodium chloride (NaCl) was added into the vial to produce greater contaminant signals during the gas chromatography analysis. Chlorobenzene was used as internal standard for diazinon samples and its stock solution was also prepared and diluted for use. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution were used to adjust pH value of the solution. Detailed information includes manufacturer, product number, and concentration of every used chemicals are listed in Table 7.

Table 7: Information of chemicals and fiber used for this project

Item	Manufacturer	Catalog number	Concentration
Diazinon	Sigma-Aldrich	49021	98.3%
Potassium ferrate (VI)	Sigma-Aldrich	723835-25G	>90%
Methanol	Fisher Scientific	67-56-1	99.9%
NaCl	Fisher Scientific	7647-14-5	≥99.5%
Chlorobenzene	Sigma-Aldrich	270644-100ml	99.9%
HCl	Fisher Scientific	7732-18-5	34-37%
NaOH	Fisher Scientific	1310-73-2	10 N
85um CAR/PDMS SPME Fiber	Supelco	57295-U	N/A

Gas Chromatography (HS-SPME) set up

Headspace Solid Phase Microextraction (HS-SPME) was used to analyze the diazinon samples. Before and after each run, blank injection and desorption steps were conducted to prevent cross-contamination of residual compounds in the SPME fiber. An 85 um CAR/PDMS fiber was used for diazinon adsorption and every new fiber was conditioned for three hours at 290°C. Extraction time for diazinon was set to be 45 minutes since heavier and less volatile compounds tend to have low diffusion coefficient and it takes longer to reach headspace equilibrium. As shown in Figure 3, the detector response increases as extraction temperature increases and reaches its highest point at 75°C (Lambropoulou, 2001). Higher temperature enhances the volatilization of diazinon as more energy is provided to diazinon particles in the form of heat.

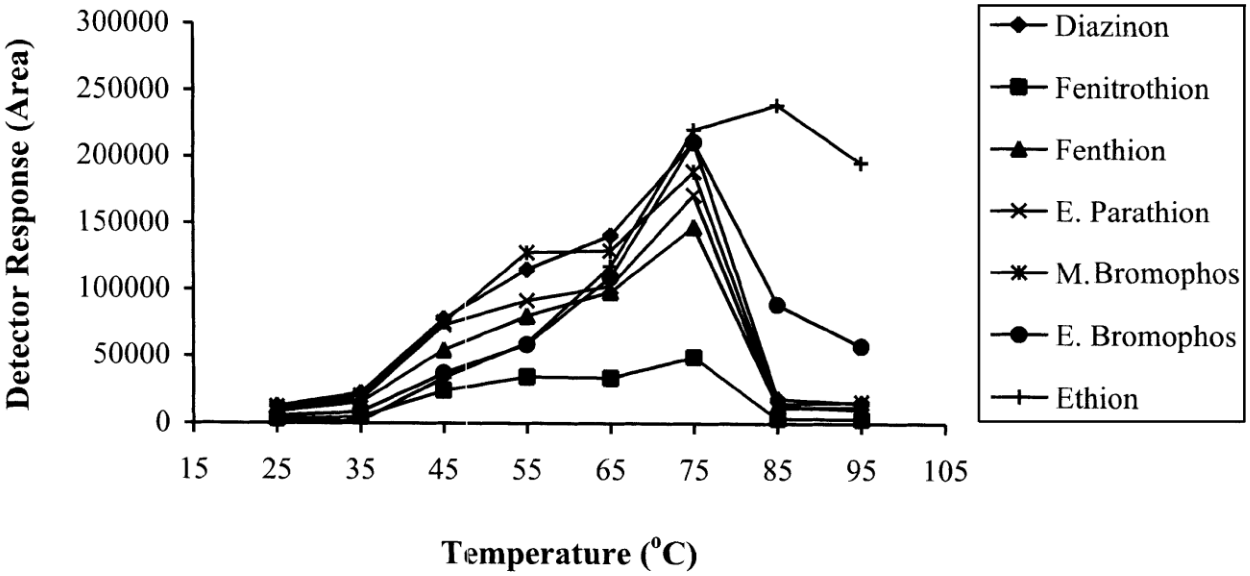


Figure 3: Influence of temperature on detector response of pesticides (Lambropoulou, 2001)

The detector response drops significantly when the temperature exceeds 75°C. This is because adsorption is an exothermic process and diazinon fails to adsorb on the fiber surface at temperature higher than 75°C. Hence, the temperature of extraction was set at 75°C to achieve the greatest adsorption to the fiber. Moreover, HS-SPME was set to agitate the diazinon solution at 950 revolutions per minute (rpm) since anything lower than 950 rpm resulted in decrease in the detector response (Lambropoulou, 2001). Table 8 and 9 show HS-SPME parameters and configurations, respectively.

Table 8. HS-SPME parameters

Extraction Time	45 mins
Extraction Temperature	75°C
Oven Temperature	290°C
Stirring Rate	960 rpm
Fiber Type	85 um CAR/PDMS SPME Fiber

Table 9: Headspace solid phase microextraction (Agilent 6890) configuration

Injector	Volume – 1.0 to 2.0 µL			
Inlet	Mode – Splitless Gas – N2 (H2) Heater – 290 °C Pressure – 14.99 psi Total Flow – 4.8 mL/min Purge flow to split vent 1.0 mL/min at 0.00 min			
Column	Mode – constant pressure Model No. Restek RTX-5 350C MAX – Capillary 30.0 m x 250 µm x 0.25 µm nominal Flow 1.6 mL/min Velocity – 36 cm/sec			
Oven	Oven Ramp	°C/min	Net °C Hold Time	Run Time
	Initial	30	4.0 min	4.0 min
	Ramp 1	50	0.0 min	16.67 min
	Ramp 2	290	2.0 min	45 min
FID Detector	Heater – 300 °C H2 flow – 40.0 mL/min Air flow – 450 mL/min Makeup N2 – 25 mL/min			
Signals	Signal 1 – 20Hz -- 0.01 min Signal 2 – 50 Hz -- 0.004 min			

Calibration curve preparation

A calibration curve was required to determine the concentration of diazinon in treatment experiments. To obtain the calibration curve, different concentration of diazinon in solution was prepared at room temperature by using serial dilution method. The highest concentration was controlled at 40 mg/L, at which diazinon is saturated in water at room temperature. Other concentrations were controlled at 20, 10, 5, 2.5, and 1.25 mg/L. Then, 10 ml of each solution was transferred to each vial with 4 g NaCl and 50 µl of 7.5 mg/L of chlorobenzene. HS-SPME was used to analyze the solution to find the peak areas responding to diazinon and chlorobenzene. The concentration of chlorobenzene was controlled at 7.5 mg/L, because it gave the area of peak ratio (diazinon to chlorobenzene) close to one when diazinon was saturated, which would provide a more accurate calibration curve. Finally, known concentrations of diazinon were plotted against the area ratio (diazinon to chlorobenzene) that was found by HS-SPME and the best fitting straight line was found using linear regression in Microsoft Excel.

Degradation with varying ferrate (VI) dose over 24 hours

Solutions of 10 mg/L diazinon with different molar ratio of potassium ferrate (VI) varying from 1:1 to 20:1 (potassium ferrate (VI) to diazinon) were investigated. The mixed solutions were sealed and constantly agitated for 24 hours on laboratory rotators at room temperature. The ferrate flocs were removed with a 0.45 µm syringe filter and the diazinon solutions were transferred to 10 ml vials and quenched with methanol. NaCl and chlorobenzene were added to each vial. The samples were analyzed with HS-SPME from the highest molar ratio to the lowest molar ratio with blank injections in between every three samples analyzed.

Effect of pH on ferrate (VI) oxidation of diazinon

Solutions of 8:1 molar ratio of potassium ferrate (VI) to diazinon were used to analyze the pH effect on degradation of diazinon. Approximately 41 mg of potassium ferrate (VI) was dissolved in 400 ml of water in a 600 ml beaker at room temperature. The pH of this ferrate solution was around 9.4. Then, 50 ml of this ferrate solution was collected into six small beakers. The pH values were adjusted by using HCl and NaOH solutions with Pasteur pipettes. The pH of one of the solutions was not adjusted so this solution was used as reference. The amount and concentration information was listed in Table 10. The pH of each solution was measured.

Table 10: pH adjustment of ferrate solution with HCl and NaOH

Amount (drops)	Solution with concentration	Adjusted pH
2	10N HCl	2.1
2	1N HCl	3.6
1	1N HCl	6.3
4	0.333N HCl	8.1
2	10N NaOH	11.8

After the solution reached the desired pH value, 50 ml of 20 mg/L diazinon solution was added to every beaker. The mixed solution had 8:1 molar ratio of potassium ferrate (VI) to diazinon. The pH value of the solution with 21 mg potassium ferrate (VI) and 400 ml of water was around 9.6. This value was very close to the pH value of 9.4 mentioned earlier. Therefore, it was assumed in the experiments that the dilution of the ferrate solution did not have great effects on the pH value of the total solution.

Every beaker was sealed and continuously agitated for 24 hour using a rotator. Then, 10 ml of each solution was transferred to HS-SPME vials and mixed with methanol, NaCl and chlorobenzene. The vials were placed into the tray and then the samples were analyzed by HS-SPME to find the ratio of the peak area of diazinon to chlorobenzene. Finally, the concentration of diazinon in each of the solutions was found using the calibration curve.

Kinetic time trials

To study the kinetics of the ferrate (VI) oxidation of diazinon, one hour time trial was conducted with initial diazinon concentration of 10 mg/L. The samples were collected and quenched shortly after each time step at 0, 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, 50, and 60 minutes at room temperature. The samples were analyzed with HS-SPME from the longest to the shortest reaction times with blank injections in between every three samples analyzed. By using a linear regression model and pseudo first and second order kinetics analysis, the order of the reaction as well as its rate constants were determined and discussed in the results section.

Temperature effect on ferrate (VI) oxidation of diazinon

Temperature was controlled at 31±1°C to investigate how temperature affects the degradation of diazinon with potassium ferrate (VI). In the experiment, 400 ml of 10 mg/L of diazinon was collected in a beaker and placed on a rotator, which agitated and heated the solution to 31°C. A thermometer was inserted into the solution to measure the temperature. After the solution reached the desired temperature, 21 mg of potassium ferrate (VI) was added into the solution, which made the molar ratio of potassium ferrate (VI) to diazinon to be 8 to 1. Then, the beaker was sealed by Parafilm. Figure 4 shows the set up for this part of experiment. Then, 10 ml of solution was collected into a vial and mixed with methanol at predetermined times: 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 40, 60 minutes, respectively after adding potassium ferrate (VI). After approximately 5 minutes, NaCl and chlorobenzene was added into the vials. The vials were placed into the HS-SPME tray and then the samples were analyzed with HS-SPME to find the ratio of the peak area of diazinon to chlorobenzene. Finally, the concentration of diazinon in each of the solution was determined from the calibration curve.

Figure 4: Set up of the experiment of temperature adjustment effect on degradation

Methanol effect on the HS-SPME analysis of diazinon

Methanol was used to quench the ferrate (VI) oxidation reactions. However, methanol had effects on the HS-SPME analysis of diazinon. An experiment was performed to investigate this effect. In the experiment, diazinon solution was prepared at 20 mg/L. After solution was prepared, 10 ml of diazinon solution was collected into four vials respectively. Different amount of methanol, 6 µl, 9 µl, 12 µl, was added into three vials respectively to make the concentration of methanol in the vials to be 500 mg/L, 750 mg/L, and 1000 mg/L. After approximately five minutes, 4 g NaCl and 50 µl of 7.5 mg/L of chlorobenzene was added into every vials. Finally, theses vials were placed into the HS-SPME tray and the samples were analyzed by the HS-SPME.

Chapter 4: Results and discussion

The objectives of the ferrate (VI) oxidation experiments were to study the kinetics of ferrate (VI) oxidation reaction and to understand the impacts of each experimental variable such as pH, temperature, ferrate (VI) dosage, and reaction time. In this section, the results of the experiments were presented, analyzed, and discussed in attempt to explain the reasons behind the trends and deviations of the data obtained. Information from published sources was also used to strengthen the arguments made in this section.

Calibration curve

A calibration curve was created, as shown in Figure 5, to determine the concentration of diazinon in later experiments. In the graph of calibration curve, the y-axis represents the peak area ratio (diazinon to chlorobenzene) that was found by HS-SPME-GC, and the x-axis represents the known concentration of diazinon. The best fit straight line was found though linear regression using Microsoft Excel. The R-squared value, representing how well the trend line fits to the data points, was found to be 0.983, indicating a good linear fit to the data.

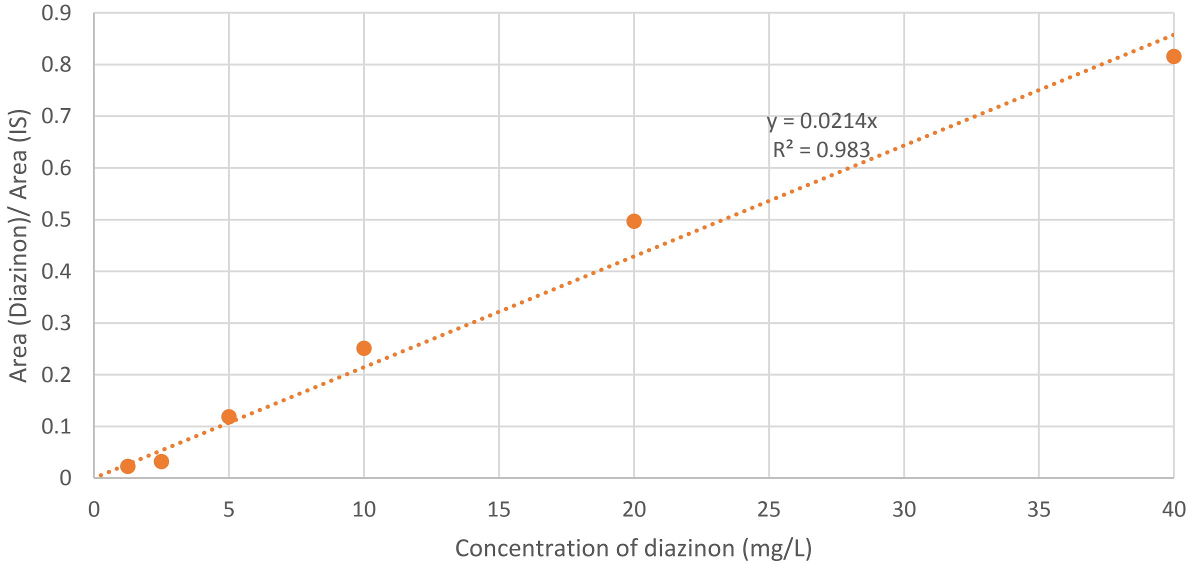


Figure 5: Calibration curve of diazinon with 7.5 mg/L of chlorobenzene as internal standard

Degradation with varying ferrate (VI) dose over 24 hours

The concentration of diazinon was found using the calibration curve after HS-SPME analysis from the ratio of the responding peak areas of diazinon and chlorobenzene. The concentration of diazinon after 24 hours reaction time at room temperature was plotted against the molar ratio of potassium ferrate (VI) to diazinon as shown in Figure 6. The initial concentration of diazinon was 10 mg/L. However, the initial concentration analyzed by HS-SPME was found to be 7.9 mg/L. This may be caused by the experimental error and uncertainties which will be discussed in the later sections. In the figure, the experimental results showed that the concentration of diazinon decreased as the amount of potassium ferrate (VI) increased. The change of concentration became smaller after the molar ratio of ferrate (VI) to diazinon past eight to one.

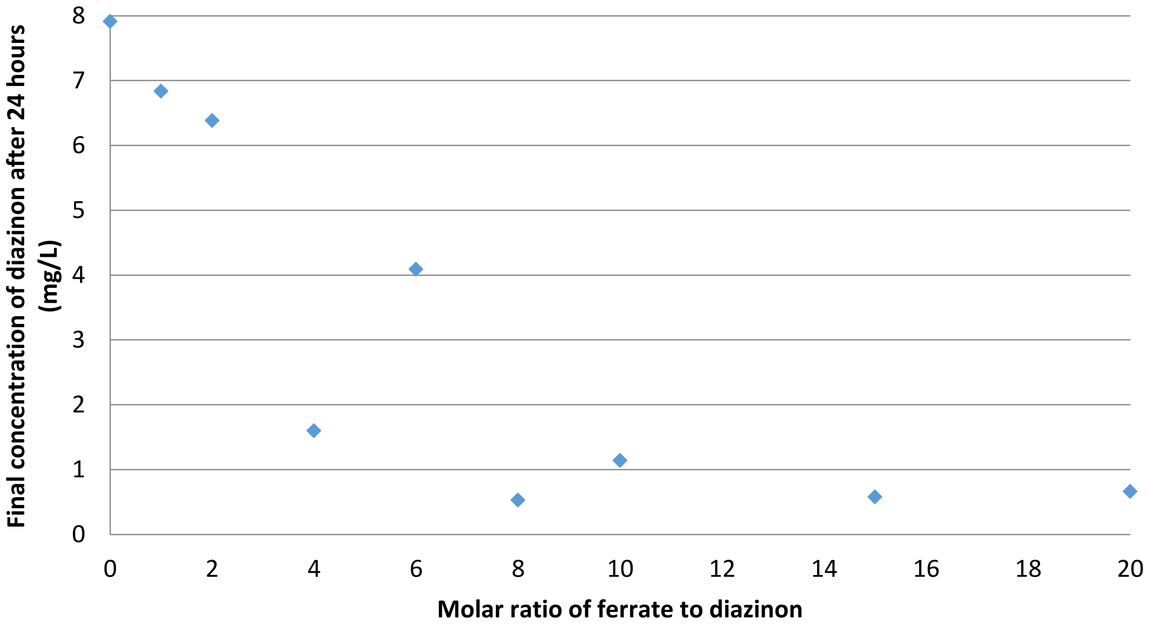


Figure 6: Degradation of 10mg/L diazinon with varying potassium ferrate (VI) dose after 24 hours at room temperature

Fraction removal of diazinon was plotted against the molar ratio of potassium ferrate (VI) to diazinon as shown in Figure 7. The highest removal fraction of diazinon was approximately 93%, showing that potassium ferrate was effective in removing diazinon from water.

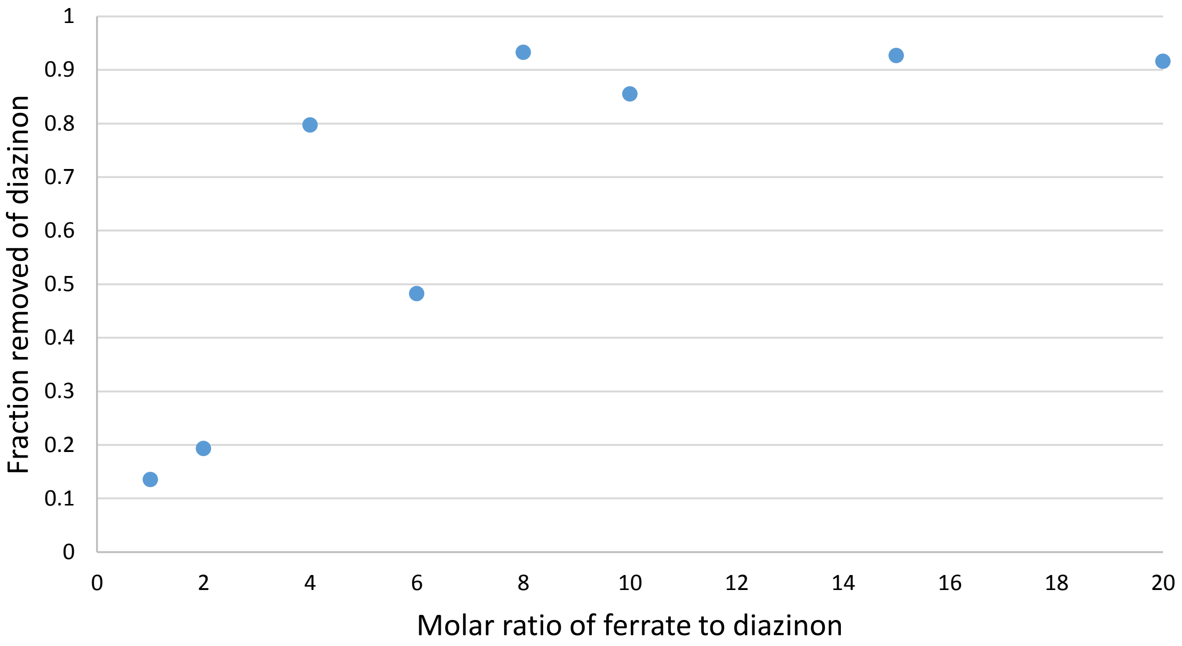


Figure 7: Fraction removed of 10 mg/L diazinon with varying potassium ferrate (VI) dose after 24 hours at pH 9.6 and room temperature

According to Figure 7, increasing the molar ratio of potassium ferrate (VI) to diazinon above eight to one did not significantly increase the removal effectiveness. Generally, higher ferrate (VI) to diazinon molar ratios resulted in greater diazinon removal. Ferrate (VI) reacted with diazinon as well as dissociated in water. An excess amount of ferrate (VI) was required to reduce the concentration of diazinon to the minimum. For further studies of ferrate (VI) oxidation in this project, ferrate solutions with molar ratio of 8 to 1 (ferrate (VI) to diazinon) were tested and analyzed under different conditions.

Effect of pH on ferrate (VI) oxidation of diazinon

The influences of pH on the ferrate (VI) oxidation reactions was studied. Ferrate solutions with molar ratios of 8 to 1 (ferrate (VI) to diazinon) had an initial pH of 9.6. The pH of the ferrate solutions were adjusted to a desired pH before and after adding the diazinon solution. A minimum amount of hydrochloric acid and sodium hydroxide solution were used to control the pH in order to avoid diluting the solution. Figure 8 showed the concentrations of diazinon in ferrate solutions for solution pH of 2.1, 3.6, 6.3, 8.1, 9.6, and 11.8 after 24 hours.

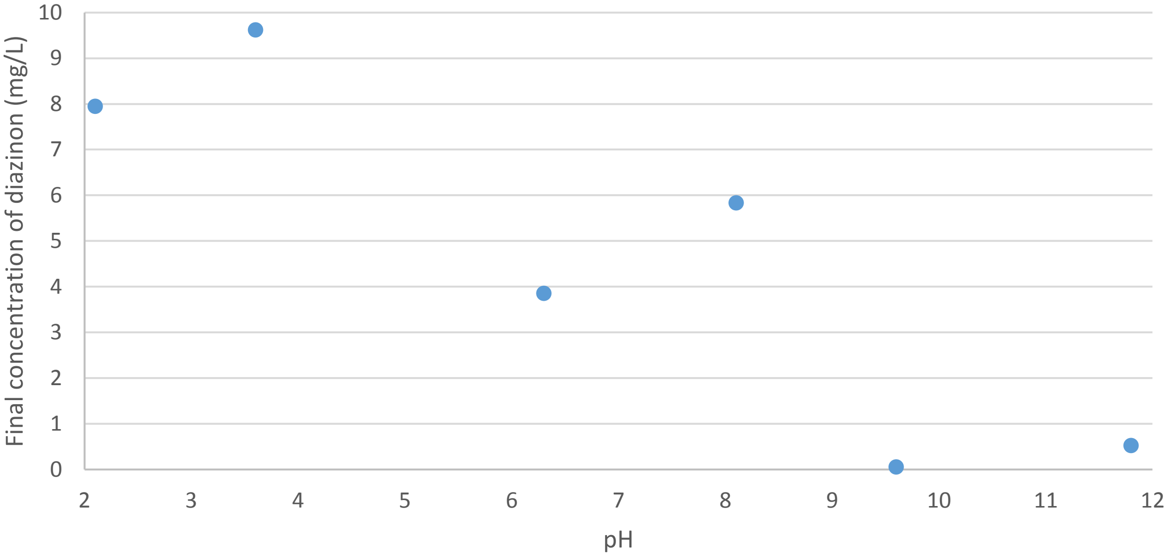


Figure 8: Degradation of 10 mg/L diazinon at 8:1 molar ratio (ferrate (VI) to diazinon) and room temperature after 24 hours at different pH

The concentration of diazinon reached the lowest point at pH 9.6, which was the initial pH of the ferrate solution. The concentration of diazinon at pH 12 was also quite low unlike those at lower pH values. In every solution pH evaluated, there was a significant change in final diazinon concentration. The poor removal at low pH was mainly due to the instability of ferrate (VI) at low pH. According to recent research, ferrate (VI) decomposed completely within 7 minutes at pH 5 while at higher pH, ferrate (VI) remained stable for around 9 hours (Sharma, 2012). When ferrate (VI) was dissolved in water, it underwent rapid decomposition due to its strong oxidizing property. The following chemical equation shows the reaction of ferrate (VI) decomposition in water.

$$4FeO_4^{2-} + 10\mathrm{H}_2O \rightarrow 4Fe(OH)_3 + 3O_2 + 8OH^-$$

Hydroxide was produced as a result of ferrate (VI) decomposition, which increased the pH of the water even more. In alkaline condition, ferrate (VI) followed a different reduction pathway, producing anionic compound. Referring to the chemical equations mentioned in the section of *Ferrate (VI) oxidation*, as shown again below, the third equation with pKa of 7.3 (Sharma, 2012).

$$FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \quad pKa = 1.6 \pm 0.2$$

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \quad pKa = 3.5$$

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \quad pKa = 7.3 \pm 0.1$$

Based on the pKa values, it was apparent that H_2FeO_4, HFe_4^-, and FeO_4^{2-} are predominant in acidic, mildly acidic to neutral, and alkaline region, respectively. Ferrate (VI), FeO_4^{2-}, was barely consumed at pKa of 7.3, indicating that ferrate (VI) remained unreacted. In alkaline conditions, ferrate (VI) was known to have a reduction potential of 0.72 V, which was surprisingly lower than its reduction potential of 2.2 V in acidic conditions (Barisci et al., 2014). As a result, ferrate (VI) remained undecomposed at high pH and reacted with diazinon for a longer period of time. In Figure 2, curves at pH 9 and 10 remained straight while those at lower pH had steeper negative slopes, indicating the rate of ferrate (VI) decomposition is faster for these curves (Tiwari, 2011).

Kinetics experiments and temperature effect on ferrate (VI) oxidation of diazinon

The kinetics of ferrate (VI) oxidation of diazinon was found by carrying out reaction time trials. The reaction time was limited to 60 minutes and samples were taken and quenched at predetermined times during the total reaction period. The HS-SPME analysis was conducted in two ways. In the first method, the samples were arranged from the lowest to the highest diazinon concentration. While in the second method, the samples were arranged from the highest to the lowest diazinon concentration. Figure 9 compared the results from these two methods.

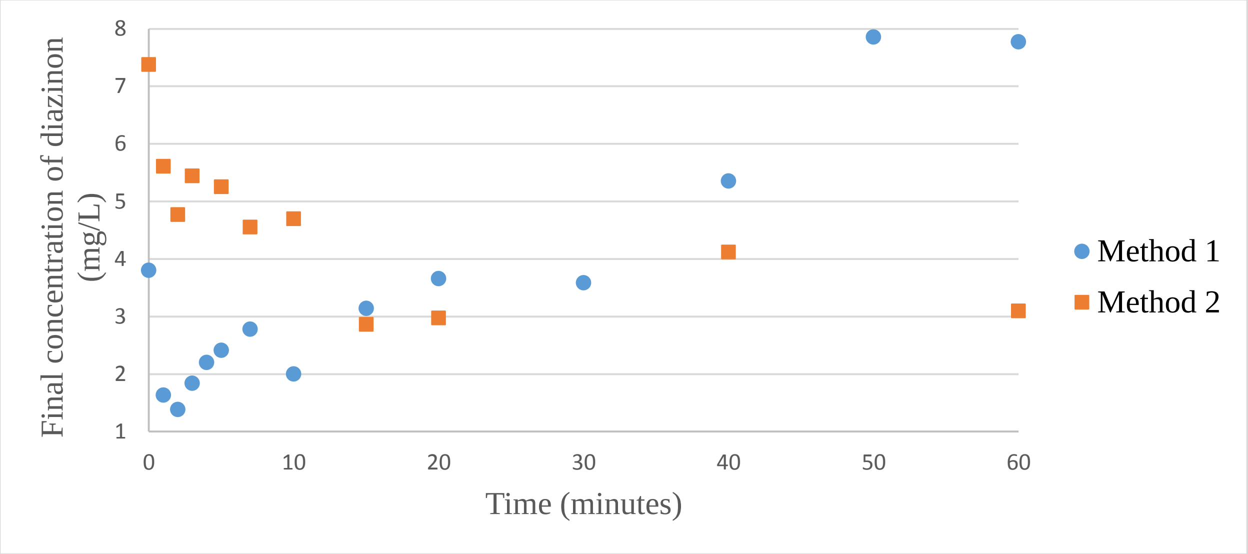


Figure 9: Comparison between two analysis methods: 10 mg/L diazinon as initial concentration, 8 to 1 ferrate (VI) to diazinon molar ratio, pH 9.6, room temperature

In Figure 9, results from method 1 showed that the concentration of diazinon increased as reaction time increased, which did not make sense. It was because during the ferrate (VI) oxidation reaction, ferrate (VI) was expected to oxidize diazinon, which should decrease the amount of diazinon with time. One of the reasons causing this improper trend was due to the time delay in the HS-SPME analysis and inadequate quenching. Each vial took around 90 minutes to analyze and thus the last vial in the sequence was analyzed approximately 12 hours after the quenching. Since the amount of methanol was not enough to quench the reaction completely, ferrate (VI) continued to react and reduce the amount of diazinon in the vials. The effect of methanol on the HS-SPME analysis was discussed in the error analysis section. Unlike the results from method 1, the results from method 2 showed a general trend that diazinon concentration decreased with time, which was expected. Hence method 2 was practiced when analyzing the samples with the HS-SPME to obtain more reliable data. Diazinon concentration was plotted against time at 20°C and 31°C, as shown in Figure 10.

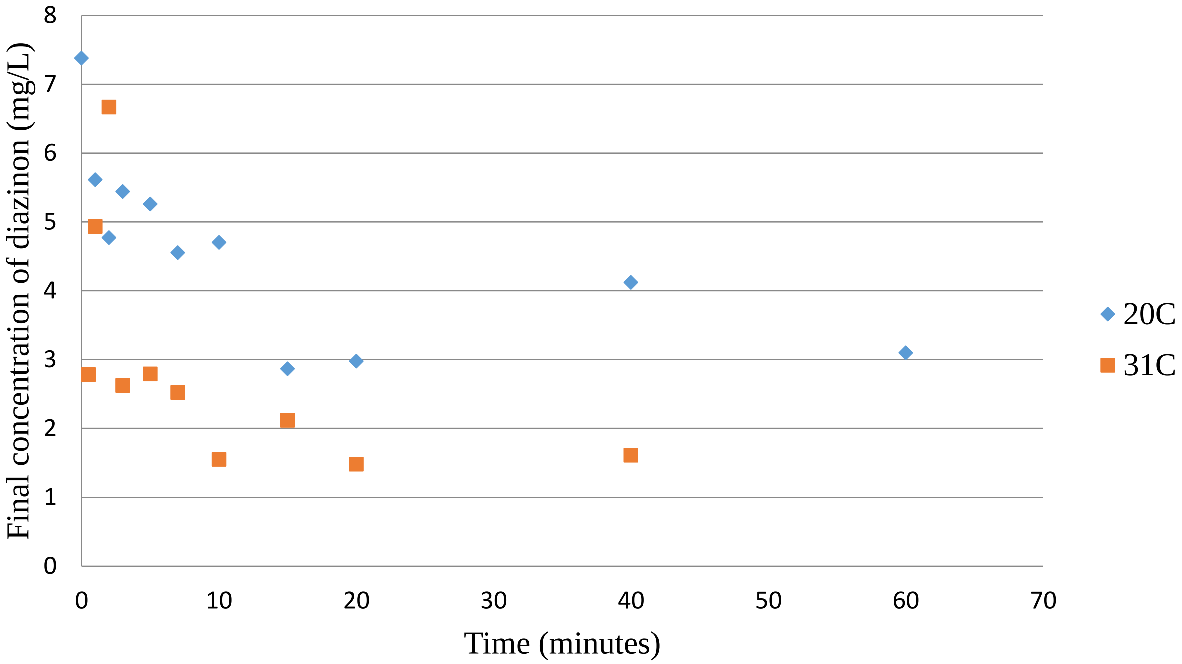
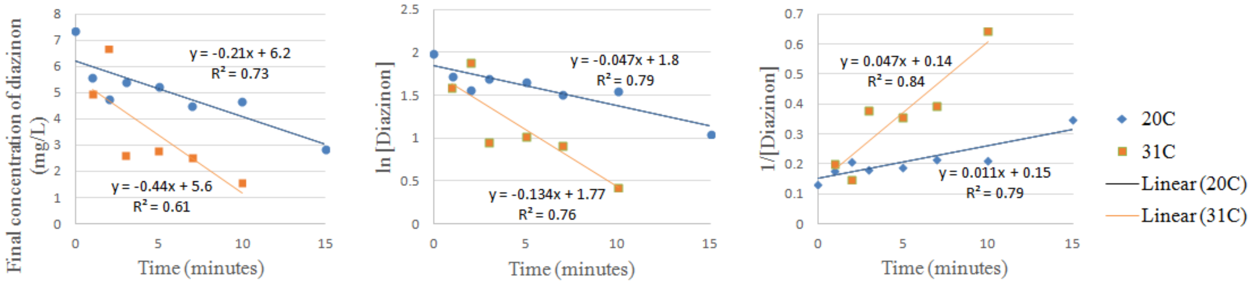


Figure 10: Temperature effect on 10mg/L diazinon removal at 8:1 molar ratio (ferrate (VI) to diazinon) and pH 9.6

In Figure 10, the initial concentration of diazinon was prepared at 10 mg/L. The result at 60 minutes reaction at 31°C was not obtained. As can be seen in Figure 10, it was found that at higher temperature, the reactions took less time to reach equilibrium and the final concentration of diazinon was lower. The results make sense as reactants can only react when they are in contact, and molecules move faster and collide more frequently at higher temperature. Therefore, higher temperature would be expected to speed up the rate of reaction.

With same molar ratio of potassium ferrate to diazinon and initial concentration of diazinon, the final concentration of diazinon for 24 hours reaction at room temperature was 0.53 mg/L, which was discussed in the previous section. When the temperature was increased to 31°C, it took 40 minutes to decrease the concentration of diazinon to 1.61 mg/L. Due to the time limitation, more experiments at higher temperatures were not conducted. It was expected that the ferrate (VI) oxidation reactions with diazinon would react faster when the temperature was increased to greater than 31°C. Also, with higher temperature, the final concentration of diazinon may approach 0.53 mg/L within one hour.

To determine the order of the reaction, the data in Figure 10 were linearized by taking natural log (first order), and inverse (second order). Zero order did not require any data linearization. The figures were generated with Microsoft Excel using linear regression as shown in Figure 11. Only the results during the first 15 minutes of the reaction were generated since the reaction reached equilibrium after that time period. The slope of the trend line of each graph represented the rate constant of the reaction at each condition. In the figure, it was observed that the rate constants at 31°C were always greater than the ones at 20°C. It proved the previous conclusion that increasing temperature helped to speed up the rate of reaction. According to Figure 11, it was found that second order had both highest R-squared values at 20°C and 31°C, indicating that the ferrate (VI) oxidation was slightly towards second order.



a) Zero order b) First order c) Second order

Figure 11: Order of the ferrate (VI) oxidation reaction with diazinon at pH 9.6, 20°C, and 31°C

As mentioned in the background chapter, previous studies reported that the reaction order of ferrate (VI) oxidation of different compounds could be first and second order. The rate law of the ferrate (VI) oxidation of diazinon was studied further by employing pseudo-first and second order kinetics. Assuming the stoichiometric ratio of ferrate (VI) and diazinon was 1:1, the concentration of diazinon would decrease significantly while that of ferrate (VI) would barely change as the oxidation reaction proceeds. Consequently, the molar ratio of ferrate (VI) to diazinon changed from 8:1 to a greater ratio. Equations 2 and 3 were the pseudo-first and second order equations, respectively, assuming constant ferrate (VI) concentration. The rate constant k' was a new constant derived by multiplying the original rate constant, k, and the concentration of ferrate (VI). Detailed derivations and calculations of the pseudo-first and second order reactions could be found in Appendix B.

$$[\text{diazinon}]_{\text{final}} = [\text{diazinon}]_{\text{initial}} \cdot \exp(-k't) \qquad \text{(Equation 2)}$$

$$\frac{1}{[\text{diazinon}]_{\text{final}}} = \frac{1}{[\text{diazinon}]_{\text{initial}}} + k't \qquad \text{(Equation 3)}$$

Using the data tabulated in Table 15 and 16 in Appendix B, a graphical representation of the pseudo first order and pseudo second order kinetic models of the ferrate (VI) oxidation reactions at 20°C and 31°C were generated as shown in Figure 12.

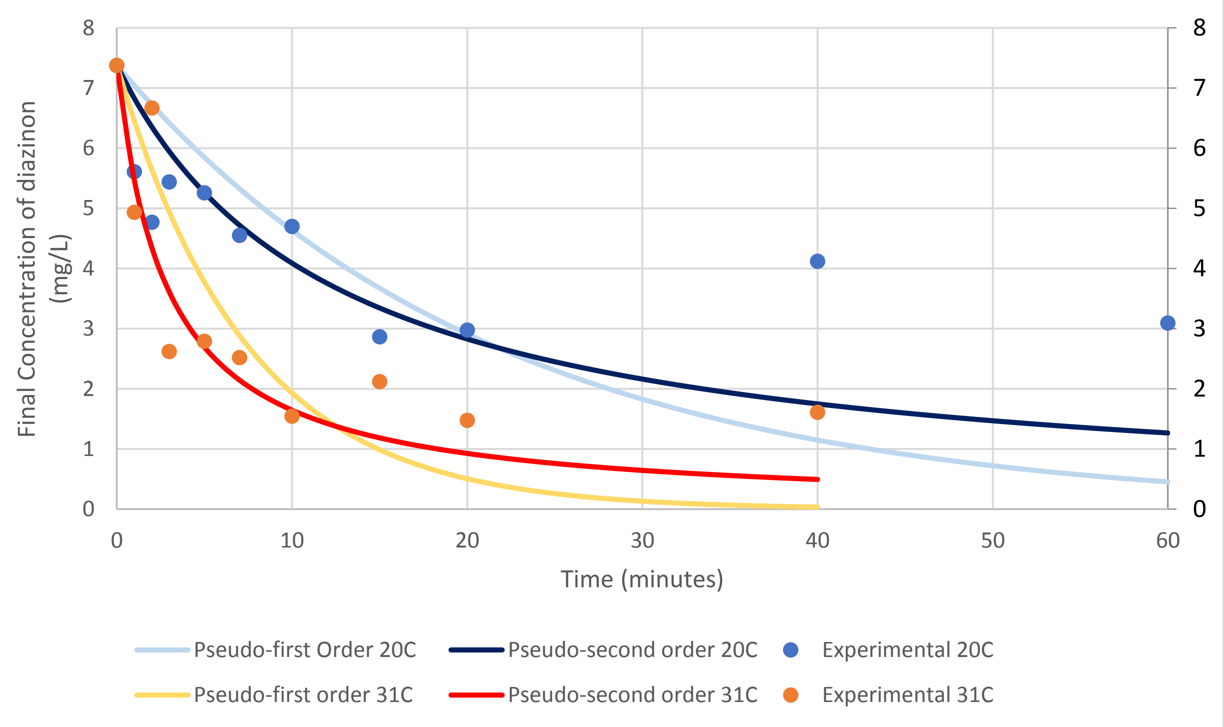


Figure 12: Pseudo 1st and 2nd order models for the ferrate (VI) oxidation reactions at pH 9.6 with initial concentration of 10 mg/L diazinon at 20°C and 31°C

Compared to the pseudo-first-order curve, the pseudo-second-order curve seemed to fit the overall trend of the ferrate (VI) oxidation of diazinon a bit better over a period time at both temperatures. Therefore, the reaction of ferrate (VI) oxidation of diazinon was concluded to be second order.

Activation energy of ferrate (VI) oxidation of diazinon

From the Arrhenius equation, the relationship between ln(k) and 1/T can be derived as shown below.

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

where k is the rate constant; A is the pre-exponential factor; and Ea is the activation energy. After two rate constants at different temperature were determined from Figure 12, a plot showing ln(k) versus 1/T was made in Excel as shown below.

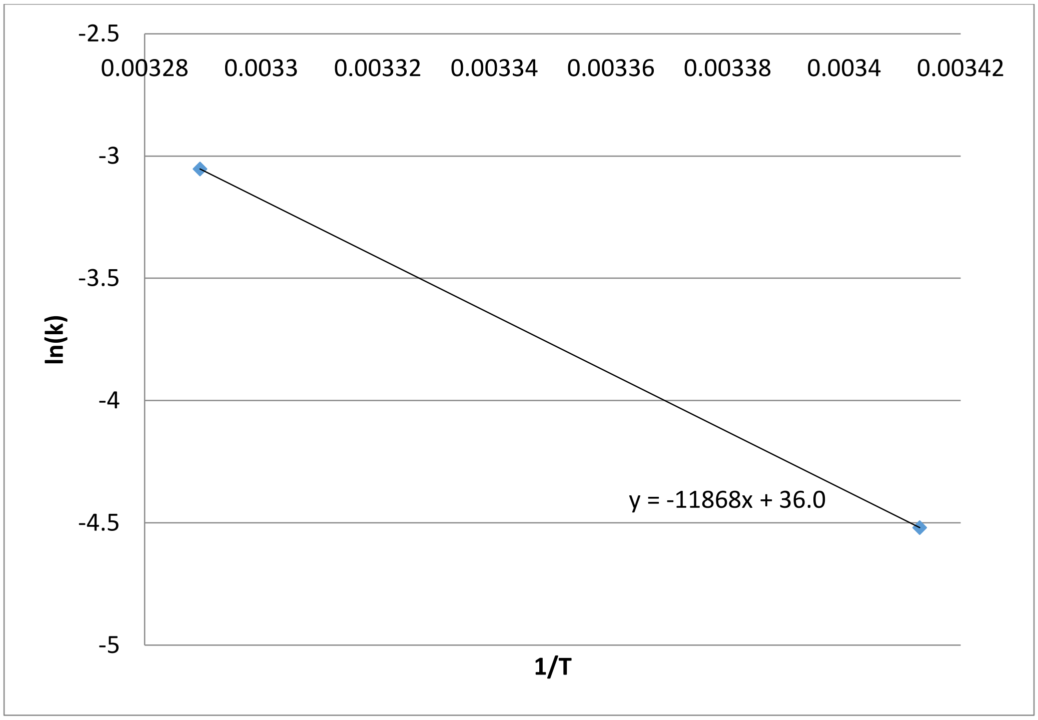


Figure 13: Determination of activation energy by Arrhenius plot method

In Figure 13, the best fit straight line was applied through linear regression to the data. The activation energy was calculated from the slope of the straight line, and was equal to $\frac{E_a}{R}$. The activation energy was found to be 98.7 KJ/mol. The pre-exponential factor was calculated to be

4.31×10^{15}. The literature value of activation energy of potassium ferrate (VI) oxidation reaction with diazinon was not found. To compare the calculated activation energy, several activation energy values of ferrate (VI) oxidation with different chemicals were referenced as shown in Table 11. Compared to these literature values, the calculated activation energy of ferrate (VI) oxidation of diazinon was a bit high, but it was still in a reasonable range.

Table 11: Activation energy of ferrate (VI) oxidation of different contaminants

Contaminants	**Activation Energy (KJ/mol)**
Ibuprofen	65.4 (Sharma & Mishra, 2006)
Thioacetamide	59.7 (Sharma et al., 2000)
Zinc-cyanide	45.7 (Yngard et al., 2007)
Aqueous cyanide	38.9 (Sharma et al., 1998b)
Thiourea	32.2 (Sharma et al., 1999)
Hydrogen sulfide	30.1 (Sharma et al., 1997)

Error Analysis

An error analysis was conducted to determine the validity of the experimental results. The use of methanol to quench the oxidation reactions was found to negatively affect the accuracy of the HS-SPME analysis for the concentration of diazinon. And it was found that the volatilization of diazinon decreases the concentration of diazinon in the solutions.

Methanol Effect

Methanol was used to quench the ferrate (VI) oxidation reactions. However, it was found that adding higher amounts of methanol into the samples has significant effect on the HS-SPME analysis of diazinon as shown in the Figure 16. Diazinon solution was prepared at 20 mg/L, but the detected concentration of diazinon by the HS-SPME was around 18.8 mg/L. This small difference might be caused by analytical error and volatilization of diazinon, which was discussed in the later sections. In the Figure 14, with same initial concentration of diazinon, when adding more methanol into the vial, the concentration of diazinon detected by the HS-SPME significantly decreased. When the methanol was controlled at 500 mg/L in the vial, the detected concentration of diazinon was decreased about 38.1%.

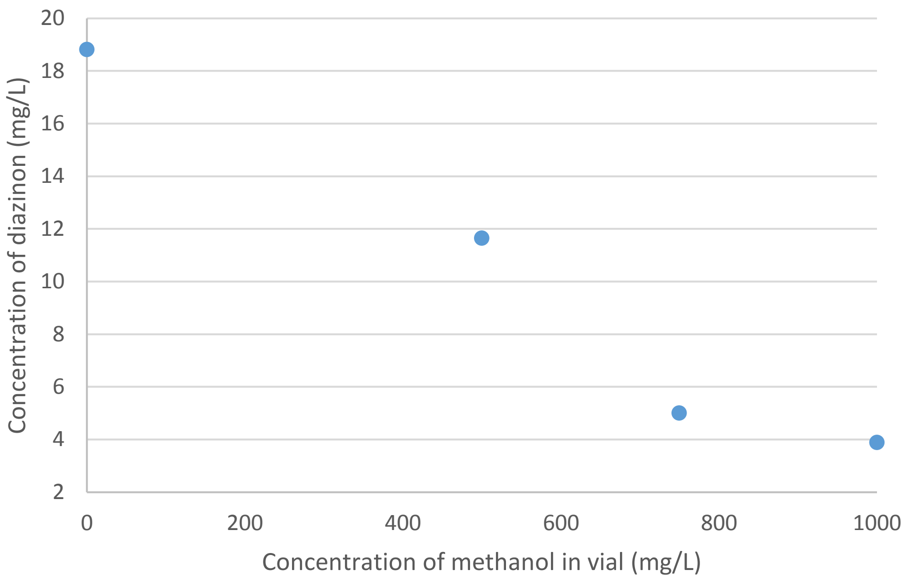


Figure 14: Effect of different amount of methanol on the HS-SPME analysis of 20 mg/L diazinon at pH 9.6

Due to the time limitation, the calibration curve with adding the methanol was not created. This decreased the accuracy of measuring the concentration of diazinon in this project. Therefore, it was highly recommended to obtain the calibration curve with methanol.

Volatilization

It was observed that the detected concentrations of diazinon were always a bit smaller than the expected value. One of the reasons might be volatilization. Stock solutions of diazinon were prepared by dissolving diazinon in purified water in a period of 24 hours at room temperature. After 24 hours, it was observed that many small droplets remained on the wall of the beaker and the sealing film. These droplets may be caused by volatilization of diazinon and vaporization of water. It was also found that with the concentration of diazinon increased, more droplets were observed. This means that these droplets may be primarily caused by the volatilization of diazinon. The vapor pressure of pure diazinon at 20°C is 1.4×10^{-4} torr, which is much smaller than the vapor pressure of pure water at same temperature, 17.5 torr (Garber et al., 2007; Lide, 2005). This information does not support the observation. One of the reasons might be that mixture of diazinon and water was used instead of pure chemicals. The volatilization was explained by Henry's law. The Henry's law constant (HLC) of diazinon highly depends on temperature. It was found that the HLC of diazinon was around 3133 M/atm at room temperature (Feigenbrugel et al., 2004). The volatilization slightly caused the concentration of diazinon solution to decrease.

In the experiment of temperature adjustment effect on degradation, certain amount of droplets was also observed on the wall of the beaker and the sealing film. Figure 15 showed an example of ferrate (VI) and diazinon solution after heating. Heating increased the rate of volatilization. These droplets may contain diazinon, which decreased the concentration of diazinon in the solution.

Figure 15: Potassium ferrate (IV) and diazinon solution after heating

Chapter 5: Conclusions and recommendations

In this project, removal of diazinon in water with potassium ferrate (VI) was conducted under varying conditions. Although there were different water treatment techniques available such as ozone and hydrogen peroxide, the ferrate (VI) oxidation process was chosen for this research because it was relatively cheaper compared other advanced oxidation processes, had the highest redox potential, and produced no toxic by-products. Furthermore, ferrate (VI) acted as an oxidant and coagulant which maximized its removal capacity of diazinon. In fact, ferrate (VI) was proven to be very effective in mineralizing diazinon in a short period of time in this research.

Under laboratory conditions, ferrate (VI) reduced the concentration of diazinon by nearly 93% over 24 hours at ferrate (VI) to diazinon molar ratio of 8:1. Higher molar ratio resulted in equally higher percentage of diazinon removal. On the other hand, anything below the molar ratio of 8:1 (ferrate (VI) to diazinon) resulted in relatively low percentage removal of diazinon. Hence, ferrate (VI) to diazinon molar ratio of 8:1 was used for the rest of the experiments. The effects of pH on the ferrate (VI) oxidation reaction was also studied by observing the reaction at varying pH values. The ideal pH value of the ferrate (VI) oxidation reaction was found to be 9.6, which was the initial pH of the ferrate (VI) solution. After 24 hours, over 95% removal of diazinon was achieved at pH 9.6 as well as at higher pH. Removal capacity of diazinon decreased significantly at lower pH. Ferrate (VI) decomposed immediately at pH lower than 4.

The time trial of the ferrate (VI) oxidation reaction over maximum 60 minutes was conducted at room temperature and 31°C. The data obtained from the time trial were linearized to determine the order of the reaction. At room temperature, the correlation for the fit, or R^2, to the first order and the second order were 0.791 and 0.794, respectively. At 31°C, R^2 of the first order and the second order were 0.755 and 0.842, respectively. Hence, the ferrate (VI) oxidation reaction with diazinon was concluded to be a second order reaction. The time trial experiment at two different temperatures revealed that the ferrate (VI) oxidation reaction was enhanced at elevated temperature. At room temperature, the concentration of diazinon was reduced to 2.98 mg/L while at 31°C, it was reduced to 1.61 mg/L in the first 20 minutes. For both cases, the concentration remained unchanged until the end of the time trial. Lastly, the activation energy of the ferrate (VI) oxidation of diazinon was found to be 98.7 KJ/mol using the modified Arrhenius equation. This value was in a reasonable range with other documented activation energy of ferrate (VI) with different compounds. In conclusion, the removal of diazinon from water using ferrate (VI) oxidation works the most effectively at higher temperature, longer reaction time, higher pH, and higher ferrate (VI) dosage.

For further studies regarding the ferrate (VI) oxidation reaction, it is recommended to have a better reaction quenching method. Adding excess amount of methanol in the samples was not adequate to quench the ferrate (VI) oxidation reaction. Moreover, high concentration of methanol reduced the gas chromatography signal of diazinon, hindering accurate measurement and analysis of the data. Also, it is recommended to prepare a stock solution of diazinon concentration of less than 10 mg/L. Due to low water solubility of diazinon, it took almost 24 hours to dissolve diazinon in water. Lower diazinon concentration will shorten the stock solution preparation time which will decrease the volatilization of diazinon. Lastly, it was recommended to repeat the procedures of experiment of *Temperature effect on diazinon degradation* at 40°C or higher temperature. It may be helpful to provide more evidence on the conclusion of the temperature effect on the reaction. Also, it may improve the accuracy of the calculation of the activation energy.

References

Aggarwal, V., Deng, X., Tuli, A., & Goh, K. (2012). Diazinon-Chemistry and Environmental Fate: A California Perspective. *Reviews of Environmental Contamination and Toxicology,223*, 107-140.

Barisci, S., Ulu, F., Sarkka, H., Dimoglo, A., & Sillampaa, M. (2014). Electrosynthesis of Ferrate(VI) ion Using High Purity Iron Electrodes: Optimization of Influencing Parameters on the Process and Investigating Its Stability. *International Journal of Electrochemical Science,9*, 3099-3117.

Basu, A., Williams, K., & Modak, M. (1987). Ferrate Oxidation of Escherichia coli DNA Polymerase-I. *The Journal of Biological Chemistry, 262*(20), 9601-9607.

Bouzek, K., Schmidt, M., & Wragg, A. (1999). Influence of anode material composition on the stability of electrochemically-prepared ferrate(VI) solutions. *Journal of Chemical Technology & Biotechnology, 74*(0268-2575), 1188-1194.

Diazinon | C12H21N2O3PS - PubChem. (n.d.). Retrieved March 1, 2015, from http://pubchem.ncbi.nlm.nih.gov/compound/diazinon

EPA. (2015, February 23). Why we use pesticides. Retrieved March 15, 2015, from http://www2.epa.gov/safepestcontrol/why-we-use-pesticides

Feigenbrugel, V., Le Calvé, S., & Mirabel, P. (2004). Temperature dependence of Henry's law constants of metolachlor and diazinon. *Chemosphere*, *57*(4), 319-327.

Garber, K., Orrick, G., Young, D., & Steeger, T. (2007, May 9). Risks of Diazinon Use to the Federally Listed Endangered Barton Springs Salamander. Retrieved February 28, 2015, from http://www.epa.gov/oppfead1/endanger/litstatus/effects/bss-diazinon-assessment.pdf

Gut, L., Schildler, A., Rufus, I., & McManus, P. (2014, December 14). Fruit Crop Ecology and Management. Retrieved March 15, 2015, from http://grapes.msu.edu/integrated_pest_management/how_pesticide_resistance_develops

Hofstrand, D. (2014, February 1). Can we meet the world's growing demand for food? Retrieved March 15, 2015, from http://www.agmrc.org/renewable_energy/renewable_energy/can we-meet-the-worlds-growing-demand-for-food/

Howard, J. (2013, August 1). An Introduction to Pesticides and Human Health. Retrieved March 15, 2015, from http://cape.ca/pesticides-2/

Howard, P. (1993). Diazinon. In *Handbook of environmental fate and exposure data for organic chemicals* (Vol. 4, pp. 211-216). Boca Raton, Florida: Lewis.

Jiang, J. (2007). Research Progress in the use of ferrate(VI) for the environmental remediation. *Journal of Jazardous Materials, 146*(0304-3894), 617-623.

Kolpin, D., Furlong, E., Meyer, M., Thurman, M., Zaugg, S., Barber, L., & Buxton, H. (2002, January 1). Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance. Retrieved February 28, 2015, from http://wsp.arizona.edu/sites/wsp.arizona.edu/files/uawater/documents/workshops/workshop2/Additional_Info.pdf

Lambropoulou, D., & Albanis, T. (2001). Optimization of headspace solid-phase microextraction conditions for the determination of organophosphorus insecticides in natural waters. *Journal of Chromatography A, 922*, 243-255.

Lide, D. ed. (2005). *CRC Handbook of Chemistry and Physics*. Boca Raton, Florida: CRC Press

Lloyd, B., & Jiang, J. (2001). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research, 36*, 1397-1408.

Noorhasan, N., Sharma, V., & Baum, C. (2009). A Fluorescence Technique to Determine Low Concentrations of Ferrate(VI). *ACS Symposium Series, 985*, 145-155.

NPIC. (2009, January 1). Diazinon Technical Fact Sheet. Retrieved February 28, 2015, from http://npic.orst.edu/factsheets/diazinontech.pdf

Satcher, D. (1996). Health Effects. In *Toxicological Profile for Diazinon* (Vol. 1, pp. 29-132). Atlanta, Georgia: U.S. Department of Health and Human Services.

Sharma, V. (2002). Potassium ferrate(VI): An environmentally friendly oxidant. *Advances in Environmental Research, 6*(1093-0191), 143-156.

Sharma, V. (2012). Ferrate (VI) and ferrate (V) oxidation of organic compounds: Kinetics and mechanism. *Coordination Chemistry Reviews, 257*(0010-8545), 495-510.

Sharma, V. K., Bloom, J. T., & Joshi, V. N. (1998a). Oxidation of ammonia by ferrate (VI). *Journal of Environmental Science & Health Part A*, *33*(4), 635-650.

Sharma, V. K., & Mishra, S. K. (2006). Ferrate (VI) oxidation of ibuprofen: a kinetic study. *Environmental Chemistry Letters*, *3*(4), 182-185.

Sharma, V. K., Mishra, S. K., & Ray, A. K. (2006). Kinetic assessment of the potassium ferrate (VI) oxidation of antibacterial drug sulfamethoxazole. *Chemosphere*, *62*(1), 128-134.

Sharma, V. K., Rendon, R. A., Millero, F. J., & Vazquez, F. G. (2000). Oxidation of thioacetamide by ferrate (VI). *Marine chemistry*, *70*(1), 235-242.

Sharma, V. K., Rivera, W., Joshi, V. N., Millero, F. J., & O'Connor, D. (1999). Ferrate (VI) oxidation of thiourea. *Environmental science & technology*, *33*(15), 2645-2650.

Sharma, V. K., Rivera, W., Smith, J. O., & O'Brien, B. (1998b). Ferrate (VI) oxidation of aqueous cyanide. *Environmental science & technology*, *32*(17), 2608-2613.

Sharma, V. K., Smith, J. O., & Millero, F. J. (1997). Ferrate (VI) oxidation of hydrogen sulfide. *Environmental science & technology*, *31*(9), 2486-2491.

Tiwari, D., & Lee, S. (2011, April 1). Ferrate (VI) in the treatment of wastewaters: A new generation green chemical. Retrieved February 28, 2015, from http://www.intechopen.com/books/waste-water-treatment-and-reutilization/ferrate-vi-in-the-treatment-of-wastewaters-a-new-generation-green-chemical

Turner, L. (2002, November 29). Diazinon Analysis of Risks to Endangered and Threatened Salmon and Steelhead. Retrieved February 28, 2015, from http://www.epa.gov/oppfead1/endanger/litstatus/effects/diazinon-analysis-final.pdf

Vtech. (2006, October 27). Quenching Reactive Substances. Retrieved March 15, 2015, from http://www.chem.vt.edu/facilities/resources/safety-quenching-pdf.pdf

Wijnja, H., Doherty, J., & Safie, S. (2013). Changes in Pesticide Occurrence in Suburban Surface Waters in Massachusetts, USA, 1999-2010. *Bull Environ Contam Toxicol*, (93(2):228-32), 228-232.

Yarkin, M. (2008). Enhancing Natural Treatment Systems by Utilizing Water Treatment Residuals. Retrieved March 15, 2015, from https://books.google.com/books?id=1UJdvZtf2ZQC&printsec=frontcover&vq=conventional treatment process pesticide#v=onepage&q=conventional treatment process pesticide&f=false

Yngard, R., Damrongsiri, S., Osathaphan, K., & Sharma, V. K. (2007). Ferrate (VI) oxidation of zinc–cyanide complex. *Chemosphere*, *69*(5), 729-735.

Zhang, S., & Starner, K. (2011, August 2). Analysis of Diazinon Agricultural Use in Regions of Frequent Surface Water Detections. Retrieved February 28, 2015, from http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/diazinon_anal_zhang_starner_final_080211.pdf

Appendices

Appendix A: Sample calculation

Pseudo first order derivation

The rate equation of ferrate oxidation reaction with diazinon can be simplified as follows.

$$\mathrm{r} = -\mathrm{k} \cdot [\mathrm{Fe(VI)}]^{\mathrm{m}} \cdot [\mathrm{diazinon}]^{\mathrm{n}}$$

where r is the rate of the reaction, also can be written as dC/dt; C is the concentration of a target compound; k is the rate constant.

Assuming the concentration of ferrate is constant, the pseudo-first order equation can be derived as shown below.

$$\mathrm{r} = -(\mathrm{k} \cdot [\mathrm{Fe(VI)}]^{\mathrm{m}}) \cdot [\mathrm{diazinon}]^{\mathrm{n}} = -\mathrm{k}' \cdot [\mathrm{diazinon}]^{1}$$

$$\mathrm{r} = \frac{\mathrm{d[diazinon]}}{\mathrm{dt}} = -\mathrm{k}' \cdot [\mathrm{diazinon}]$$

$$\int_{[C]_i}^{[C]_f} \frac{\mathrm{d[diazinon]}}{[\mathrm{diazinon}]} = \int_0^t -\mathrm{k}'\mathrm{dt}$$

$$\ln\left(\frac{[\mathrm{diazinon}]_{\mathrm{f}}}{[\mathrm{diazinon}]_{\mathrm{i}}}\right) = -\mathrm{k}'\mathrm{t}$$

$$[\mathrm{diazinon}]_{\mathrm{f}} = [\mathrm{diazinon}]_{\mathrm{i}} \cdot \exp(-\mathrm{k}'\mathrm{t})$$

Pseudo second order derivation

Pseudo second order equation can be derived following the same analogy as in pseudo first order derivation except the order of the reaction is two instead of one.

$$\mathrm{r} = \frac{\mathrm{d[diazinon]}}{\mathrm{dt}} = -\mathrm{k}' \cdot [\mathrm{diazinon}]^{2}$$

$$\int_{[C]_i}^{[C]_f} \frac{\mathrm{d[diazinon]}}{[\mathrm{diazinon}]^2} = \int_0^t -\mathrm{k}'\mathrm{dt}$$

$$-\left(\frac{1}{[\mathrm{diazinon}]_{\mathrm{f}}} - \frac{1}{[\mathrm{diazinon}]_{\mathrm{i}}}\right) = -\mathrm{k}'\mathrm{dt}$$

$$\frac{1}{[\mathrm{diazinon}]_f} = \frac{1}{[\mathrm{diazinon}]_i} + k'dt$$

Activation energy and the pre-exponential factor

From Figure 14(c), k_{20C} was the slope of the straight line at 20°C, which was 0.0109. The $\ln(K_{45C})$ and 1/T were calculate as shown below.

$$\ln(k_{45C}) = \ln(0.0109) = -4.52$$

$$\frac{1}{T} = \frac{1}{273 + 20} = 0.00341K^{-1}$$

The slope of the straight line on the chart of lnk vs 1/T was -11868. Based on the Arrhenius equation, the activation of energy was calculated as shown below.

$$\mathrm{Slope} = -\frac{Ea}{R}$$

$$Ea = -(-11{,}868K) \cdot \left(\frac{8.314J}{mol} \cdot K\right) \cdot \frac{1kJ}{1{,}000J} = \frac{98.7kJ}{mol}$$

The pre-exponential factor was calculated from the y-intercept of the straight line as shown below.

$$y - \mathrm{intercept} = 36 = \ln(A)$$

$$A = 4.31 \times 10^{15}$$

Appendix B: Raw data

Table 12. Calibration curve data at different diazinon concentrations

Concentration of diazinon (mg/L)	Signal Area (D)	Concentration of chlorobenzene (mg/L)	Signal Area (IS)	Area (D)/Area (IS)
40	822.2	7.5	1008.7	0.815
20	579.5	7.5	1167	0.496
10	365.4	7.5	1457.7	0.250
5	156.5	7.5	1318	0.118
2.5	28.01	7.5	883.3	0.031
1.25	29.9	7.5	1323	0.022

Table 13. Ferrate (VI) oxidation at different molar ratios over 24 hours with 500mg/L methanol

ratio	[D]	D signal	[IS]	IS signal	ratio	concentration mg/L	Removal Eff.
N/A	10mg/L	107	7.5mg/L	631.9	0.169	7.913	-
1:1	10mg/L	163.6	7.5mg/L	1117.9	0.146	6.839	0.136
1:2	10mg/L	161.4	7.5mg/L	1181.4	0.137	6.384	0.193
1:4	10mg/L	53.06	7.5mg/L	1547.4	0.034	1.602	0.798
1:6	10mg/L	122.9	7.5mg/L	1403.12	0.088	4.093	0.483
1:8	10mg/L	13.7	7.5mg/L	1205.6	0.011	0.531	0.933
1:10	10mg/L	36.47	7.5mg/L	1490	0.024	1.144	0.855
1:15	10mg/L	19.4	7.5mg/L	1565.7	0.012	0.579	0.927
1:20	10mg/L	21.02	7.5mg/L	1475.82	0.014	0.666	0.916

Table 14. pH effect on ferrate (VI) oxidation reaction over 24 hours

pH	ratio	Initial dizinon concentration [D]	Internal standard concentration [IS]	D signal	IS signal	ratio	Final concentration mg/L
2.1	8:1	10mg/L	7.5mg/L	327	1922	0.170	7.95
3.6	8:1	10mg/L	7.5mg/L	463	2249	0.206	9.62
6.3	8:1	10mg/L	7.5mg/L	86.9	1053	0.083	3.86
8.1	8:1	10mg/L	7.5mg/L	358	2868	0.125	5.83
9.6	8:1	10mg/L	7.5mg/L	1.9	1641	0.001	0.05
11.8	8:1	10mg/L	7.5mg/L	20	1775	0.011	0.53

Table 15. Pseudo first and second order at 20°C

Time (min)	Zero order Concentration (mg/L)	Pseudo 1st order Concentration (mg/L)	Pseudo 2nd order Concentration (mg/L)
0	7.378259	7.378259	7.378259
1	5.612233	7.043016	6.828825
2	4.77327	6.723013	6.35574
3	5.443428	6.41755	5.943957
4	-	6.125966	5.582286
5	5.258249	5.84763	5.262103
6	-	5.581941	4.976657
7	4.5532	5.328323	4.720586
8	-	5.086228	4.489578
9	-	4.855133	4.280124
10	4.700224	4.634538	4.089343
11	-	4.423966	3.914843
12	-	4.222961	3.754626
13	-	4.031089	3.607008
14	-	3.847934	3.470558
15	2.865456	3.673102	3.344056
16	-	3.506213	3.226451
17	-	3.346906	3.116837
18	-	3.194838	3.014426
19	-	3.049679	2.918531
20	2.978972	2.911116	2.82855
21	-	2.778848	2.74395
22	-	2.65259	2.664265
23	-	2.532068	2.589077
24	-	2.417023	2.518016
25	-	2.307204	2.450752
26	-	2.202375	2.386988
27	-	2.102309	2.326457
28	-	2.00679	2.268921
29	-	1.915611	2.214162
30	-	1.828574	2.161984
31	-	1.745492	2.112209
32	-	1.666185	2.064673
33	-	1.590481	2.019231
34	-	1.518217	1.975745
35	-	1.449236	1.934093
36	-	1.383389	1.894162
37	-	1.320534	1.855845

38	-	1.260535	1.819048
39	-	1.203262	1.783682
40	4.123145	1.148592	1.749665
41	-	1.096405	1.716921
42	-	1.046589	1.68538
43	-	0.999037	1.654977
44	-	0.953645	1.625651
45	-	0.910316	1.597347
46	-	0.868955	1.570011
47	-	0.829474	1.543596
48	-	0.791786	1.518054
49	-	0.755811	1.493344
50	-	0.721471	1.469425
51	-	0.68869	1.446261
52	-	0.657399	1.423816
53	-	0.62753	1.402056
54	-	0.599018	1.380952
55	-	0.571801	1.360474
56	-	0.545821	1.340594
57	-	0.521022	1.321287
58	-	0.497349	1.302528
59	-	0.474752	1.284294
60	3.097047	0.453181	1.266563

Table 16. Pseudo first and second order at 31°C

Time (min)	Zero order Concentration (mg/L)	Pseudo 1st order Concentration (mg/L)	Pseudo 2nd order Concentration (mg/L)
0	7.378259	7.378259	7.378259
1	4.935521	6.452944	5.472313
2	6.668997	5.643681	4.348997
3	2.624272	4.935907	3.60831
4	-	4.316895	3.083203
5	2.793148	3.775514	2.691514
6	-	3.302027	2.388128
7	2.524	2.88792	2.146208
8	-	2.525746	1.948793
9	-	2.208992	1.784637
10	1.549167	1.931963	1.645987
11	-	1.689675	1.527328
12	-	1.477773	1.424627

13	-	1.292446	1.334867
14	-	1.13036	1.255748
15	2.120155	0.988602	1.185483
16	-	0.864621	1.122664
17	-	0.756189	1.066168
18	-	0.661356	1.015086
19	-	0.578415	0.968675
20	1.480028	0.505876	0.926322
21	-	0.442434	0.887518
22	-	0.386949	0.851834
23	-	0.338421	0.818908
24	-	0.29598	0.788433
25	-	0.258861	0.760145
26	-	0.226397	0.733817
27	-	0.198005	0.709251
28	-	0.173173	0.686277
29	-	0.151455	0.664744
30	-	0.132461	0.644522
31	-	0.115849	0.625493
32	-	0.101321	0.607556
33	-	0.088614	0.590619
34	-	0.077501	0.574601
35	-	0.067782	0.559429
36	-	0.059281	0.545037
37	-	0.051847	0.531367
38	-	0.045345	0.518366
39	-	0.039658	0.505986
40	1.610179	0.034684	0.494184

Table 17. Activation energy of ferrate (VI) oxidation reaction

Temperature (°C)	Temperature (K)	1/T	k	ln(k)
20	293	0.003413	0.0109	-4.51899
31	304	0.003289	0.0472	-3.05336

Table 18. Methanol effect on HS-SPME detection of diazinon

Methonal concentration (mg/L)	Initial diazinon concentration [D]	Diazinon signal	IS signal	ratio	Final concentration (mg/L)
0	10mg/L	478	1187	0.403	18.82
500	10mg/L	425	1704	0.249	11.65
750	10mg/L	90	839	0.107	5.01
1000	10mg/L	75	900	0.083	3.89