Thesis for the Degree of Master of Engineering

Degradation of Hazardous Organic Contaminants using Ferrate(VI) Synthesized by Wet Oxidation Method

by

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Major of Environmental Engineering

The Graduate School

Pukyong National University

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습식 산화공정 Ferrate(VI)를 이용한 유해 유기 오염물질의 분해특성 연구

Advisor: Prof. Il-Kyu Kim

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Abstract

Trichloroethylene (TCE) and perchloroethylene (PCE) are representative volatile organic compounds that the International Agency for Research on Cancer considers to be a likely carcinogen. Due to being non-inflammable, chemically stable, and an excellent washing solvent, TCE and PCE are frequently used in commercial processes such as machine manufacturing, metal degreasing, and dry cleaning; and as a result, many cases ground water and soil contamination have been reported. 2,4,6-trichlorophenol (TCP) is one of organic contaminants that present in wastewater. This compound is widely used in pesticides, antiseptics and wood preservation and can enter the environment when these products are being made or used. Toxicity studies showed that TCP was carcinogenic to three laboratory animals, causing liver tumors in mice and inducing forms of leukemia/lymphoma in male rats. TCP

also classified as Group B2 (probable human carcinogen) by the United States Environmental Protection Agency. Advanced Oxidation Processes (AOP's) has become interesting technology that many researchers try to develop and improve to overcome many contamination cases. Since late 90's until nowadays ferrate(VI) technology has been developed and discussed as a hazardous organic contaminants degradation material. Degradation of TCE, PCE, and TCP using ferrate(VI) synthesized by wet oxidation method were conducted in closed free head-space reactor. In synthesis, several source of precursors, procedural variations in filtering and variation in concentration of sodium hydroxide (NaOH) were used to obtain the highest concentration of Ferrate(VI) can be produced by wet oxidation method. The Ferrate(VI) produced by optimum condition were applied in the degradation experiment with several parameters such as pH (acid, base and neutral), ferrate(VI) concentration (14, 28, 42, and 56 ppm), target compound initial concentration (0.1, 0.25, 0.5, and 1ppm) and temperature (10^oC, 25^oC, 35^oC, and 45^oC). A second order reaction was observed in the all target compound degradation processes with TCE have more rapidly degraded than PCE while TCP has the higher degradation efficiency. The k_{app} value of TCE was 1,029.8 $M^{-1}s^{-1}$, the k_{app} value of PCE was 315.19 $M^{-1}s^{-1}$, and TCP was 1489.7 $M^{-1}s^{-1}$. Even though activation energy showed that PCE has lower activation energy than TCE in acid condition, TCE was more degraded compare to PCE because PCE

degradation product was TCE. In the pH experiment, neutral condition has identified as the optimum condition for degradation with 70% TCE and 60% PCE removed followed by acid and base condition. TCP optimum condition for degradation was in acid condition with 95% TCP removed. The efficiency of degradation were depend on the amount of ferrate(VI) available on the reactor, this trend was shown in the effect of ferrate(VI) dosage and initial concentration. Degradation efficiency increased as increasing of ferrate(VI) amount or decreasing of target compound concentration. Temperature parameter showed that degradation by ferrate(VI) was significantly affected, since temperature has been reported as one of the most significant parameters that increasing temperature caused an enhancement of the homogeneous ferrate(VI) decomposition kinetics. The optimum temperature was obtained in 25°C and degradation efficiency decreased as temperature increased. Degradation pathways were proposed based on intermediate product identified by GC/MS.

습식 산화공정 Ferrate(VI)를 이용한 유해 유기 오염물질의 분해특성 연구

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요약

Trichloroethylene (TCE)과 perchloroethylene (PCE)은 국제 암 연구소에서 발암 물질로 간주하고 있는 대표적인 휘발성 유기 화합물이다. 불연성이고 화학적으로 안정하며 우수한 세정 용매이기 때문에, TCE와 PCE는 흔히 기계 제조, 금속 탈지, 세정 및 건조와 같은 상업적 공정에서 사용된다. 그 결과로, 지하수 및 토양 오염이 많이 보고되었다. 2,4,6-trichlorophenol (TCP)는 폐수에 존재하는 유기 오염 물질 중 하나이다. 이 화합물은 살충제, 방부제, 목재 보존에 널리 사용되며 이 제품들을 제조 또는 사용하는 경우, 환경에 영향을 줄 수 있다. TCP의 독성에 대한 연구는 쥐에서 간 종양의 원인과 수컷 쥐에서 백혈병/림프종의 형태를 유도하는 등, 세 가지의 동물 실험을 한 결과, 동물에 발암을 일으키는 것으

로 나타났다. TCP는 미국 환경 보호국(EPA)에서 그룹 B2(인체에 발암 가능한 물질)로 분류하였다. 고도산화공정(AOP)은 많은 연구자들이 많은 오염 사례들을 극복하기 위하여 개발하고 개선하기 위해 노력하는 기술이다. 습식 산화 방법으로 합성한 ferrate(VI)를 사용한 TCE와 PCE, TCP의 분해연구는 밀폐시킨 반응기의 윗부분에서 수행하였다. 여러 합성 전구체의 자료에서 수산화 나트륨(NaOH)의 농도 변화와 여과의 절차상의 변화는 습식 산화 방법으로 ferrate(VI)를 제조하여 가장 높은 농도를 얻기 위해 사용하였다. 최적의 조건으로 제조된 Ferrate(VI)는 pH(산, 염기 및 중성)와 Ferrate(VI)의 농도(14, 28, 42, 56 ppm), 표적 화합물의 초기 농도(0.1, 0.25, 0.5, 1ppm), 온도 (10 ℃, 25 ℃, 35 ℃, 45℃)와 같은 몇 가지 변수를 주어 분해 실험에서 적용하였다. TCP는 높은 분해 효율을 갖는 반면, TCE가 PCE보다 더 급격하게 분해되는 2차 반응이 모든 표적 화합물 분해 공정에서 관찰되었다. TCE의 k_{app}값은 1,029.8 $m^{-1}s^{-1}$이었으며, PCE의 k_{app}값은 315.19 $m^{-1}s^{-1}$, TCP의 k_{app}값은 1489.7 $m^{-1}s^{-1}$이었다. PCE는 산성 조건에서의 TCE 보다 낮은 활성화 에너지를 갖는 것으로 나타났음에도 불구하고 PCE 분해 산물이 TCE이기 때문에 TCE는 PCE와 비교할 때 더 분해된 것을 보여주었다. pH 실험에서는 중성 조건에서 70%의 TCE가 제거되고 60%의 PCE가 제거되어 적정 조건임을 확인하였으며, 뒤이어 산성 조건, 그리고 염기 조건임을 확인하였다. TCP가 분해되기 위

한 최적의 조건은 95%의 TCP가 제거되는 산성 조건이였다. 분해효율은 반응기에서 반응한 Ferrate(VI)의 양에 의존되는데, 이러한 추세는 Ferrate(VI)의 양과 표적 화합물의 초기 농도의 영향으로 보여진다. Ferrate(VI)의 양을 증가시키거나 표적 화합물의 농도를 감소시키면 분해 효율은 증가되었다. 온도 매개 변수는 균일한 Ferrate(VI)의 분해 반응 속도의 향상에 의해 온도가 증가하므로 가장 중요한 변수 중 하나로 보고되었기 때문에, Ferrate(VI)에 의한 분해에 중요하게 영향을 받는 것으로 나타났다. 최적 온도는 25 ℃이며, 온도가 증가할수록 분해 효율이 감소했다. 분해 경로는 GC/MS에 의해 확인된 중간 생성물을 기반으로 제시하였다

I. Introduction

1.1 Ferrate(VI)

Iron (Fe) commonly exists in the +2 (ferrous) and +3 (ferric) oxidation states. Under strong oxidizing environments, iron moves to higher oxidation states such as +6 (ferrate). Hexavalent iron or ferrate(VI) is a strong oxidizing chemical throughout the entire pH range, from 2.2 V in acid and 0.7 V in base (Sharma, V. K., 2003), as listed in the following equations:

$$FeO_4^{2-} + 8H^+ + 3\,e^- \quad Fe^{3+} + 4H_2O \qquad E^o = 2.2\ V$$

$$FeO_4^{2-} + 4H_2O + 3e^- \, Fe(OH)_3 + 5OH^- \qquad E^o = 0.7\ V$$

Fe(VI) oxidation with a large number of organic compounds has been studied and it has been shown that Fe(VI) is a selective oxidant (Carr et al., 1985, Li, C., Li, X. Z., and Graham, N., 2005). In aqueous solutions, the infrared spectrum of ferrate is consistent with a tetrahedral geometry (Griffith, 1966) and isotopic oxygen exchange studies have indicated that all oxygen are kinetically equivalent (Goff and Murmann, 1971). From the knowledge that metal-oxygen bonds were strongly polarized (Howard and Parkin, 1994), it can be concluded that the ferrate ion is best visualized as a positively charged iron cation surrounded by four equivalent oxygen, each bearing a partial negative charge; i.e. a resonance hybrid of three canonical structures, a-c, as shown in Figure 1.

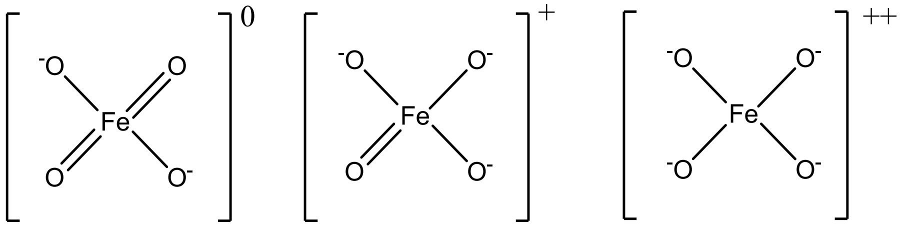


Figure 1 Ferrate structure (Norcross *et al.,* 1997)

In aqueous solution, the ion remains monomeric, and its four oxygen atoms become equivalent and exchange slowly with the solvent (Goff and Murmann, 1971). In acidic or neutral solution the ferrate ions are quickly reduced by water. Oxygen is evolved, and ferric complexes and precipitating hydrous iron (III) oxide, are formed.

Table 1 shows the comparison of reduction potential of Ferrate(VI) with other oxidant used in water treatment processes. Ferrate(VI) has the higher oxidation potential with the widest range of pH. Ferrate(VI) became the most prominent technology in AOP’s technologies.

Table 1. Comparison of Reduction Potential of Fe(VI) with Oxidants Used in Water Treatment

Oxidants	pH	Reaction	Potential, V
Ferrate	acidic	$FeO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Fe^{3+} + 4H_2O$	2.20
	basic	$FeO_4^{2-} + 4H_2O + 3e^- \Leftrightarrow Fe(OH)_3 + 5OH^-$	0.70
Hypochlorite	acidic	$HClO + H^+ + 2e^- \Leftrightarrow 2Cl^- + H_2O$	1.48
	basic	$ClO^- + H_2O + 2e^- \Leftrightarrow 2Cl^- + 2OH^-$	0.84
Ozone	acidic	$O_3 + 2H^+ + 2e^- \Leftrightarrow O_2 + H_2O$	2.08
	basic	$O_3 + H_2O + 2e^- \Leftrightarrow O_2 + 2OH^-$	1.24
Hydrogen peroxide	acidic	$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O$	1.78
	basic	$H_2O_2 + 2e^- \Leftrightarrow 2OH^-$	0.88
Permanganate	acidic	$MnO_4^- + 4H^+ + 3e^- \Leftrightarrow MnO_2 + 2H_2O$	1.68
	basic	$MnO_4^- + 2H_2O + 3e^- \Leftrightarrow MnO_2 + 4OH^-$	0.59

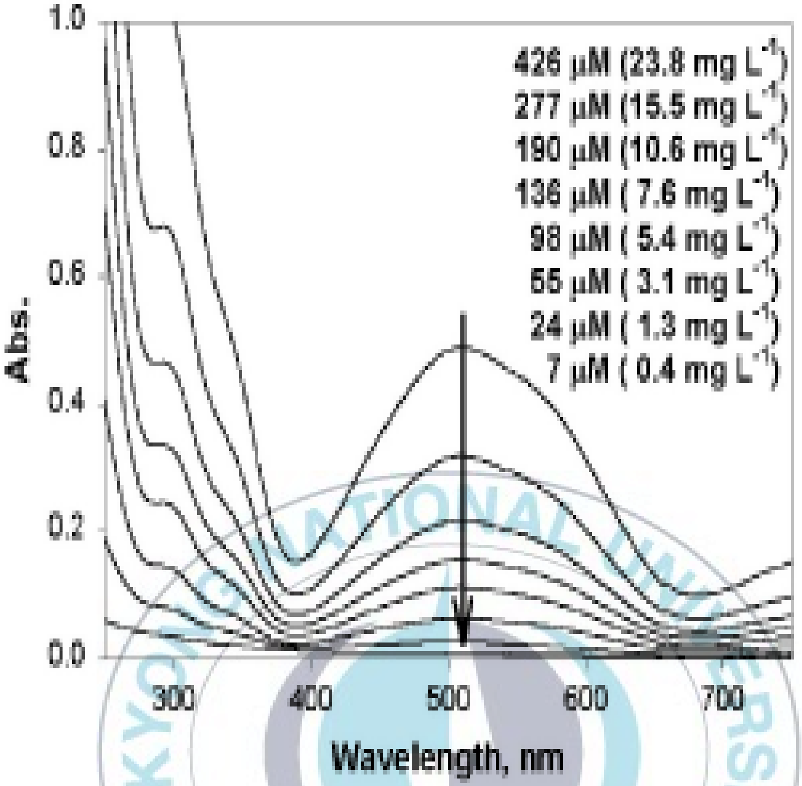


Fig. 2 UV/Vis absorption spectrum of Fe(VI) in aqueous solution as function of its concentration, pH= 9.2, 25 mM phosphate buffer

Ferrate(VI) has the characteristic red-violet color in aqueous solution. Fig. 2 shows the UV/Vis absorption spectrum in phosphate buffer solution (pH 9.2), 25 mM phosphate buffer (Y.H. Lee, M. Cho, and J. Yoon, 2003). The spectrum has its maximum absorption at wavelength of 510 nm and the molar absorption coefficient at this wavelength in 1150 $M^{-1}cm^{-1}$.

1.2 Synthesis of Ferrate

As early as 1702, it was mentioned by the German chemist and physician Stahl the appearance of an unstable purplish red colour when the molten mass (mixture of saltpetre and iron) was dissolved in water. In 1834, Eckeberg and Becquerel both found that a solid resulting from the fusion of iron oxide with potassium hydroxide when dissolved in water, formed a purplish red color solution, which decomposed with the evolution of oxygen. It was not until 1844 though, when Fremy suggested a formula of the Fe03 to the unknown purplish-red compounds described above. Fremy was the first to form ferrate in solution by passing chlorine gas through a concentrated solution of potassium hydroxide containing ferric oxide. The equation for synthesis of this method was shown by:

$$Fe_2O_3.3H_2O + 10\ KOH + 3\ Cl_2 \rightarrow 2\ K_2FeO_4 + 6\ KCl + 8\ H_2O$$

In 1897, Moeser was the first to write a detailed review of ferrates and their chemistry describing three methods of preparation of potassium ferrate, namely:

- Dry method - heating to red various potassium- and iron-containing minerals. Dry reactions imply detonation and elevated temperatures, which are considered dangerous and too difficult to implement;

- Electrochemical method - electrolyzing a potash solution with an iron anode. This method remains another access to ferrates that has retained only marginal interest. Ferrate (VI) was prepared in an electrochemical way for the first time as early as 1841 by Poggendorf. Since then, it has benefited from recent improvements though, such as superposition of an alternative current to the direct current for electrolysis (Bouzek et al.,1998) and;

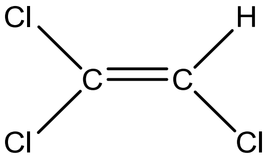
- Wet method - oxidizing a basic solution of a Fe (III) salt by a hypochlorite or hypobromite. Among the above three approaches, the wet method was the primary one in the 20' century. In 1948, Schreyer prepared potassium ferrate by bubbling chlorine through a potassium hydroxide solution containing a suspension of hydrous ferric oxide.

1.3 Trichloroethylene (TCE)

Trichloroethylene (TCE) is a volatile organic compound that has been proven to cause liver damage and kidney failure in humans and was assessed as carcinogenic to animals. TCE is produced worldwide in very large quantities due to its extensive use in the chemical industry. Trichloroethylene is also used as an extraction solvent for greases, oils, fats, waxes, and tars, a chemical intermediate in the production of other chemicals, and as a refrigerant (E.C. Butler, K.F. Hayes, 1999). Leakage from storage tanks and, sometimes, improper disposal practices led to soil, groundwater, and surface water contamination with TCE. Consequently, trichloroethylene is listed as a priority pollutant on the U.S. EPA Chemical Contaminant List and is strictly regulated in drinking water to a maximum contaminant level of 0.005mg/L (EPA-USA, 2012)

Table 2 chemical identity of TCE

Characteristic	**Trichloroethylene**
synonyms	Acetylene trichloride Ethylene trichloride 1-chloro-2,2-dichloroethylene 1,1-dichloro-2-chloroethylene Ethinyl trichloride Trichloroethene 1,1,2-trichloroethylene 1,1,2-trichloroethene
Molecular formula	C_2HCl_3, $ClHC=CCl_2$

Chemical structure	
CAS number	79-01-6
Molecular weight	131.39
Freezing point	-73°C
Boling point	87°C
Density	1.46 g/cm^3 (liquid) at 20°C
Solubility in water	1.280 g/L (25°C)
Appearance	Colorless liquid

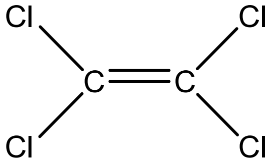
1.4 Perchloroethylene (PCE)

Perchloroethylene (PCE) is a representative volatile organic compound that the International Agency for Research on Cancer considers to be a likely carcinogen. Due to being non-inflammable, chemically stable, and an excellent washing solvent [Martha, W., Susan, B., Lorraine, Y.S., Margaret, N. F., 1983], PCE is frequently used in commercial processes such as machine manufacturing, metal degreasing, and dry cleaning. The primary effects from chronic (long term) inhalation exposure are neurological, including impaired cognitive and motor neurobehavioral performance.

Perchloroethylene exposure may also cause adverse effects in the kidney, liver, immune system and hematologic system, and on development and reproduction. Studies of people exposed in the workplace have found associations with several types of cancer including bladder cancer, non-Hodgkin lymphoma, and myeloma (EPA-USA, 2012).

Table 3 chemical identity of PCE

Characteristic	**Perchloroethylene**
synonyms	Perchloroethene Tetrachloroethylene

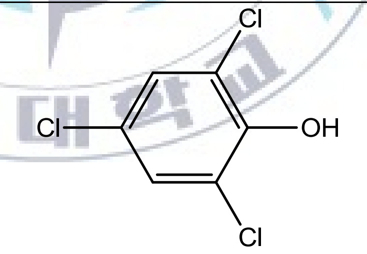
Molecular formula	C_2Cl_4, $Cl_2C{=}CCl_2$
Chemical structure	
CAS number	127-18-4
Molecular weight	165.83
Freezing point	-19°C
Boling point	121.1°C
Density	1.622 g/cm^3 (liquid) at 20°C
Solubility in water	1.5 g/L (25°C)
Appearance	Colorless liquid

1.5 2,4,6-Trichlorophenol (TCP)

2,4,6-Trichlorophenol is a chlorinated phenolic compound that exists at room temperature as colorless to yellow crystals with a strong phenolic odor (IARC 1979, 1999, HSDB 2009). It is practically insoluble in water but soluble in ethanol, diethyl ether, hot acetic acid, benzene, carbon tetrachloride, methanol, Stoddard solvent, toluene, and turpentine. It is stable under normal temperatures and pressures (Akron 2009). Physical and chemical properties of 2,4,6-trichlorophenol are listed in the following table.

2,4,6-Trichlorophenol has been used primarily in various pesticide formulations and as a wood preservative. It has been used as a fungicide, glue preservative, insecticide, bactericide, defoliant, herbicide, and anti-mildew agent for textiles. The routes of potential human exposure to 2,4,6-trichlorophenol are inhalation, ingestion, and dermal contact. The general population may be exposed to 2,4,6-trichlorophenol through ingestion of contaminated food or water or inhalation of contaminated air (IARC 1979, HSDB 2009). According to the National Cancer Institute (NCI 1979), substantial exposure of the general population was questionable; however, residues may be present throughout the environment, because 2,4,6-trichlorophenol was widely used as a pesticide. 2,4,6-Trichlorophenol can also form when industrial wastewater containing phenol or certain aromatic acids is treated with hypochlorite or during the disinfection of drinking-water sources.

Table 4 chemical identity of TCP

Characteristic	**2,4,6-Trichlorophenol**
synonyms	TCP Phenachlor Dowicide 2S
Molecular formula	$C_6H_2Cl_3OH$
Chemical structure	
CAS number	88-06-2
Molecular weight	197.5
Melting point	69 °C

Boling point	246°C
Density	1.4901 g/cm^3 (liquid) at 20°C
Solubility in water	0.008 g/L (25°C)
Appearance	Colorless to yellow crystals

II. Materials and Methods

2.1 Materials

All chemicals used were reagent grade or higher purity reagent. For synthesis ferrate(VI) iron source obtain from $Fe(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ all from Junsei chemicals Japan. As oxidizing agent sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) all chemicals also provided by Junsei Japan was used in this experiment.

and $Na_2HPO_4.12H_2O$ from Crown reagent Japan was used for buffer solution in the ferrate concentration measurement by Spectrophotometer Hach DR5000. Trichloroethylene (TCE) was provided by Wako Pure Chemical Industries (Ltd., Japan) and Perchloroethylene (PCE) by Daejung Chemical with extra pure grade. 2,4,6-Trichlorophenol (TCP) was purchased by Aldrich. Nitrogen gas for GC-ECD was supplied from Daesung Industrial Gases with 99.999% concentration of purity. HCl for controlling pH condition obtained from crown reagent Japan was used. Mercuric Thiocyanate solution and Ferric Ion solution both was purchased from Hach reagent. Filter paper Whatman 110 mm diameter and distilled water also used in this study.

2.2 Methods

2.2.1 Synthesis of ferrate(VI)

This experiment procedure started with adding sodium hydroxide (NaOH) to the hypochlorite solution (NaOCl) until all sodium hydroxide dissolved and well mixed. To the solution Fe-source were added and as the results ferrate(VI) produced. Ferrate(VI) generated from synthesis then analyzed using spectrophotometer DR 5000, HACH Company at 505 nm in buffer solution. Three different sources were used including $Fe(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$. Different treatment such as filtering and no-filtering mixture of sodium hydroxide and hypochlorite was carried out to examine the effect to the concentration ferrate

Another study was variation of sodium hydroxide (NaOH) concentration as the oxidizing agent. All variations done in this experiment in order to obtain the highest concentration of ferrate (Fe^{6+}) in the solution using wet oxidation method.

2.2.2 TCE and PCE stock solution preparation

TCE and PCE stock solution were made in 1 ppm concentration by stirring and heating for 2 days. Both compounds were very slightly soluble in water. Stock of target compounds was prepared in a stirred glass flask, which was sealed by Teflon-covered rubber stopper to prevent organic vapor from escaping, by dissolving a given amount of this organic chemical in deionized water it took several days to complete the dissolution. Heating and stirring help compounds to dissolve more easily.

2.2.3 Degradation experiment

The experiment was carried out in closed zero-head space glass reactor, sealed with Teflon covered rubber stoppers and operated in the batch mode Fig. 3. In this experiment pH, initial concentration of TCE, ferrate dosage and temperature has been studied as a variation condition to determine the degradation process of TCE.

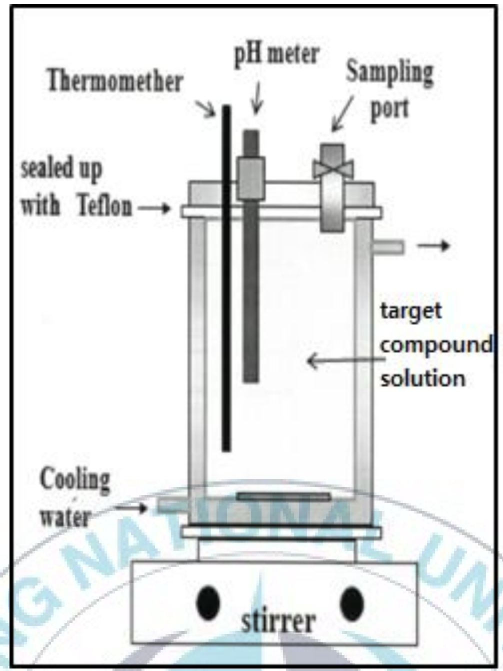


Fig. 3 Reactor for Degradation Experiment

In the variation condition for pH 3 different conditions were carried out from acid pH 3-4, neutral 6.5-7.5, and base 9-11. For the ferrate dosage variations were started with 14 mg/L, 28 mg/L, 42 mg/L, and 56 mg/L, while in the initial concentration of target compound variations starting from 0.1, 0.25, 0.5 and 1 mg/L. Temperature experiment varied from 10^{o}C, 25^{o}C, 35^{o}C and 45^{o}C. To measure the TCE concentration remained after degradation, Agilent Gas Chromatograph with ECD was used. The GC-ECD used HP-5 column with 15m length 0.53 I.D 1.5micrometer film coating from J&W Scientific USA. Temperatures hold in 35^{o}C for 5 minutes and then increased with 5^{o}C/min until 50^{o}C and hold for 1 minute. Inject temperature was 100^{o}C and detect temperature was 200^{o}C. Sample from degradation were volatilizing using vortex for one minute before injected to the GC-ECD.

2.2.4 TCE and PCE Intermediate study and degradation pathway

This experiment was performed to find out the intermediate product from degradation of TCE and PCE by ferrate(VI). Sample from the degradation reactor were analyzed using GC/MS Mass Spectrometer Systems (GCMS-QP2010Plus, Shimadzu, Japan) and AT-1 capillary column (60m x 0.32mm I.D x 1.0micrometer film thickness). To prevent further degradation by ferrate, sample taken from reactor were quenched using NaOH.

2.2.5 Cl^- Formation on the TCP Degradation

This experiment was to provide information about degradation of Cl from TCP and formation of Cl^- as the result of the degradation. The analysis Cl- generated from degradation in reactor using UV-Vis Spectrophotometer

DR-5000 from Hach Company. In this experiment, TCP degradation conduct at acid condition in the ferrate(VI) dosage was 0.23mM with initial concentration 1 ppm 25^{o}C. The method to determine concentration of Cl- was based on standard method in the UV-Vis Spectrophotometer.

III. Results and Discussion

3.1 Synthesis of ferrate(VI)

In the synthesis of ferrate(VI), previous experiment showed that from different source of precursor different concentration of a ferrate(VI) will be occurred. Thompson et al. 1951 tried some experiment conduct to various kind source of precursor in his experiment [Chengchun, J., chen, L., Shichao, W., 2008]. This study were used three kind of precursor to compare, $Fe(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$. Wet oxidation method use the oxidizing agent such strong oxidant to transform iron (Fe) from low oxidation states to the highest oxidation states [Chengchun, J., chen, L., Shichao, W., 2008]. The mixture of this to compound has a powerful energy, but when sodium hydroxide added to the hypochlorite solution a lot of foam and colloidal solution appeared in the mixture. In the variation of sources the highest concentration was obtained in the $FeCl_3.6H_2O$ as the precursor with 27.08 ppm (in thousand) followed by $FeSO_4.7H_2O$ and $Fe(NO_3)_3.9H_2O$. To determine the effect of the foams in the ferrate(VI) production, variation of filtering and no-filtering was carried out. The results of this variation of procedure has determine that no-filtering procedure have higher concentration since filtering will remove some of oxidant agent to transform iron into 6+ ion state. Oxidizing process is the key of making iron (Fe) in the high oxidation states. The concentration of sodium hydroxide (NaOH) as the oxidizing agent should be investigated to obtain the information about optimum condition in making high concentration of ferrate(VI) [Sharma, V. K., 2003]. The variations were started from 7, 9, 11,13 and 15 M. From the experiment the optimum variation of sodium hydroxide for synthesis of ferrate(VI) was 13 M with the concentration 70,870 ppm (Fig. 4).

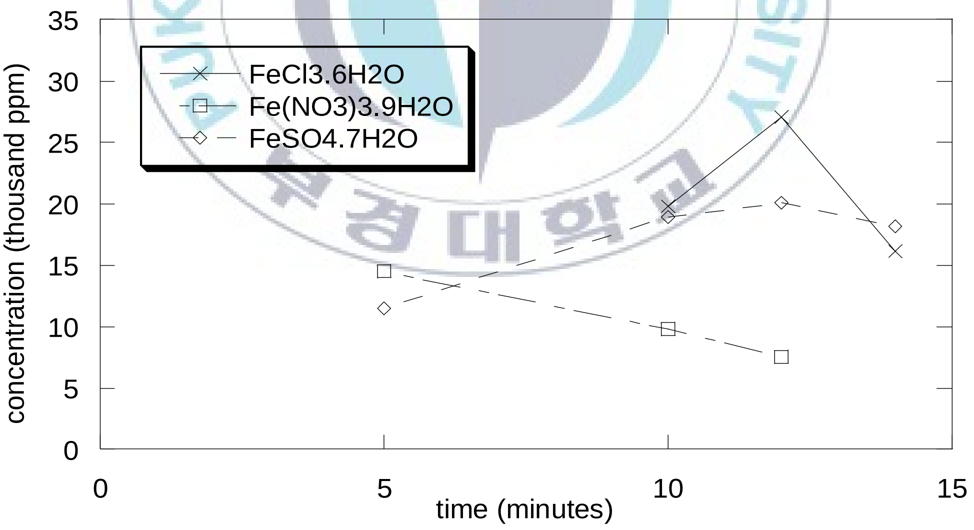


Fig. 4 Ferrate concentration in various kind of precursor, 300 mL NaOCl and 180 g NaOH

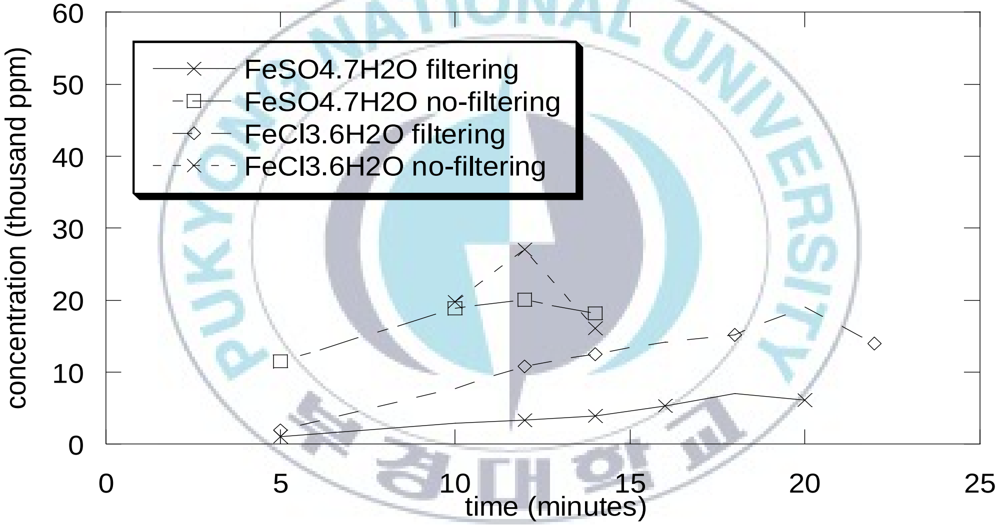


Fig. 5 Ferrate concentration with filtering and no-filtering in 300 mL NaOCl and 180g NaOH

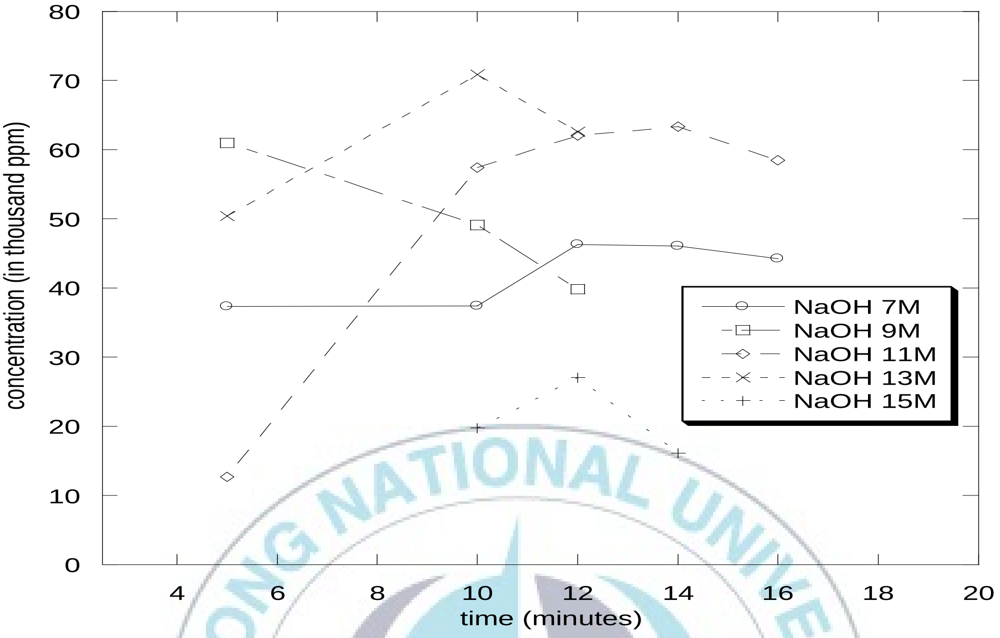


Fig. 6 Ferrate concentration with concentration variation of sodium hydroxide experiment conditions: 20 g $FeCl_3.6H_2O$, 300 mL NaOCl

Fig. 5 was the effect of filtering and no-filtering in the production of ferrate(VI) in two different sources. Fig. 6 was ferrate(VI) concentration by NaOH variation.

The best condition on the synthesis of ferrate was obtained with 13M NaOH using $FeCl_3.6H_2O$ as the precursor and without filtration. By this condition ferrate(VI) for the degradation experiment were produced.

3.2 Degradation experiment

Ferrate(VI) generated from the synthesis were used to degrade TCE and PCE in closed zero-head space glass reactor figure 3. In order to obtain the greatest amount of TCE and PCE degraded from the reactor, several parameters were carried out such as pH, ferrate dosages, target compound initial concentration and temperature. All experiment will provide information about the effect of every parameters to the degradation efficiency of TCE and PCE degraded by ferrate(VI). The degradation efficiency rates were measured by approaching ferrate degradation with target compounds and the ferrate degradation by itself as the ferrate exposure.

3.2.1 Effect of pH

pH condition was one of the most important parameter in the degradation of ferrate(VI) [Schreyer, J. M., Ockerman, L. T., 1952]. Technical literature suggests that Ferrate oxidation proceeds more efficiently at pH lower than 10 [Li, C., Li, X. Z., and Graham, N., 2005] because the maximum stability of Ferrate is at pH 10 [Li, C., Li, X. Z., and Graham, N., 2005]. Ferrate(VI) ion reduced rapidly to Fe (III) and oxygen in strong acids, while the oxygen ligand of ferrate(VI) exchanged very slow with water at pH 10 [Sharma, V. K., 2003, Sharma, V. K., 2010]. In the pH experiment C_0 of the target compound was 1 ppm while ferrate(VI) was 0.5 mL (±28 mg/L) in the temperature of 25^{o}C. The variation carried out in acid condition pH 3-4, neutral condition pH 6.5-7.5, and base condition pH 9-11.

3.2.1.1 Acid condition

Ferrate(VI) generated from synthesis has very high concentration of hydroxide (OH^-) to control pH in this experiment hydrochloric acid was used. HCl was added to the solution in reactor before ferrate(VI) added. In acid condition more hydrochloric acid added than in neutral condition. Acid condition set in the pH ranging from 3 to 4.

In acid condition, TCP was observed to be more degraded than in other pH variation experiment with 95% TCP degraded. In the present study, the ionic species of phenol is predominant when the pH exceeds 10.0 (equal to pKa value of phenol at 25 ºC), but the molecular species predominates when pH is less than the pKa. The fraction in the molecular state of phenol was larger when the pH was smaller [Graham, 2004].

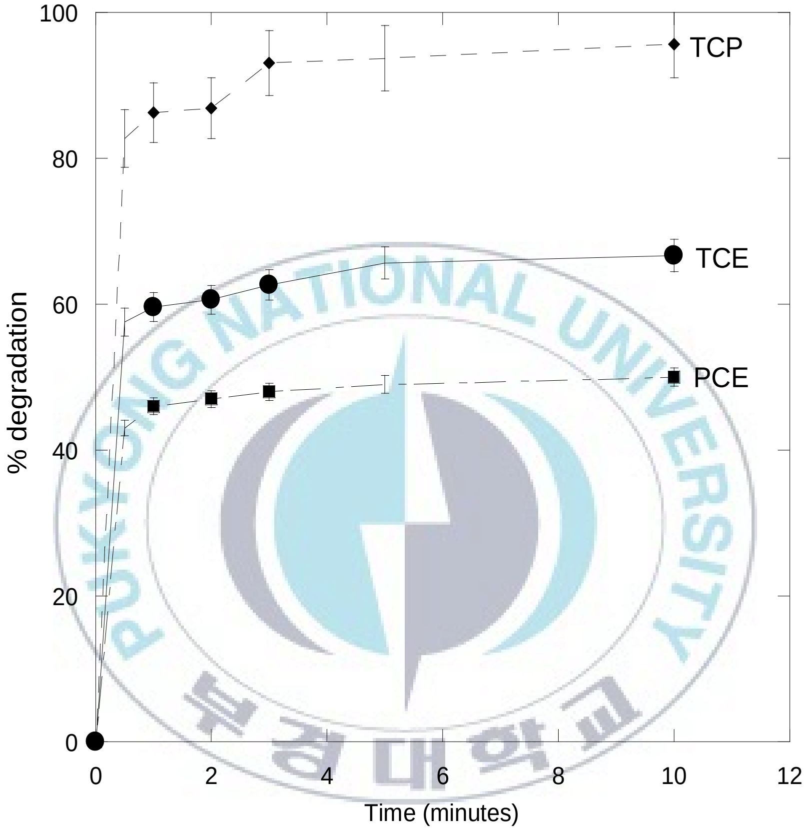


Fig. 7 Target compounds degradation in pH acid variation, $C_o = 1$ppm,

Ferrate concentration 28 ppm

3.2.1.2 Neutral condition

In the experiment for neutral condition, degradation efficiency was observed as the highest compare to acid and base condition for TCE and PCE. Neutral condition has more difficulties to obtained since pH was very sensitive parameter even though very slightly different amount of HCl and ferrate(VI) were added it would be create lot of differences in the pH condition. Neutral condition experiment was set at pH 6.5 to 7.5.

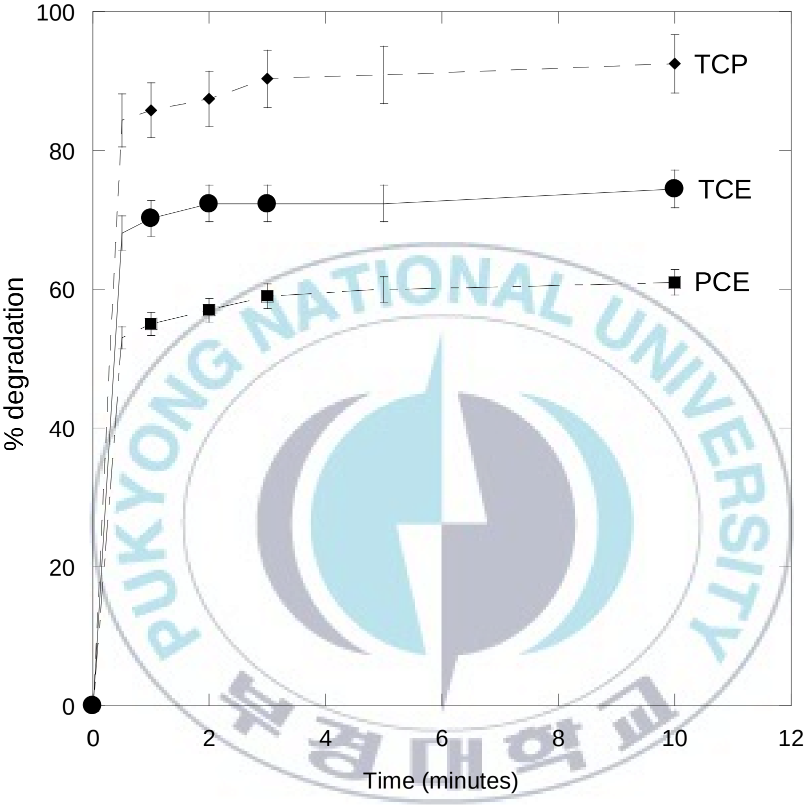


Fig. 8 Target compounds degradation in pH Neutral variation, $C_o = 1$ppm, Ferrate concentration 28 ppm

3.2.1.3 Base condition

For the basic condition, since ferrate(VI) has high hydroxide and high pH condition hydrochloric acid was not used. The range of pH for this experiment was 9-11. Compare to other parameter, base condition has the lowest degradation efficiency. In the basic condition ferrate(VI) has the lower energy and more stable as the effect of this status ferrate(VI) degrade less target compound.

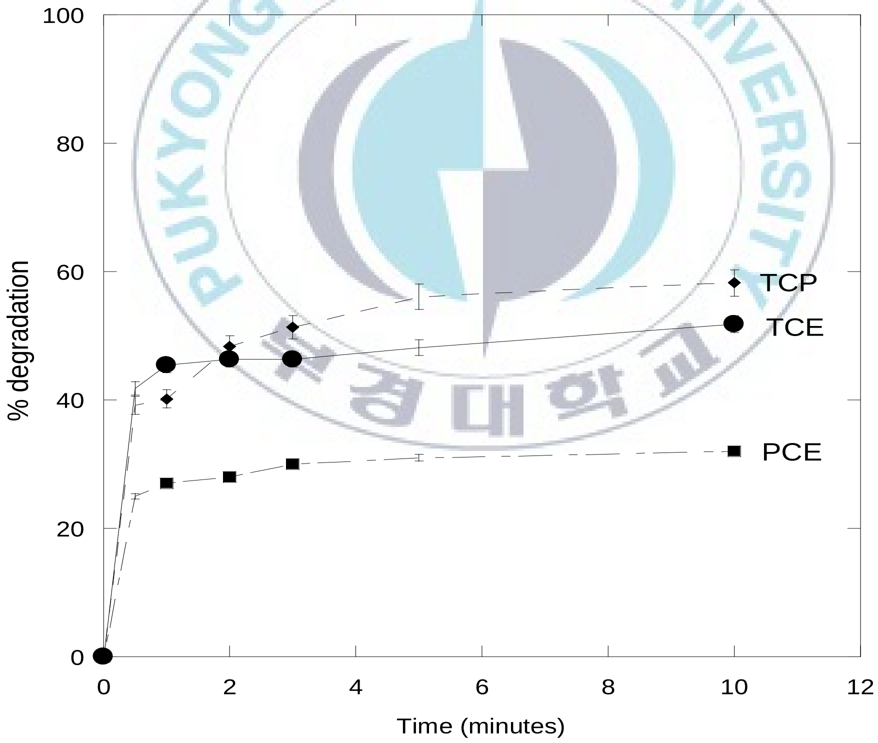


Fig. 9 Target compounds degradation in pH base variation, $C_o = 1$ppm, Ferrate concentration 28 ppm

In the pH experiment ferrate (FeO_4^{2-}) decomposed very fast as decreasing of pH. From the experiment in pH acid, ferrate(VI) decomposed 34-40% and pH neutral 25-29% decomposed during first 30 second. According to the previous studies on ferrate(VI) reaction with organic compound, second order reaction rate obtained [Yang Bin, Ying Guang-Guo Zhang Li-Juan, 2011]. Second order reaction rate law can be described by eq (1).

$$-d[\text{Target Compound}]/dt = k_{app}[FeO_4^{2-}][\text{ Target Compound}] \qquad (1)$$

Eq(1) is rearranged and d[Target Compound]/dt is integrated to become

$$\text{Ln}(\text{Target Compound}]/[\text{ Target Compound}]_0) = -k_{app}\int_0^t [FeO_4^{2-}]\,dt$$

Where, $\int_0^t FeO_4{}^{2-}$ is concentration of ferrate(VI) exposure, and the k_{app} is the apparent second order reaction rate constant [Yang Bin, Ying Guang-Guo Zhang Li-Juan, 2011, V. K. Sharma, 2013, Yang Bin, Ying Guang-Guo, 2011].

The value of k_{app} could be obtained by plotting the natural logarithm of target compounds concentration (ln C/C_o) vs. the ferrate exposure (Fig.10, 11, and 12). From this plotting, the rate of degradation process could be determined. This approaching method was used to measure all k_{app} in different variation of parameters from the degradation experiment including temperature variations.

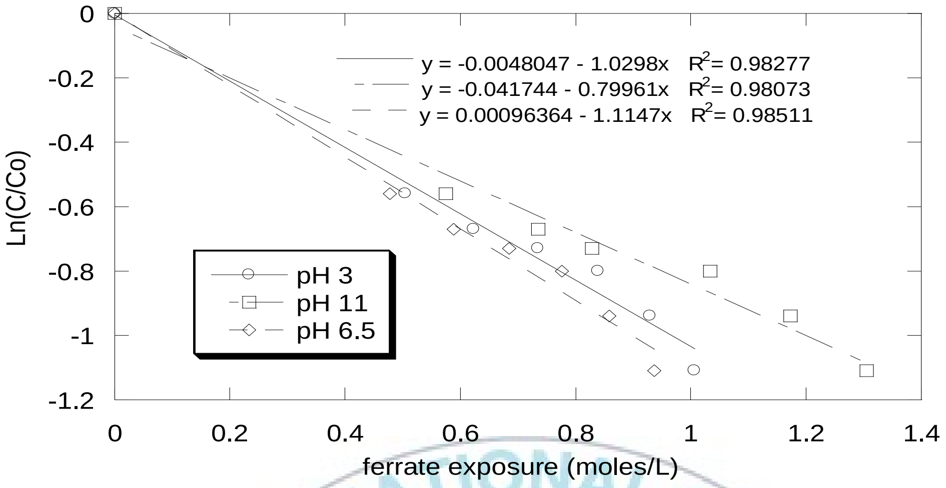


Fig. 10 Ferrate exposure plot versus concentration in the determination of k_{app} value TCE degradation by ferrate(VI).

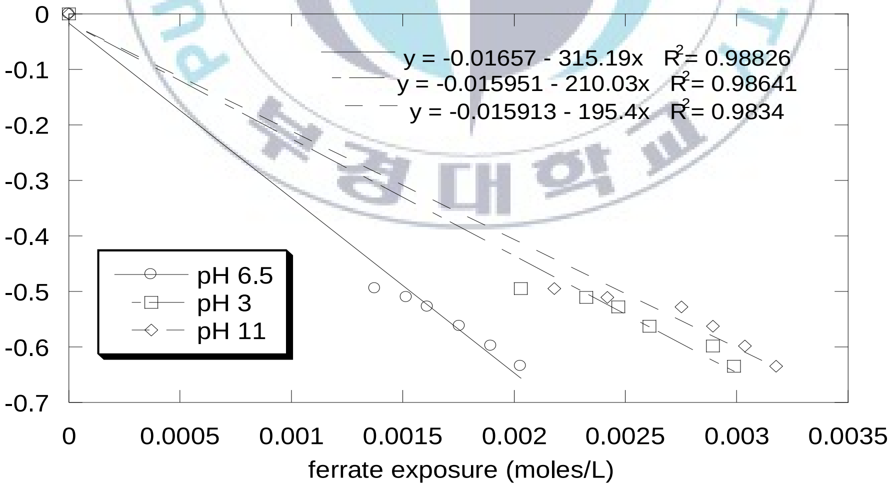


Fig. 11 Ferrate exposure plot versus concentration in the determination of k_{app} value PCE degradation by ferrate(VI).

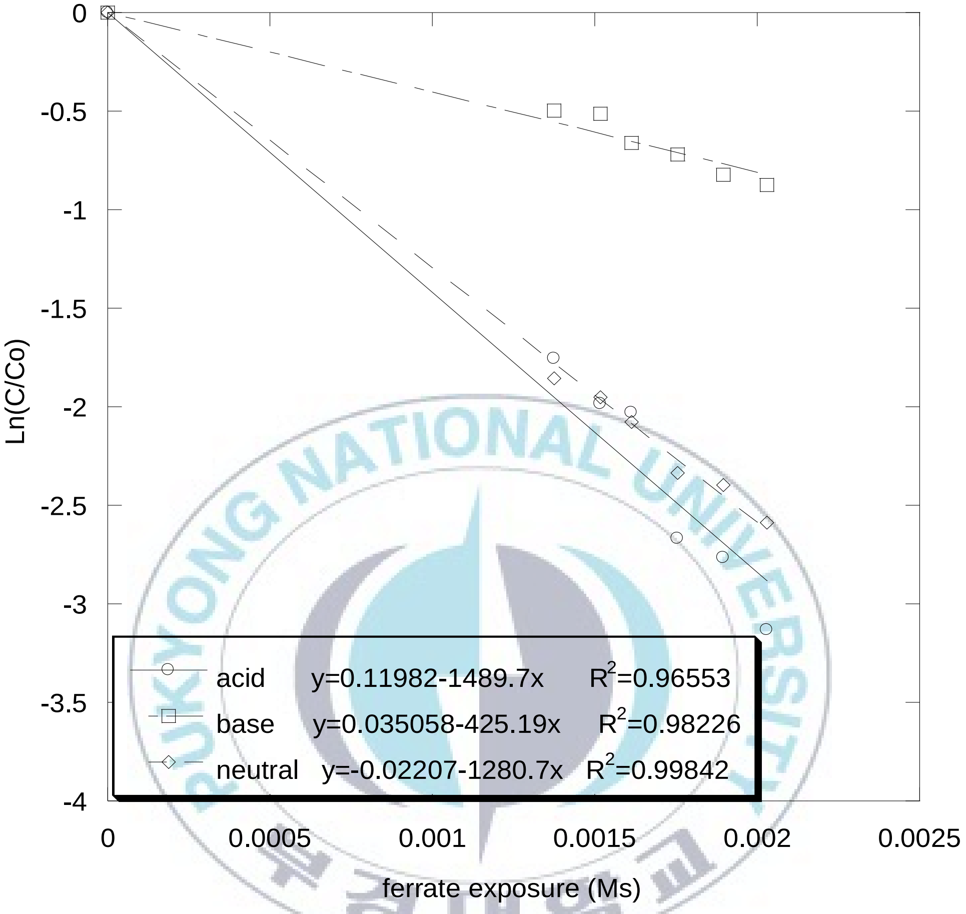


Fig. 12 Ferrate exposure plot versus concentration in the determination of k_{app} value TCP degradation by ferrate(VI).

TCE has higher degradation efficiency compare to PCE. The k_{app} value showed that TCE has higher rate than PCE. In neutral condition k_{app} value TCE was 1,114.7 $M^{-1}s^{-1}$with 70% TCE degraded in the reactor while PCE k_{app} value was 315.19 $M^{-1}s^{-1}$. Compared to TCE and PCE, TCP has more high degradation efficiency. The k_{app} value 1,489.7 $M^{-1}s^{-1}$ with 95% TCP degraded in the reactor, TCP was observed greatly removed by ferrate(VI).

Even though pH neutral showed the highest degradation efficiency, the pH controlling was very difficult at neutral condition. Acid condition was used for other parameter experiments. For TCP as acid condition was observed to be optimum condition for degradation, for the next parameter TCP also proceed in acid condition.

3.2.2 Effect of ferrate(VI) dosage

Another important factor in the degradation was ferrate(VI) dosage. The amount of the ferrate(VI) put on the reactor will definitely affect in the degradation efficiency. The ferrate dosage experiments were used dosage varies from 56 mg/L, 42 mg/L, 28 mg/L and 14 mg/L. Target compounds Degradation by each variations show linear trend, as increasing ferrate(VI) dosage will increase the degradation efficiency to degrade the target compounds. The effect of the ferrate dosage on the degradation of TCE is shown in Fig.13, in Fig. 15. for PCE and Fig. 17 for TCP. The degradation of Target compounds were strongly depend on the dosage of ferrate(VI) added to the reactor [Yu Myongjin, Park Guisu, and Kim HyunoOk, 2008] more ferrate(VI) added more TCE and PCE degraded. The initial concentration (C_0) was constant in this experiment. From this experiment degradation of TCE showed more degraded than PCE but compare to TCP, TCP has the highest degradation efficiency. The amount of the ferrate(VI) put on the reactor will definitely affect in the degradation efficiency. The increasing of degradation efficiency was because the ferrate(VI) dosage increased, which increasing the amount of ferrate available for degradation. Ferrate(VI) is a stronger oxidant upon protonation; the reaction rate is expected to increase [Wust, Wolfgang. F., Kober, Ralf.,Schlicker, Oliver., and Dahmke, Andreas., 1999, V. K. Sharma, 2013]. With the increasing of ferrate dosage the efficiency on the degradation was observed increase. Fig. 14, Fig. 16, and Fig. 18 informed the target compounds degradation in mg/L for every variation of ferrate(VI) dosage.

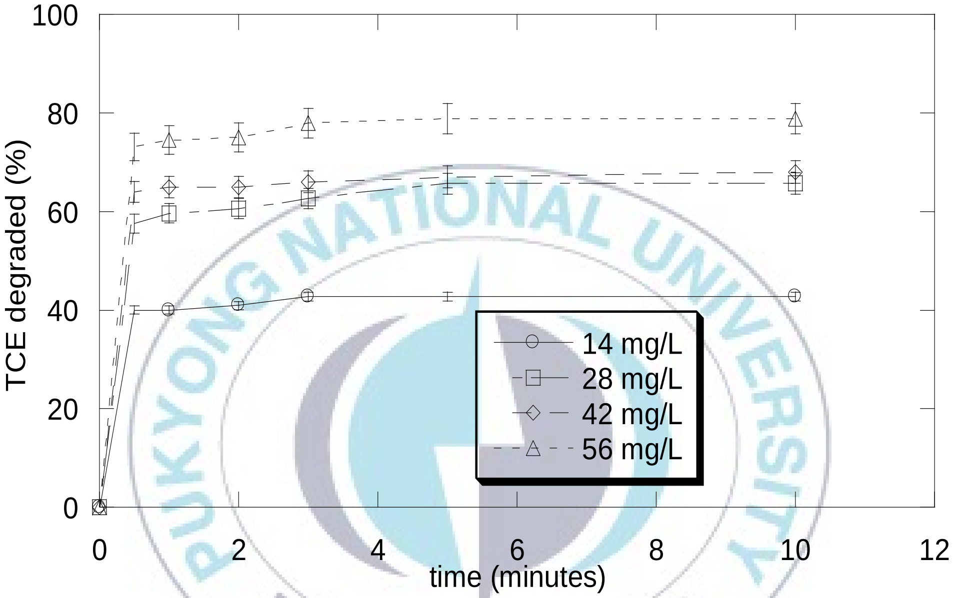


Fig. 13 TCE degradation (%) in Ferrate dosage variation, pH 3-4 with 1 ppm initial concentration

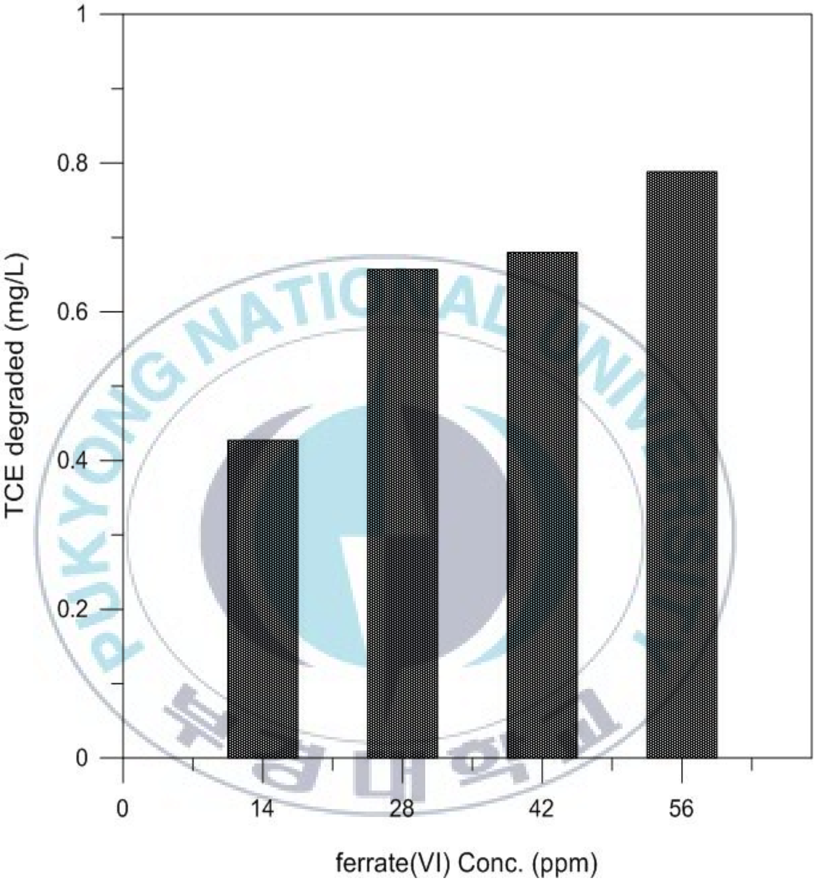


Fig. 14 TCE degraded (mg/L) in ferrate dosage variations, pH 3-4 with 1 ppm initial concentration

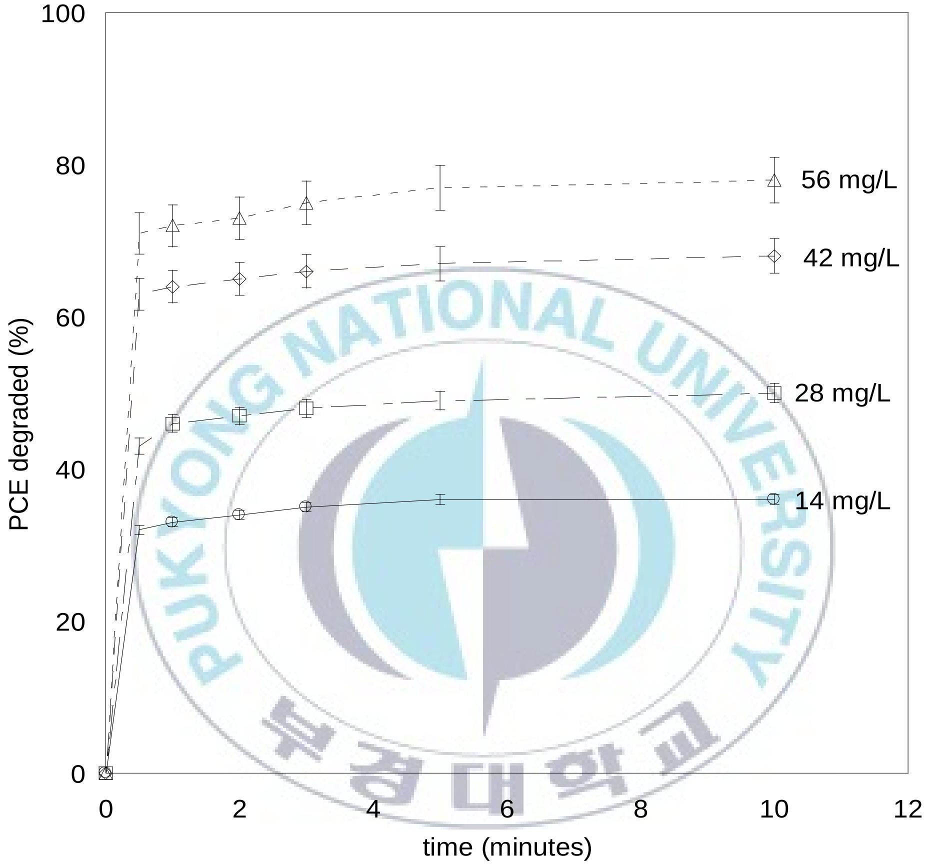


Fig. 15 PCE degradation (%) in Ferrate dosage variation, pH 3-4 with 1 ppm initial concentration

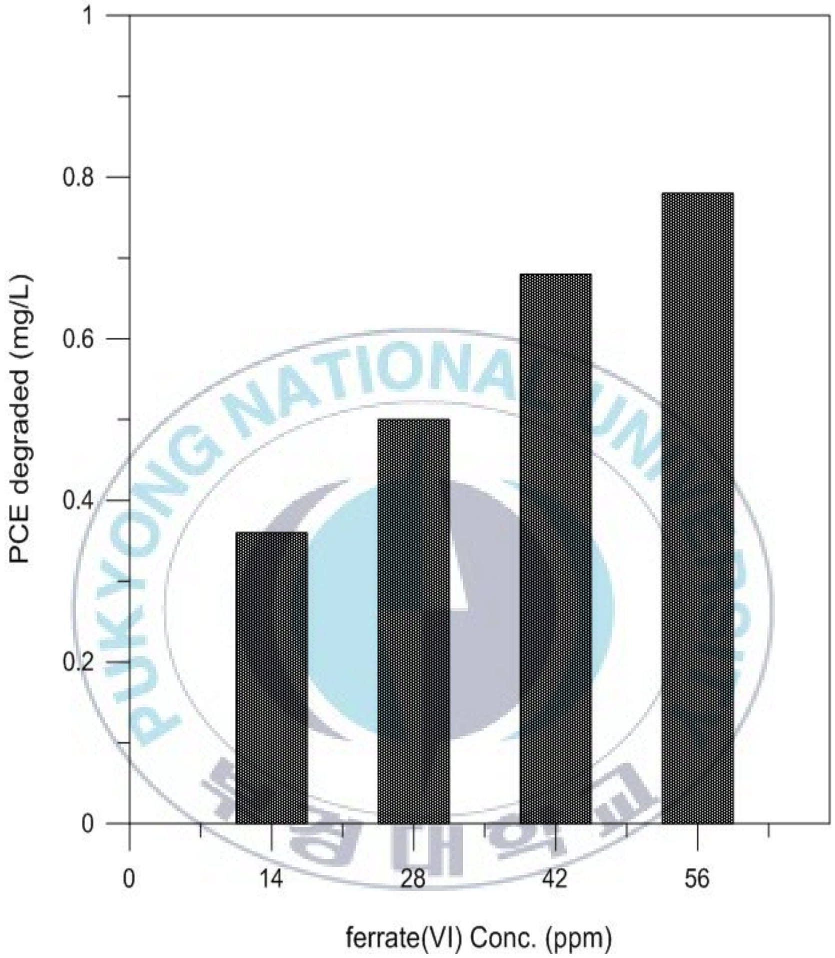


Fig.16 PCE degraded (mg/L) in ferrate dosage variations, pH 3-4 with 1 ppm initial concentration

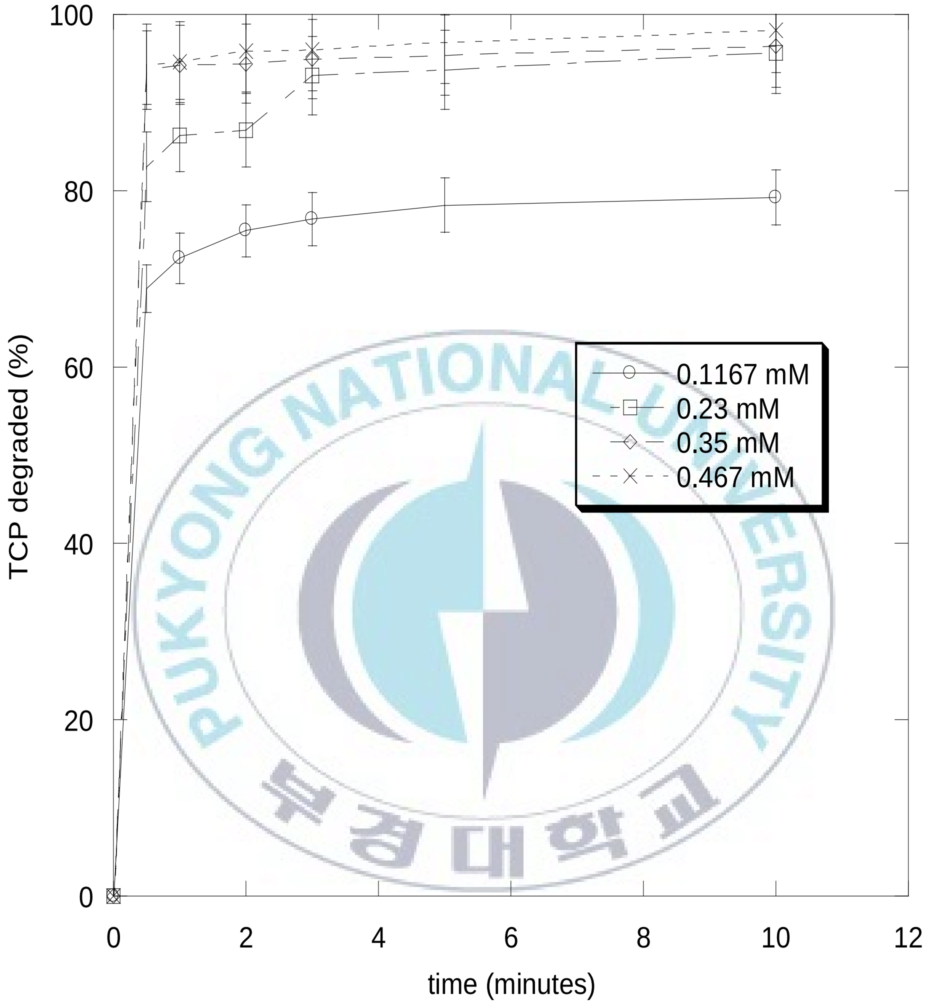


Fig. 17 TCP degradation(%) in Ferrate dosage variation, acid condition with 1 ppm initial concentration temperature 25^{o}C.

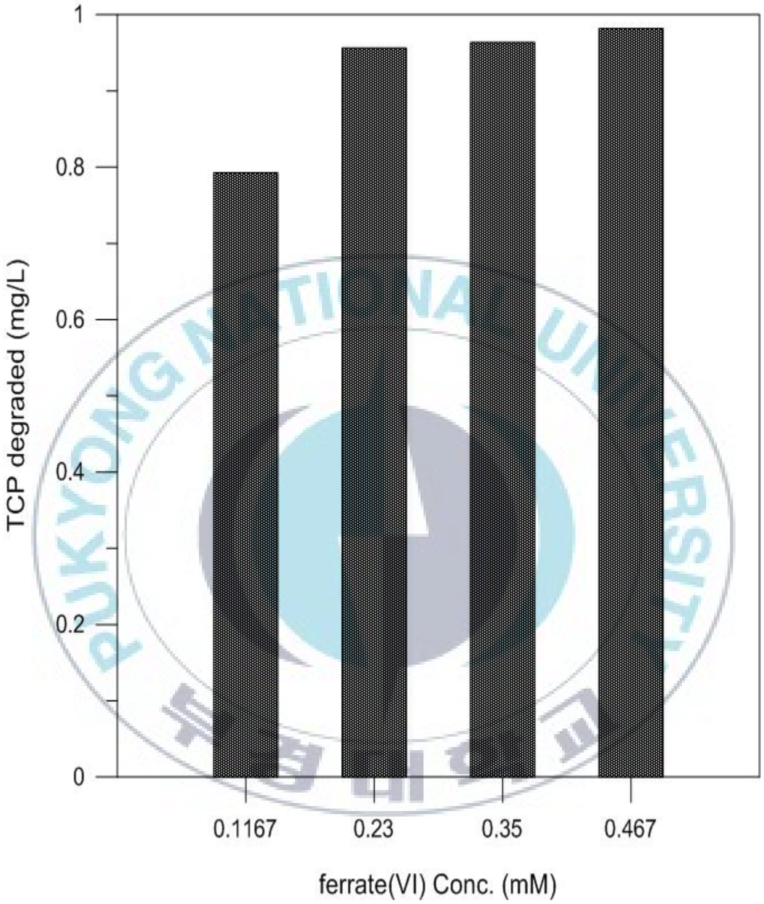


Fig. 18 TCP degraded (mg/L) in ferrate dosage variations, acid condition, 1 ppm initial concentration, temperature 25°C, with contact time 10 minutes.

3.2.3 Effect of target compounds initial concentration

Same as the effect of the ferrate dosage, the initial concentration of target compounds (C_0) has been determined by this experiment and showed the same trend. Starting from 0.1 ppm, 0.25 ppm, 0.5 ppm and 1 ppm the degradation of TCE, PCE and TCP were showed in linear trends with increasing of target compounds initial concentration will decrease the degradation efficiency of ferrate(VI). The low range of initial concentration of target compound was because the analytical instrument used (GC/ECD) is very sensitive analytical equipment which can detect in the range of ppb (part per billion) or even ppt (part per trillion) level. More over in the contamination case, the real concentration of target compound was found only in low concentration. The target compounds initial concentration increase and ferrate (VI) dosage constant the degradation efficiency will decrease since in the reactor more target compounds concentration available to degrade with the same dosage of ferrate(VI). Degradations of TCE from 0.1 ppm to 1 ppm were: 98%; 82%; 60% and 54% shown in the Fig. 19. Fig. 21 was showed PCE degradation in initial concentration variation and Fig. 23 was showed TCP degradation in initial concentration variation. The degradation of target compounds were strongly depending on the dosage of ferrate(VI) added to the reactor [Yang Bin, Ying Guang-Guo Zhang Li-Juan, 2011]. More amount of ferrate(VI) more degradation reaction can be proceed in the reactor. Another studies need to be conducted to identify the maximum amount of ferrate can be added for degradation since ferrate in excess amount will proceed auto-degradation among ferrates(VI) itself.

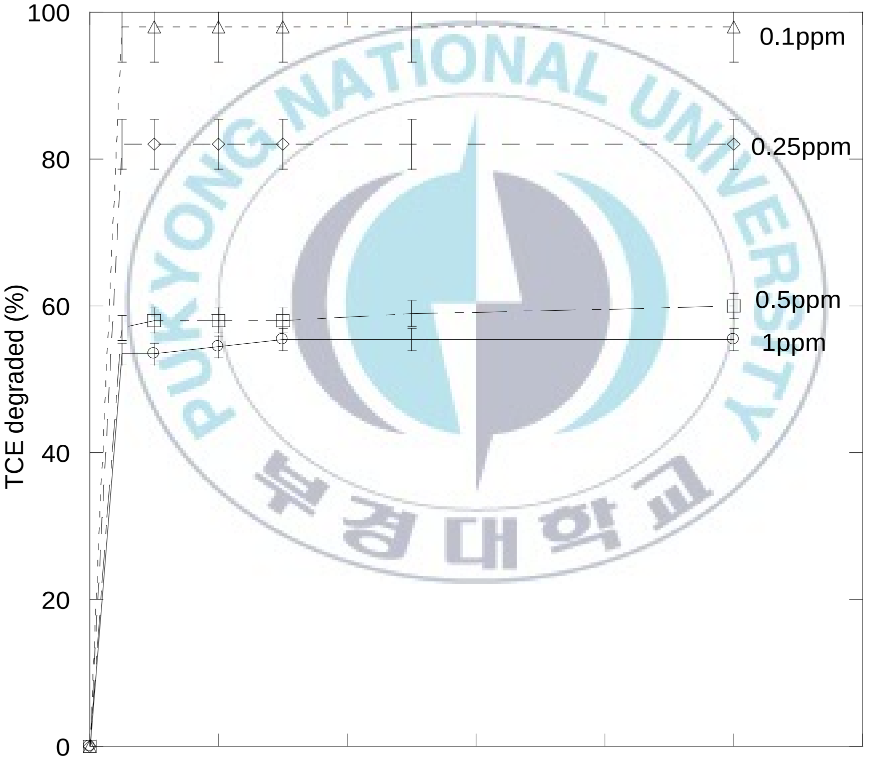


Fig. 19 TCE degradation (%) in TCE initial concentration variation, pH 3-4 with 1 ppm initial concentration.

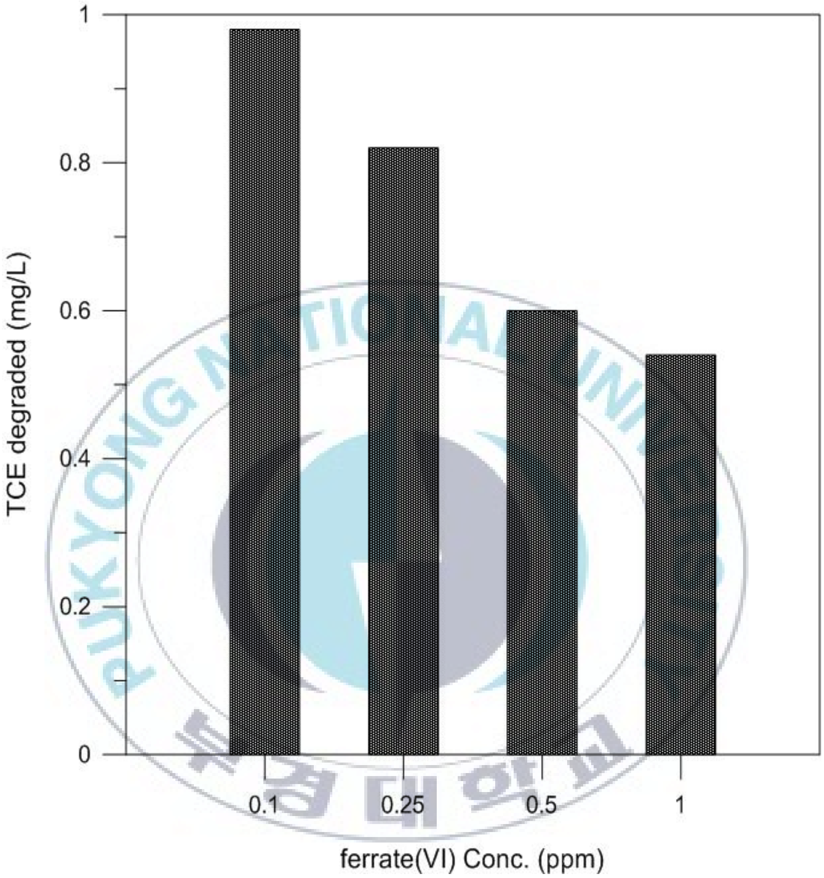


Fig. 20 TCE degraded (mg/L) in initial concentration variations, pH 3-4 with 1 ppm initial concentration

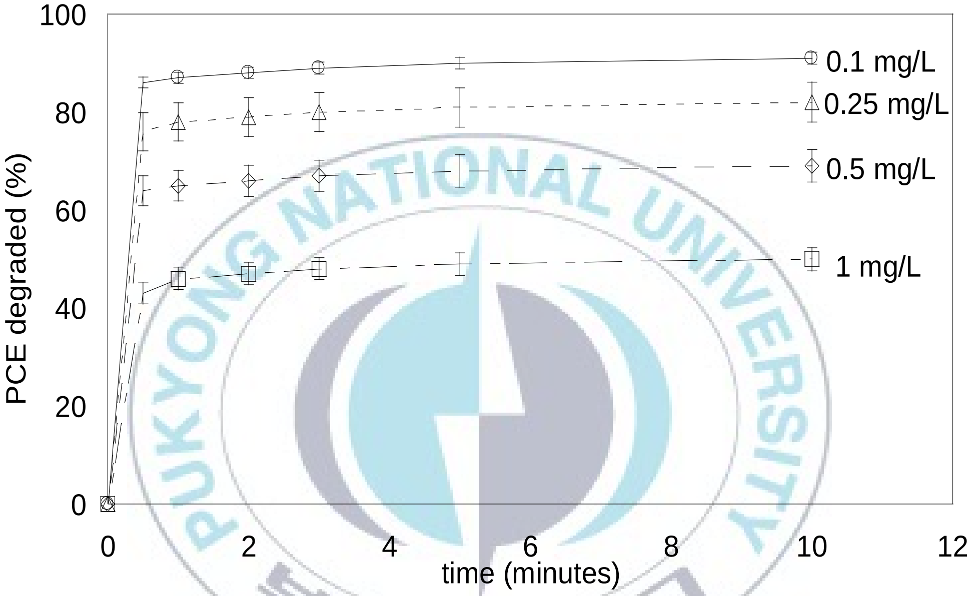


Fig. 21 PCE degradation (%) in PCE initial concentration variation, pH 3-4 with 1 ppm initial concentration

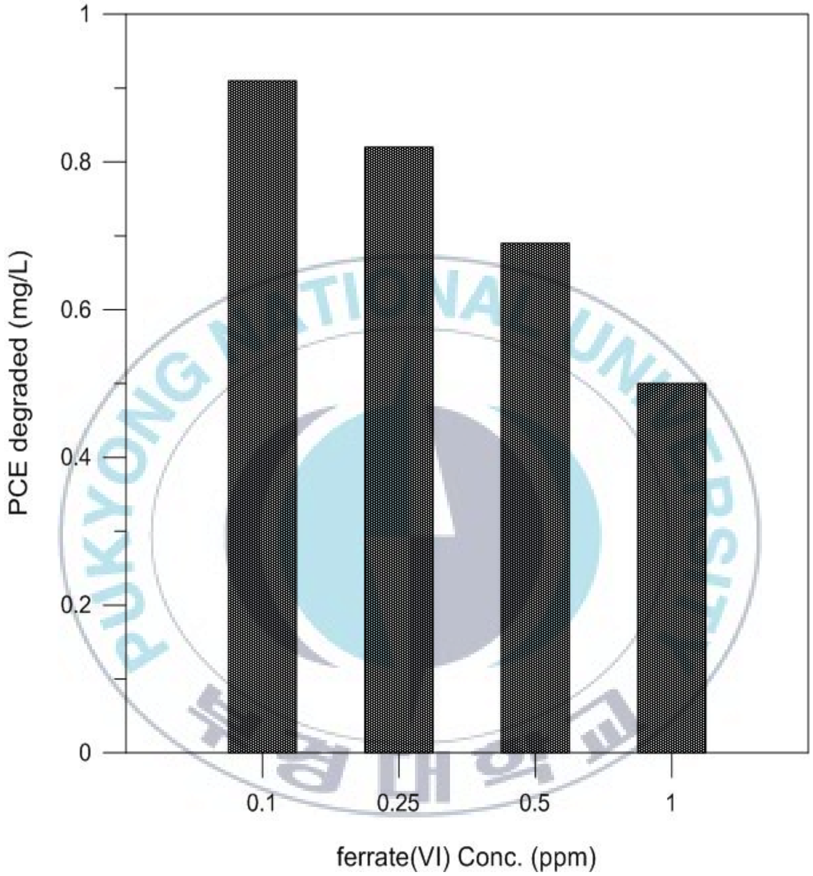


Fig. 22 PCE degraded (mg/L) in PCE initial concentration variations, pH 3-4 with 1 ppm initial concentration

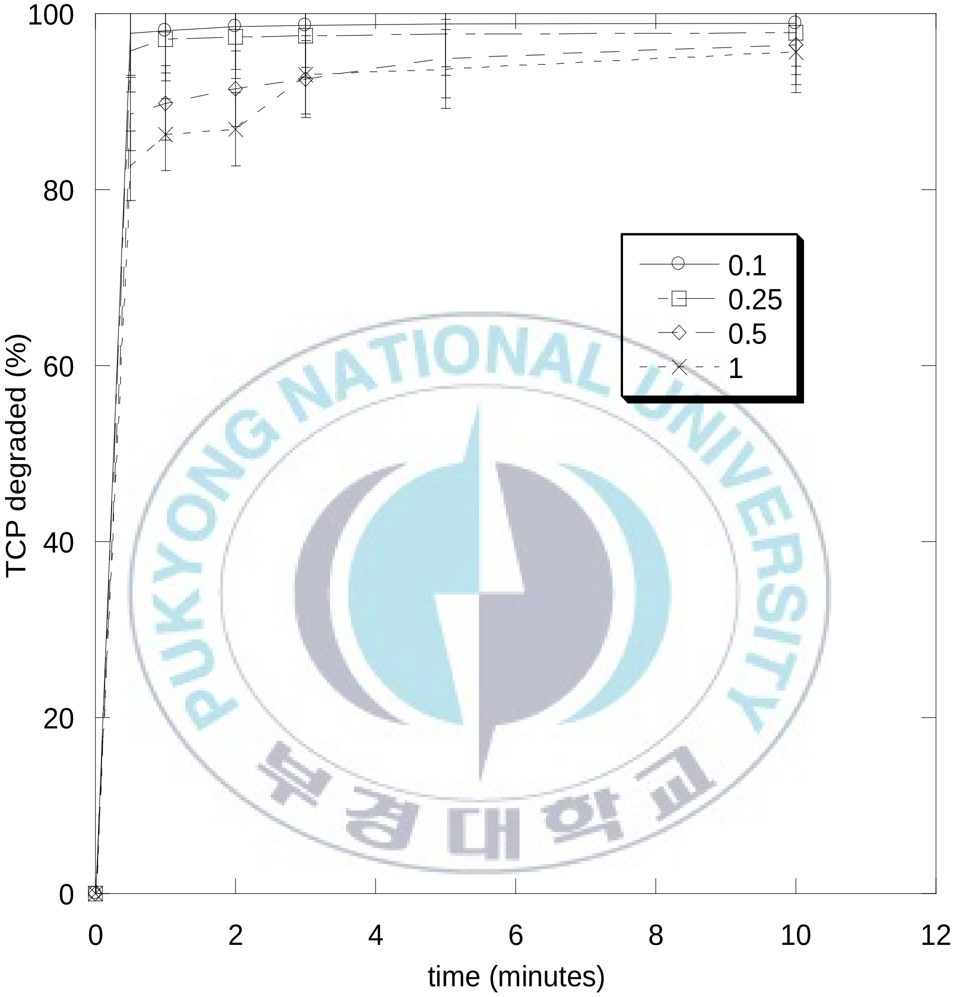


Fig. 23 TCP degradation (%) in TCP initial concentration variation, acid condition, 0.23mM ferrate(VI) dosage, and temperature 25°C.

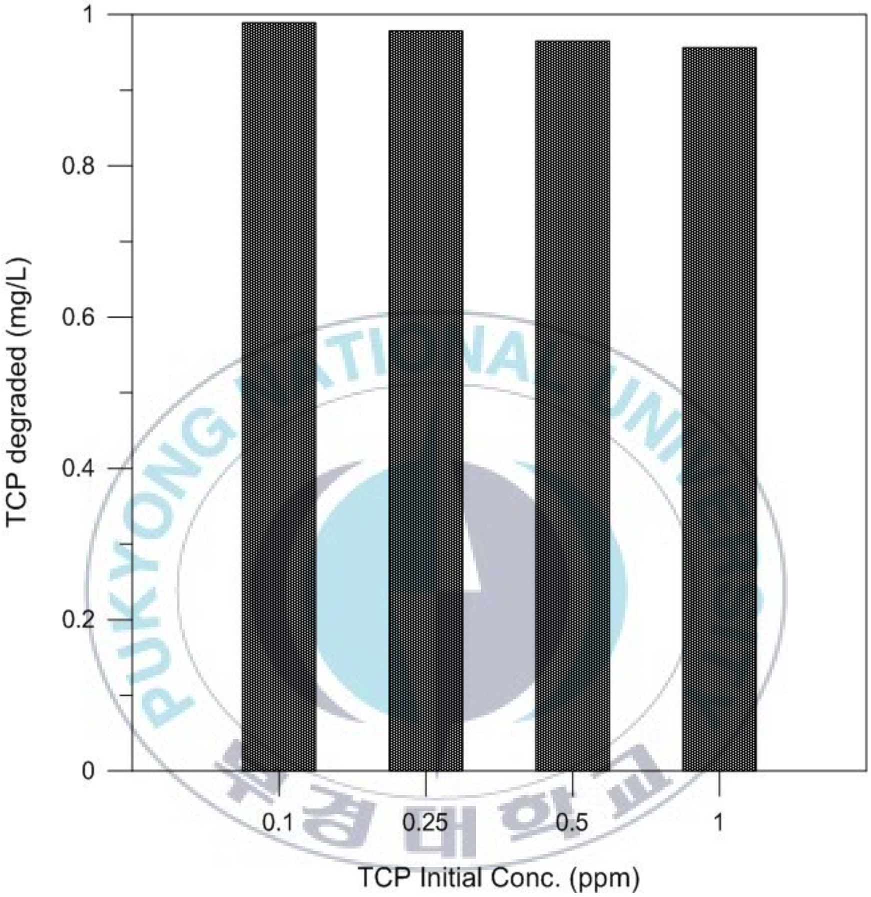


Fig. 24 TCP degraded (mg/L) in TCP initial concentration variation, acid condition, 0.23mM ferrate(VI) dosage, temperature 25°C, with contact time 10 minutes.

3.2.4 Effect of temperature

The temperature has been reported as one of the most significant parameters, its effect on ferrate(VI) stability has been observed in the previous researches. Increasing temperature caused an enhancement of the homogeneous ferrate(VI) decomposition kinetics [W.F.Wagner, J.R.Gump, E.N. Hart, 1952, T.Svanks, 1976, Z.Macova, K.Bouzek, J.Hives, V.K.Sharma, R.J.Terryn, J.C.Baum, 2009]. To determine effect of temperature in the degradation efficiency of target compounds by ferrate(VI) produced from synthesis, temperature experiments were conduct. Varying from 10^{o}C, 25^{o}C, 35^{o}C and 45^{o}C, the experiment of temperature variation showed that optimum temperature of TCE degradation by ferrate(VI) was 25^{o}C with 67% TCE degraded by 0.5 mL ferrate(VI) (28ppm) in acid condition C_0 1ppm. Fig. 25 showed degradation TCE in various temperature variations. In PCE with the same condition showed that only 50% of PCE were degraded (Fig. 28). With 95% degraded from the reactor (Fig. 30), TCP was identified as the highest degradation efficiency. From this experiment also observed a second order reaction in the degradation of TCE, PCE and TCP by ferrate(VI) generated from the synthesis. The activation energy for TCE degradation reaction was 63.70 kJ/mol as measured by

Arrhenius equation from experiment data, while PCE activation energy was 35.70 kJ/mol and TCP was 30.69 kJ/mol. The equation used to measure activation energy was:

$$\ln\frac{rate_1}{rate_2} = -\frac{ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2)$$

Fig. 26 was showed the k_{app} value of TCE, Fig. 29 was k_{app} value of PCE, and Fig. 31was k_{app} value of TCP in temperature range from 10°C to 45°C with the highest k_{app} value obtained in 25°C for all target compounds. The k_{app} value of TCP was 1489.7 $M^{-1}s^{-1}$ the highest k_{app} value compared to TCE and PCE. In 25°C the degradation reached the maximum efficiency because ferrate(VI) in this temperature still in low homogenous condition [Yang Bin, Ying Guang-Guo Zhang Li-Juan, 2011]. In the low homogenous condition ferrate(VI) freely to move to attack the target compounds in reactor.

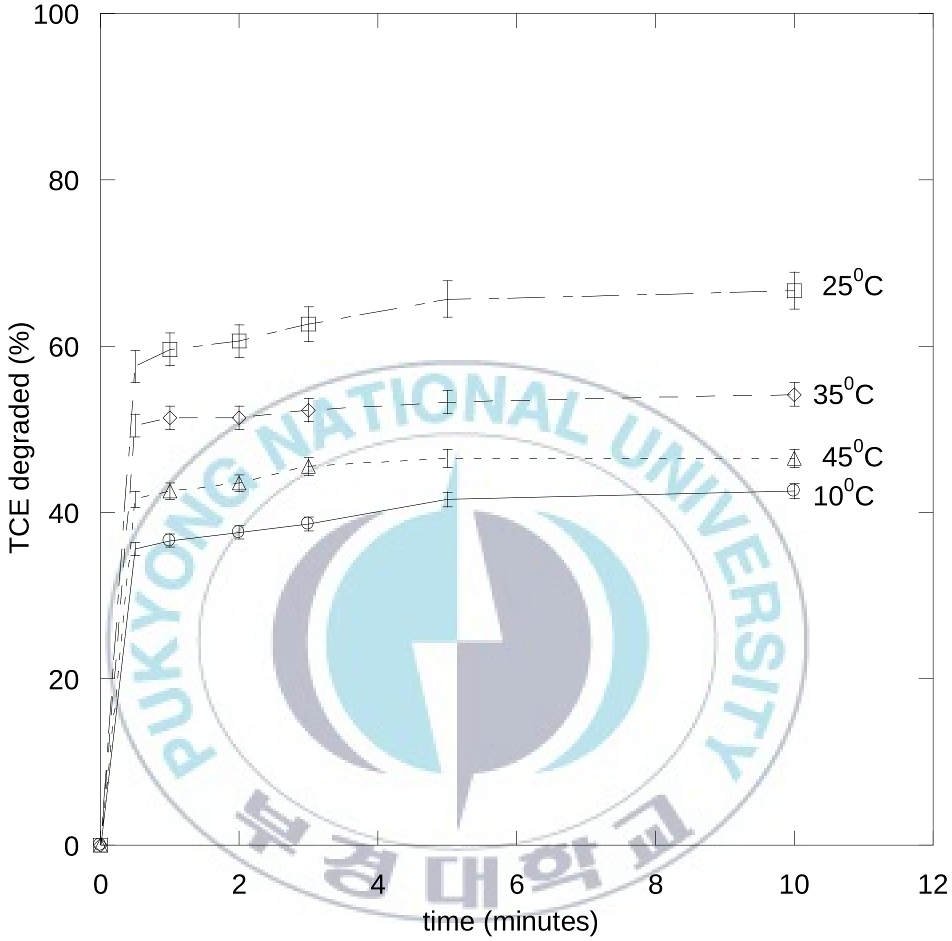


Fig. 25 TCE degradation in Temperature variation, pH 3-4 with 1 ppm initial concentration and 28 ppm ferrate concentration

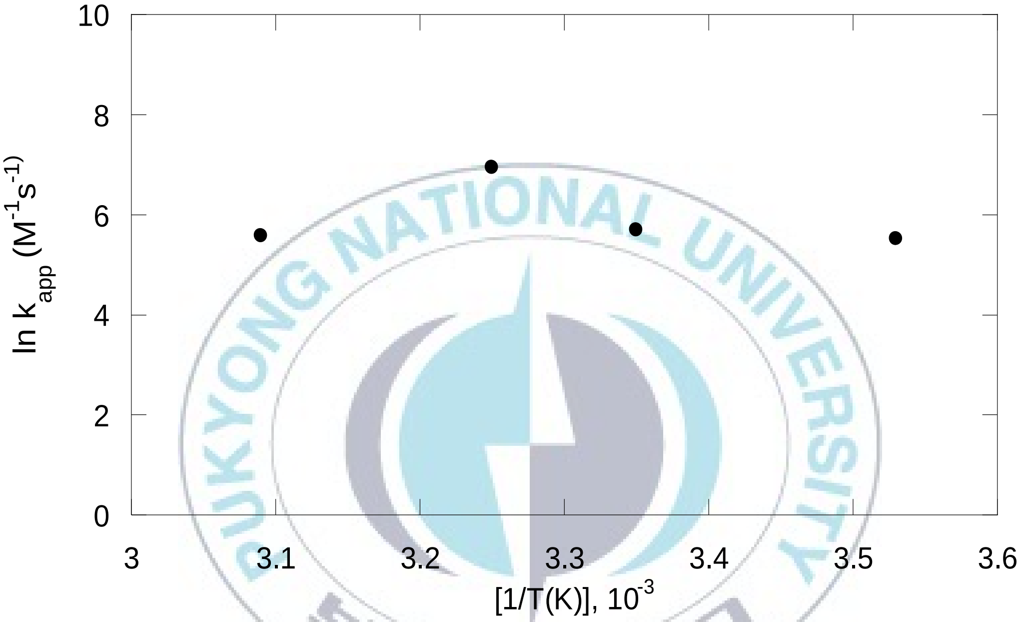


Fig. 26 TCE k_{app} value in temperature variation, pH 3-4 with 1 ppm initial concentration and 28 ppm ferrate concentration

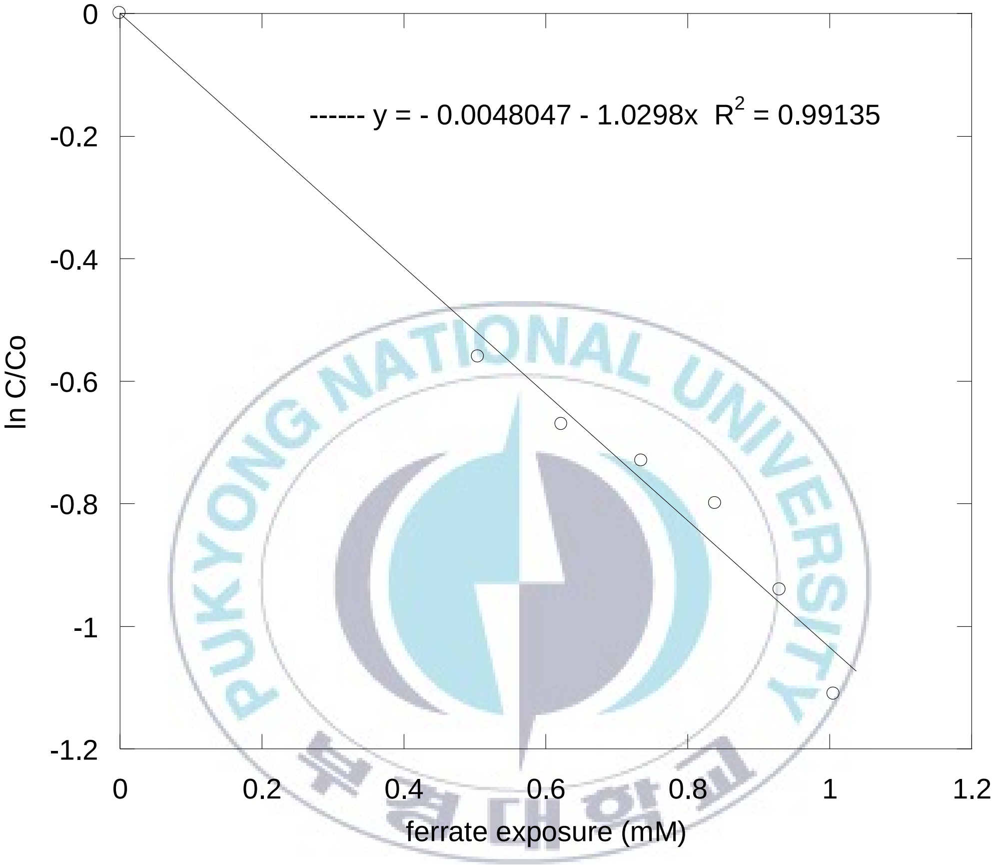


Fig. 27 TCE k_{app} value in temperature variation, pH 3-4 with 1 ppm initial concentration and 28 ppm ferrate concentration

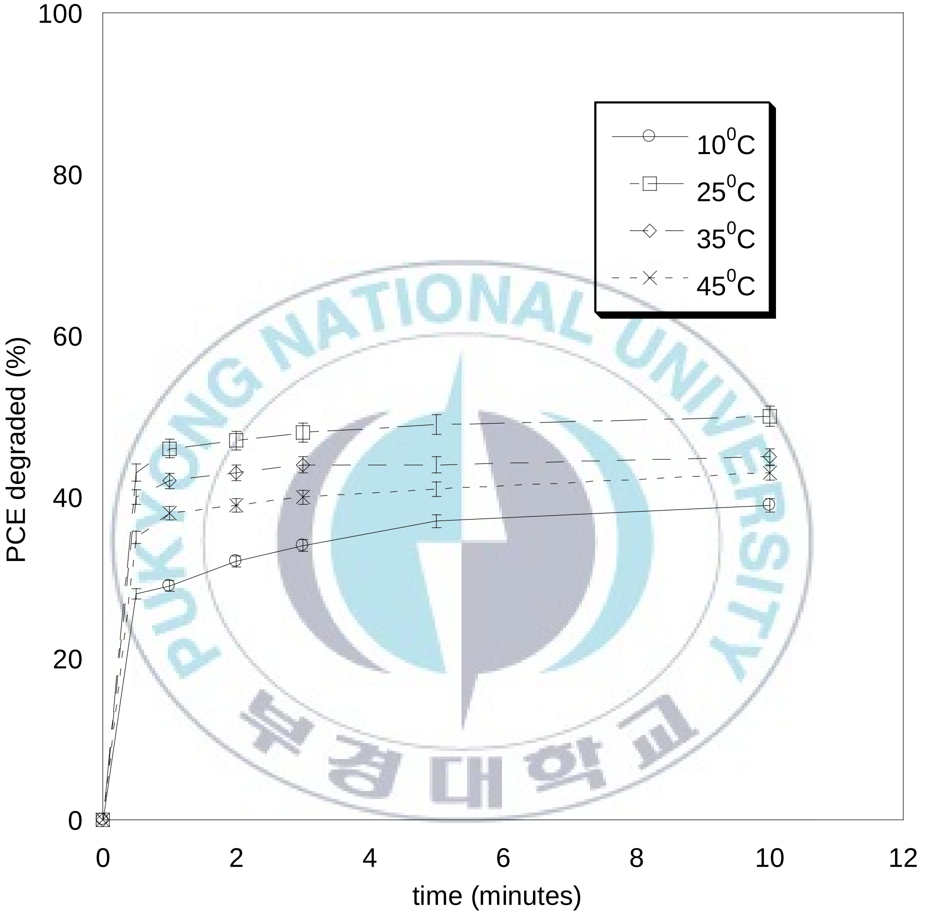


Fig. 28 PCE degradation in Temperature variation, pH 3-4 with 1 ppm initial concentration and 28 ppm ferrate concentration

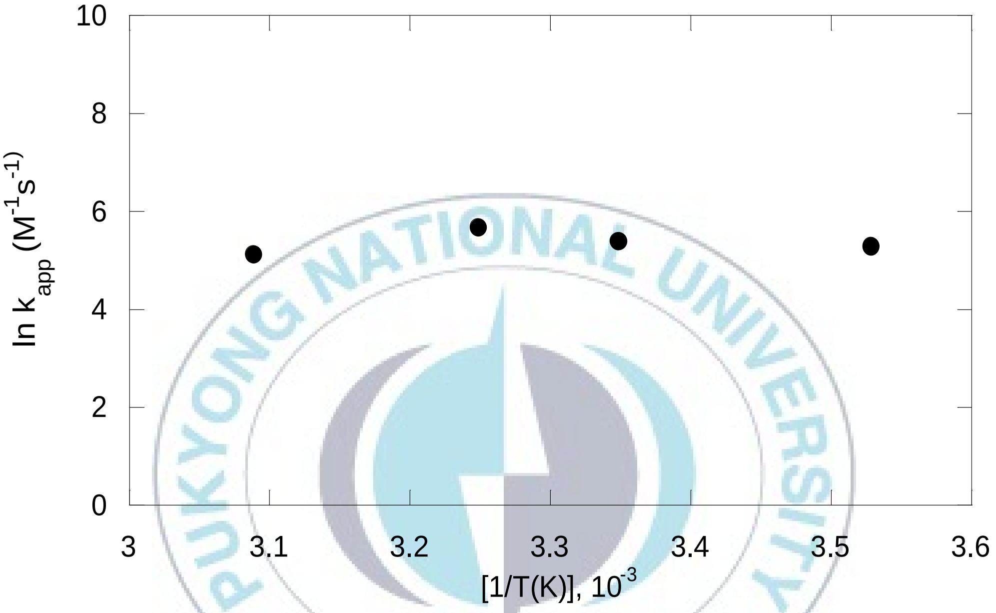


Fig. 29 PCE k_{app} value in temperature variation, pH 3-4 with 1 ppm initial concentration and 28 ppm ferrate concentration

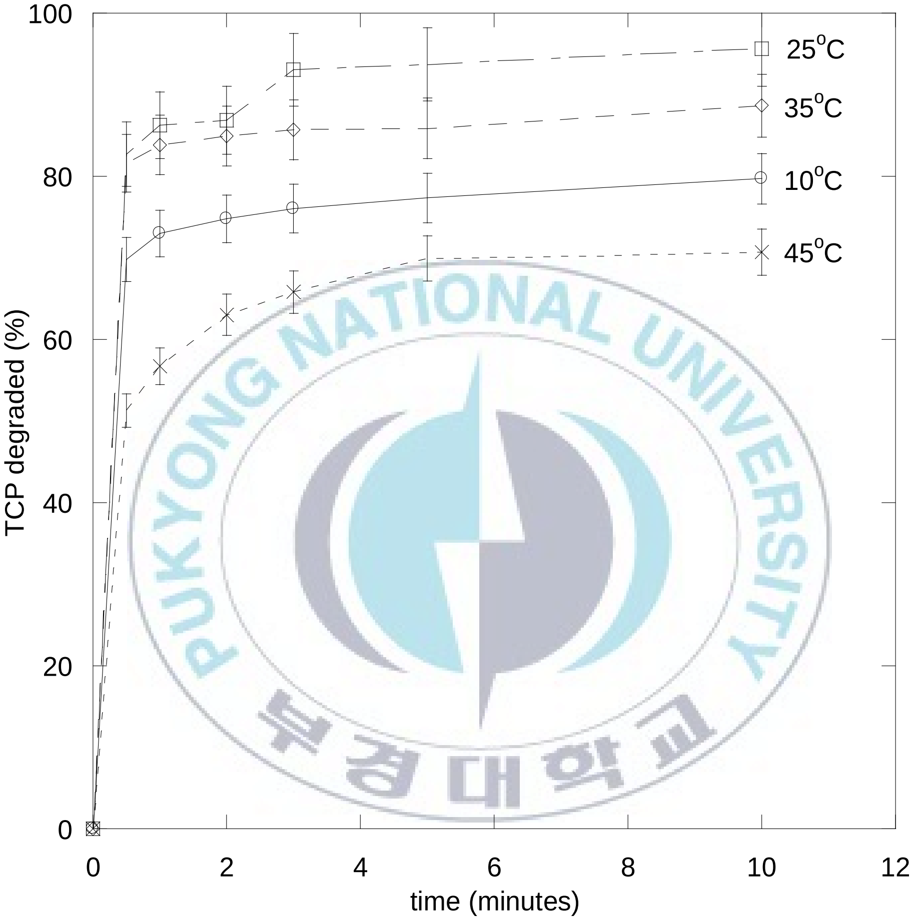


Fig. 30 TCP degradation (%) in Temperature variation, acid condition, 1 ppm initial concentration and 0.23mM ferrate(VI) concentration.

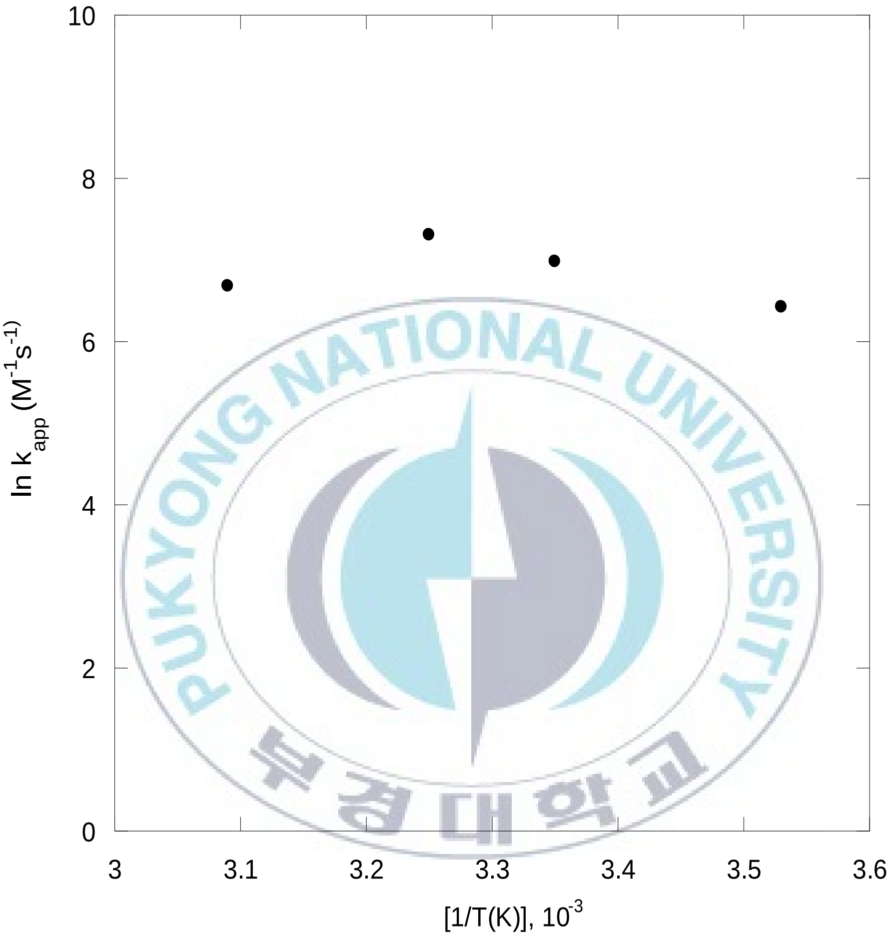


Fig. 31 TCP k_{app} value in temperature variation acid condition, 1 ppm initial concentration and 0.23mM ferrate(VI) concentration.

3.3 Intermediate study and degradation pathway

3.3.1 TCE Intermediate study and degradation pathway

This experiment was performed to find out the intermediate product from degradation of TCE and PCE by ferrate(VI). Sample from the degradation reactor were analyzed using GC/MS Mass Spectrometer Systems. The mechanism of the reactions between ferrate(VI) and organic/inorganic matters can be divided into three categories. In general, ferrate(VI) was known to allow organic/inorganic matters to oxidized either by providing oxygen or by taking away electron or hydrogen atom from organic/inorganic matters. The reaction was brought about by providing oxygen, which was provided mainly from ferrate(VI) [Sharma, V. K., 2003, J.Q. Jiang, B. Lloyd, 2002].

Fig. 25 showed the possible reaction pathways involving oxygen. The first step was the oxygen transfer and proton addition produced 1,1,2-trichloroethane, Dichloroethylene, and chloroform. 1,1,2-trichloroethane could be changed to 1,2-Dichloroethane by second oxygen transfer. After second oxygen transfer, 1,2-Dichloroethane could be changed to ethyl chloride by third oxygen transfer. Dichloroethylene could be changed to vinyl chloride by second oxygen transfer. After second oxygen transfer, vinyl chloride could be changed to ethylene by third oxygen transfer. Further decomposition would generate ethane [E.C. Butler, K.F. Hayes, 1999, H.Y. Jeong, H. Kim, K.F. Hayes, 2007, W.A. Arnold, A.L. Roberts, 2000]. The ethane would convert to glycolic acid and glyoxylic acid. Then it was proposed that further decomposition of intermediates led to end products like carbon dioxide [M. Kang, J.H. Lee, S.H. Lee, C.H. Chung, K.J. Yoon, K. Ogino, S. Miyata, S.J. Choung, 2003].

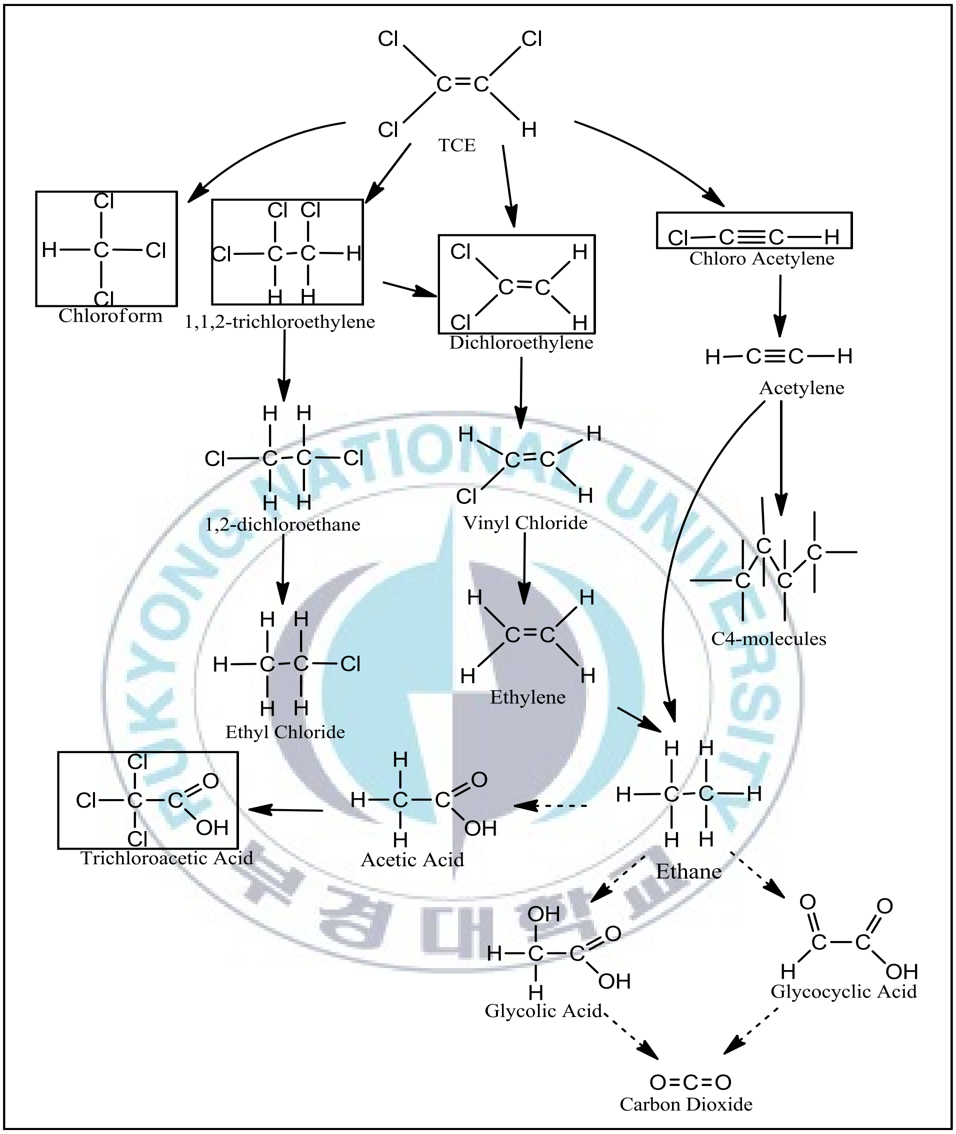


Fig. 32 Degradation reaction pathway for TCE by ferrate(VI) species in the boxes are detected in this experiment. pH 3-4 with 10 ppm TCE initial concentration and 280 ppm ferrate dosage

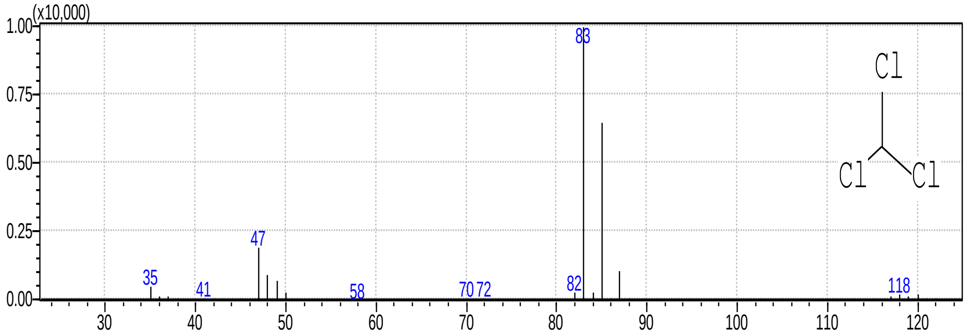


Fig. 33 Mass spectrum of Chloroform (Ret. time: 7.258 min.).

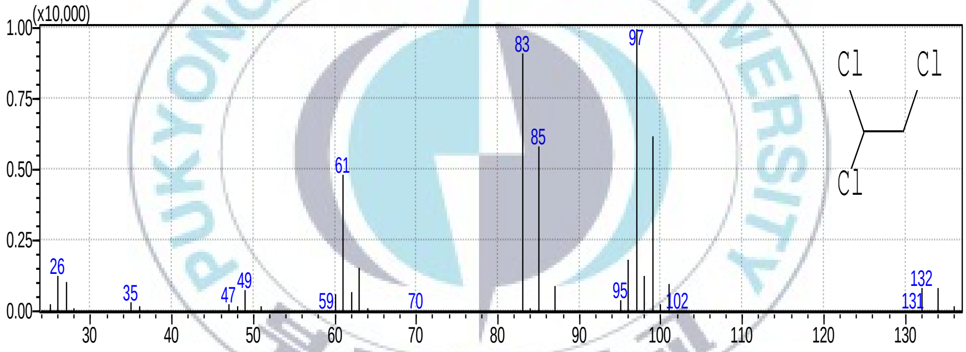


Fig. 34 Mass spectrum of 1,1,2-trichloroethane (Ret. time: 14.875 min.).

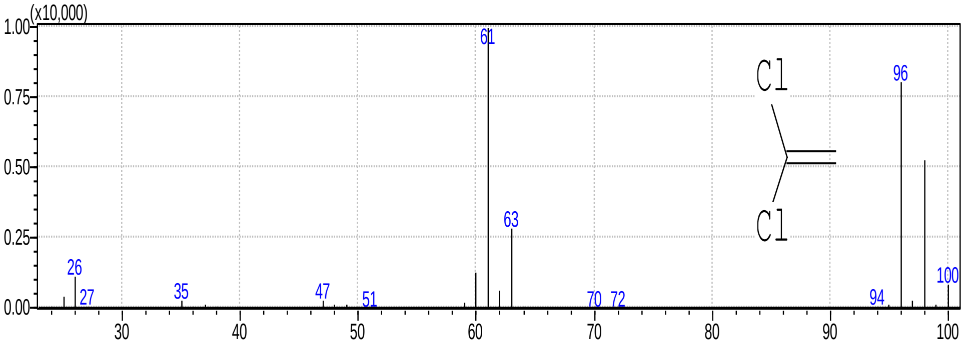


Fig. 35 Mass spectrum of 1,1-dichloroethylene (Ret. time: 4.708 min.).

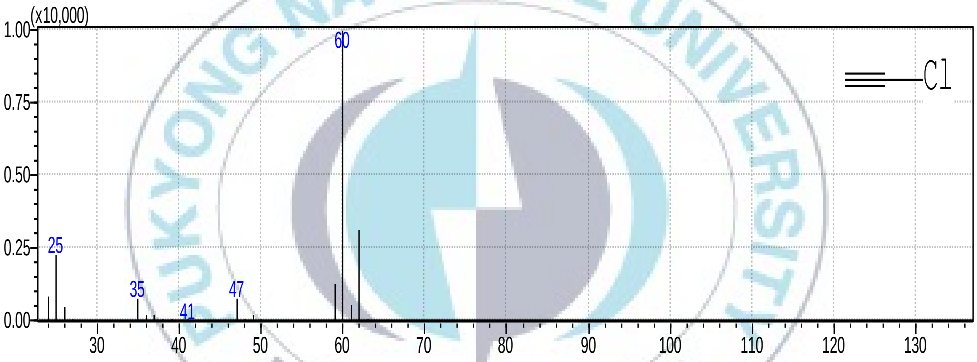


Fig. 36 Mass spectrum of Chloroacetylene (Ret. time: 12.075 min.).

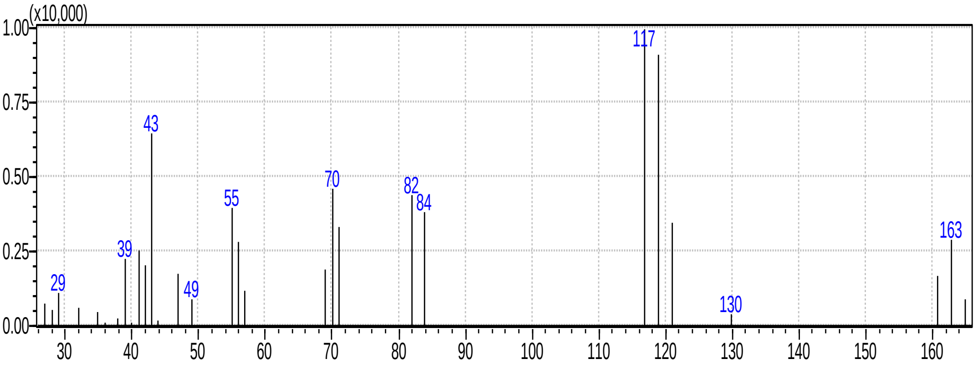


Fig. 37 Mass spectrum of Trichloroacetic Acid (Ret. time: 15.008 min.).

3.3.2 PCE intermediate study and degradation pathway

This experiment was performed to find out the intermediate product from degradation of PCE by ferrate(VI). The mechanism of the reactions between ferrate(VI) and PCE has similarity with TCE

The first step was the oxygen transfer and proton addition produced trichloroethylene, Dichloroacetylene, and chloroform. trichloroethylene could be changed to 1,2-DCE by second oxygen transfer. After second oxygen transfer, 1,2-DCE could be changed to vinyl chloride by third oxygen transfer. Dichloroacetylene could be changed to chloroacetylene by second oxygen transfer. After second oxygen transfer, vinyl chloride could be changed to ethylene by third oxygen transfer. Further decomposition would generate ethane and ethylene [H.Y. Jeong, H. Kim, K.F. Hayes, 2007, W.A. Arnold, A.L. Roberts, 2000]. As TCE degradation pathways proposed the ethane would convert to glycolic acid and glyoxylic acid. Then it was proposed that further decomposition of intermediates led to end products like carbon dioxide [M. Kang, J.H. Lee, S.H. Lee, C.H. Chung, K.J. Yoon, K. Ogino, S. Miyata, S.J. Choung, 2003]. Fig. 26 shows the degradation pathway of PCE pH 3-4 with 10 ppm TCE initial concentration and 280 ppm ferrate dosage

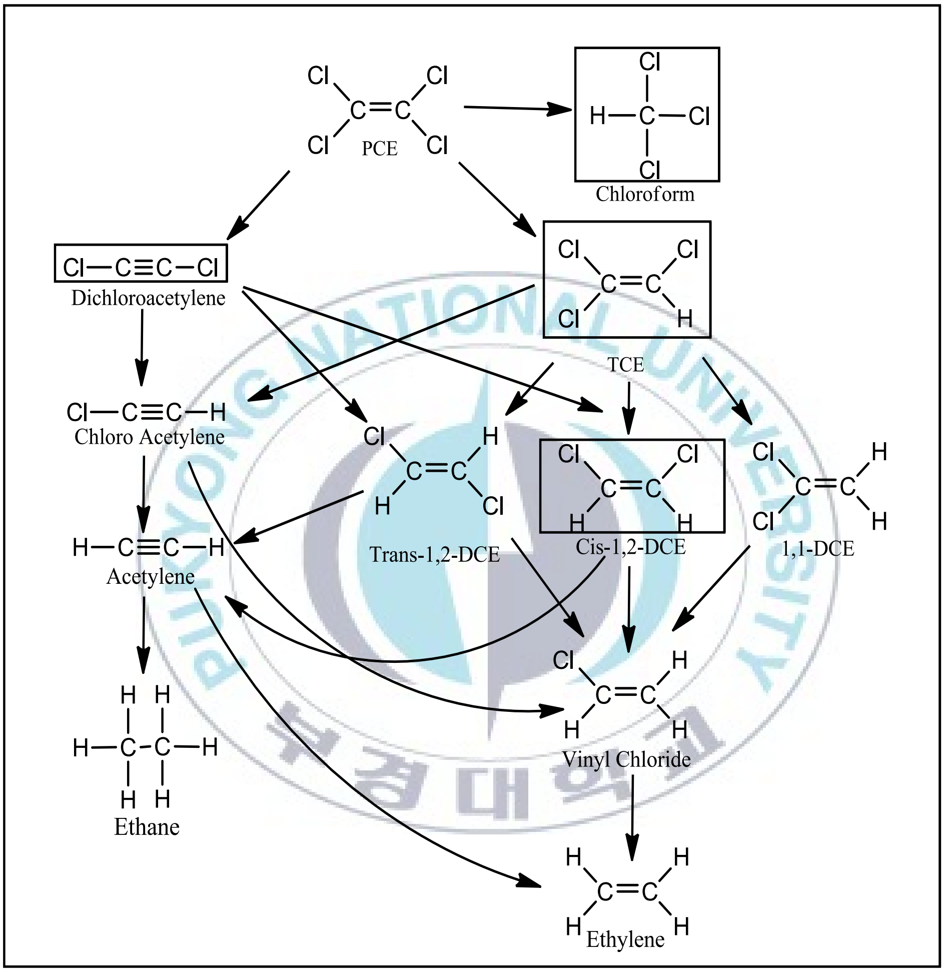


Fig. 38 Degradation reaction pathway for PCE by ferrate(VI) species in the boxes are detected in this experiment. pH 3-4 with 10 ppm TCE initial concentration and 280 ppm ferrate dosage

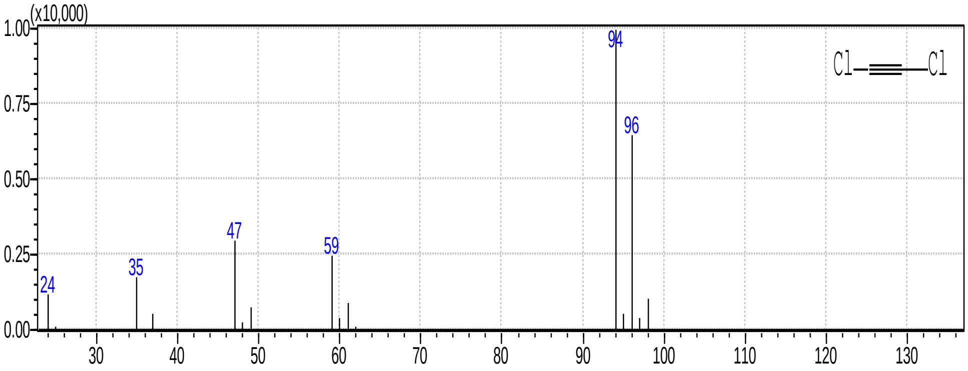


Fig. 39 Mass spectrum of Dichloroacetylene (Ret. time: 12.092 min.).

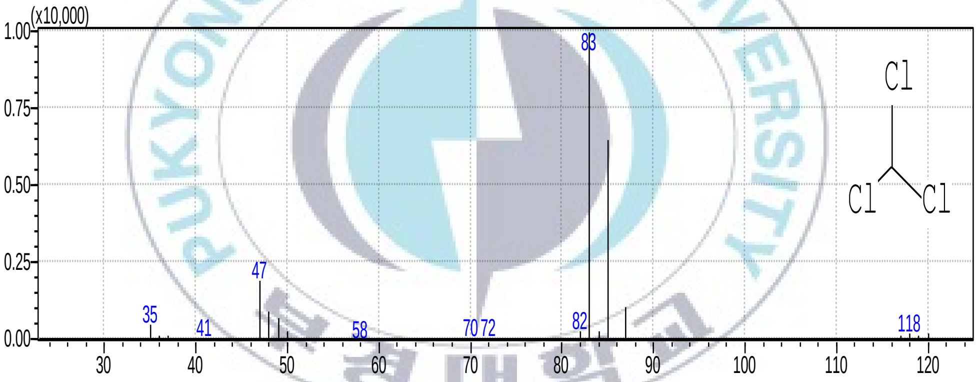


Fig. 40 Mass spectrum of Chloroform (Ret. time: 7.250 min.).

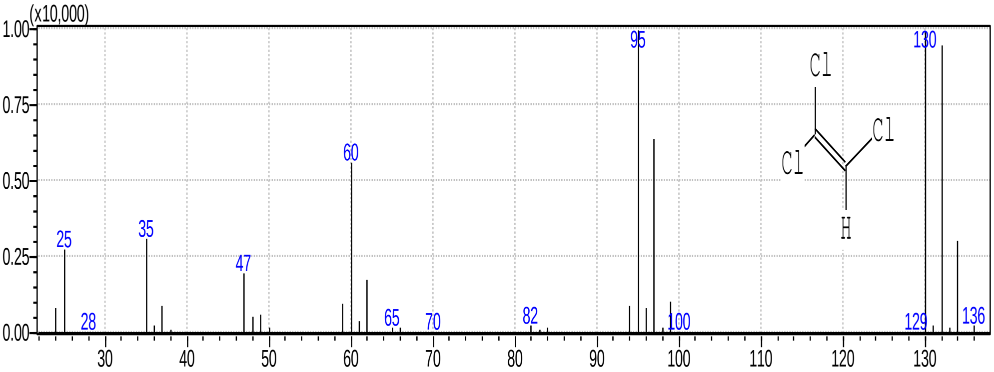


Fig. 41 Mass spectrum of Trichloroethylene (Ret. time: 10.083 min.).

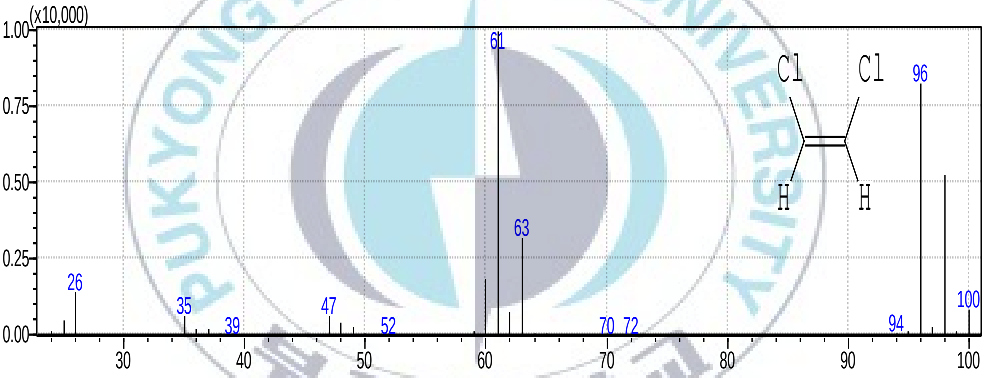


Fig. 42 Mass spectrum of Cis-1,2-dichloroethylene (Ret. time: 4.692 min.).

3.4 Cl^- Formation on the TCP Degradation

The formation of Cl^- from TCP degradation was showed in the Fig. 9. The concentration of Cl in the TCP and the formation of Cl^- were measured using UV-Vis spectrophotometer DR5000 from Hach to provide information on how Cl in TCP degraded. The amount of Cl- detected on the TCP degraded was 0.022400 mM while Cl concentration degraded 0.02698 mM.

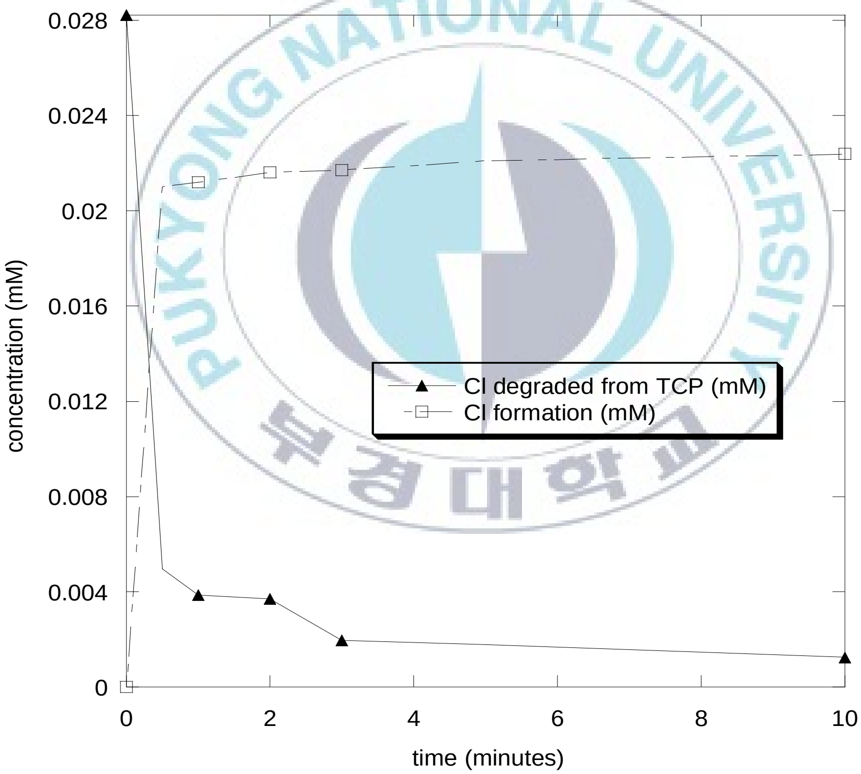


Fig. 43 Comparison of Cl^- degraded from TCP to Cl^- formation. (Experimental condition: Co=1ppm, ferrate(VI) dosage=0.23mM, acid condition in 25°C).

IV. Conclusions

Ferrate (VI) is a powerful oxidizing agent and its oxidizing power can be used in advanced oxidizing process. Due to range of pH and by product of the reaction, ferrate(VI) is a promising technology. From this study of organic contaminants (TCE, PCE, and TCP) Degradation using Ferrate(VI) by Wet Oxidation Method. An optimum condition of ferrate(VI) synthesis has been reached with several variations of parameter including precursor, procedural experiment and concentration of sodium hydroxide (NaOH). 70,870 ppm concentration of ferrate(VI) obtained with $FeCl_3.6H_2O$ as the source of precursor without filtering in 13M concentration of sodium hydroxide. From this experiment a second order reaction obtained with k_{app} value 1,029.8 $M^{-1}s^{-1}$ determined in acid condition for TCE, PCE with the same condition has k_{app} value 315.19 $M^{-1}s^{-1}$while TCP has k_{app} value 1489.7 $M^{-1}s^{-1}$. Compare to PCE, TCE has more degrade since TCE has less halogenated substitution. Even though activation energy showed than PCE has less energy than TCE, PCE k_{app} value much lower compare to TCE. Among 3 target compounds, phenol (TCP) was observed to be the highest degraded compared to TCE and PCE. Phenol has aromatic ring which has double bond that can easily attack by ferrate(VI)

Under the experimental conditions, five reaction intermediates were detected in TCE degradation using GC/MS; chloroacetylene, dichloroethylene, chloroform, trichloroacetic acid and trichloroethane. For PCE the intermediate product were; TCE, dichloroacetylene, dichloroethylene, and chloroform. From the product identified by GC/MS the degradation reaction pathway was proposed. Instead of intermediate study, Cl^- formation from TCP degradation using ferrate(VI) synthesized by wet oxidation method was carried out. This experiment showed that the degradation of TCP were followed by formation of chloride ion (Cl^-)

References

Audette, R.J., Quail, J.W., Smith, P.J., 1971.”Ferrate (VI) ion, a novel oxidizing agent.”TetrahedronLett. 3, 279-281

Williams, D. H., Riley, J. T., 1974. “Preparation and Alcohol Oxidation Studies of the Ferrate (VI) ion FeO_4^{2-}.”InorganicaChim.Acta. 8, 177-183

Tsuda, Y., Nakajima, S., 1978. “Potassium Ferrate , a new selective oxidizing agent.” Chem. Lett. 1397-1398

Carr et al., 1985. “Properties of Ferrate(VI) in aqueous solution: an alternate oxidant in waste water treatment.” In: Jolley, R. L. (Ed), Proceedings of Conference on Water Chlorination Chem. Environment Impact Health Eff Lewis Chelsew, pp. 1285-1298

Delaude and Laszlo., 1996. “A novel oxidizing reagent based on Potassium Ferrate (VI).” J. Org. Chem. 61, 6360-6370

Li, C., Li, X. Z., and Graham, N., 2005. “A Study of the preparation and reactivity of potassium ferrate.”Chemosphere, 61. 537-543

Moeser, L., 1897. J. Prakt. Chem. 56, 425

Bouzek, K., Rousar, I., 1993. Elektrochim.Acta, 38. 1717-1720

Bielski, B. H., 1991. “Studies of hypervalent ion.” Free. Rad. Res. Commns. 12-13, 469-477

Thompson, M., Ockerman, L. T., and Schreyer, J. M., 1951.“Preparation and Purification of Potassium ferrate (VI).” J. Am. Chem. Soc., 73, 1379-1381

Schreyer, J. M., Thompson, W., Ockerman, L. T., 1953. “Potassium Ferrate (VI).”Inorg.Synthesis, 4. pp. 164-169

White, D. A., and G. S. Franklin., 1998.“A Preliminary Investigation into the Use of Sodium Ferrate in Water Treatment.”Environmental Technology. 19(11), 1157-1160

Chengchun, J., chen, L., Shichao, W., 2008. “Preparation of potassium ferrate by wet oxidation method using waste alkali: Purification and reuse of waste alkali.”ACS Symposium Series, 985. 94-101

Hrostowski, H., Scott, A., 1960. J. Chem. Phys., 18, p. 105

Li, K., Stefan, M.T., Crittenden, J. C., 2007. “Trichloroethene Degradation by UV/H_2O_2 Advanced Oxidation Process : Product Study and Kinetic Modelling.” Environ. Sci. Technol, 41. 1696-1703

Schreyer, J. M., Ockerman, L. T., 1952. “Stability of the ferrate (VI) iom in aqueous solution.”Anal.Chem, 23. 1312-1314

Sharma, V. K., 2003. “Potassium Ferrate (VI): An environmentally friendly oxidant.” Adv. Environ. Res., 6(2), 143-156

Sharma, V. K., 2010. “Oxidation of Inorganic Compounds by Ferrate(VI) and Ferrate(V): one-electron and two-electron transfer steps.” Environ. Sci. Technol, 56. 949-956

Wust, Wolfgang. F., Kober, Ralf.,Schlicker, Oliver., and Dahmke, Andreas., 1999. “Combined Zero- and First-Order Kinetic Model of the Degradation of TCE and cis-DCE with Commercial Iron.” Environ. Sci. Technol, 33, 4304-4309

Yang Bin, Ying Guang-Guo Zhang Li-Juan. Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles. (2011) Water Research, 45, 2261-2269

V. K. Sharma Ferrate(VI) and ferrate(V) oxidation of organic compounds: kinetics and mechanism. (2013) Coordination chemistry Reviews, 257 (2), pp. 495-510

Yang Bin, Ying Guang-Guo. Oxidation of triclosan by ferrate: Reaction kinetics, products identification and toxicity evaluation. (2011) Journal of Hazardous Materials 186, pp.227-235

Yu Myongjin, Park Guisu, and Kim HyunoOk.Oxidation of Nonylphenol Using Ferrate. (2008) American Chemical Society (24), pp. 389-403

W.F.Wagner, J.R.Gump, E.N. Hart, Factors affecting stability of aqueous potassium ferrate(VI) solutions, Anal. Chem., 24 (1952) 1497-1498.

T.Svanks, Oxidation of ammonia in water by and ferrates(VI) and(IV), Water Resources Center, Engineering Experiment Station, The ohio state university, Columbus,1976.

Z.Macova, K.Bouzek, J.Hives, V.K.Sharma, R.J.Terryn, J.C.Baum, Research progress in the electrochemical synthesis of ferrate(VI), ElectrochimicaActa., 54(2009) 2673-2683.

J.Q. Jiang, B. Lloyd, Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Res., 36 (2002) 1397-1408

E.C. Butler, K.F. Hayes, Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide, Environ. Sci. Technol., 33 (1999) 2021-2027.

H.Y. Jeong, H. Kim, K.F. Hayes, Reductive dechlorination pathways of tetrachloroethylene and trichloroethylene and subsequent transformation of their dechlorination products by mackinawite(FeS) in the presence of metals, Environ. Sci. Technol., 41 (2007) 7736-7743.

W.A. Arnold, A.L. Roberts, Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles, Environ. Sci. Technol., 34 (2000) 1794-1805.

M. Kang, J.H. Lee, S.H. Lee, C.H. Chung, K.J. Yoon, K. Ogino, S. Miyata, S.J. Choung, Preparation of TiO_2 film by the MOCVD method and analysis for decomposition of trichloroethylene using in situ FT-IR spectroscopy, J. Molecular Catalysis A: Chem., 193 (2003) 273-783.

Hirata, K., 1996. Counterplan of Soil and Groundwater Pollution, first ed. Nihon kankyo sokuteibunsekikyokai, pp. 3-1 Johnson, M. D., Hornstein, B. H., Wischnewsky, J. M., 2008. “Ferrate(VI) Oxidation of Nitrogenous Compounds.” Amer. Chem. Soc. Symposium Series, 987. 177

Johnson, Michael. D., and Read, John. F., 1996. “Kinetics and Mechanism of the Ferrate Oxidation of Thiosulfate and Other Sulfur-Containing Species.” Inorg. Chem, 35, 6795-6799

Kirchner K., Helf D., Ott P., and Vogt S., 1990.“The reaction of OH radicals with 1, 1-di-,tri-and tetrachloroetylene.”Ber.Bunsenges. Phys. Chem. 94, 77-83

Kutsuna S., Ebihara Y., Nakamura K., and Ibusuki T., 1993.“Heterogenous Photochemical reactions between volatile chlorinated hydrocarbons (trichloroethylene and tetrachloroetylene) and titanium dioxide.” Atmos. Environ. 27, 599-604

Lee,Yun-Ho., Zimmermann, S. G., Kieu, A. T., and Gunten, U.V., 2009. “Ferrate (Fe(VI)) Application for Municipal Wastewater Treatment: A Novel Process for Simultaneous Micropollutant Oxidation and Phosphate Removal.” Environ. Sci. Technol, 43,3831-3838

Murmann, R. K. and Robinson, P. R., 1974. Experiments Utilising Ferrate Ion for Purifying Watcr. Water Research, 8.

Norcross, B. E., Lewis, W. C., Gai, H. F., Noureldin, N. A. and Lee, D. G., 1997. The oxidation of secondary alcohols by potassium tetraoxoferrate(VI). Canadian Journal of Chemistry-Revue Canadienne De Chimie, 75(2): 129-139.

Y.H. Lee, M. Cho, and J. Yoon, J, Environ, Hi-tech, 12, 52 (2003)

P. de Morais, T. Stoichev, M.C.P. Basto, M.T.S.D. Vasconcelos, Extraction and preconcentration techniques for chromatographic determination of chlorophenols in environmental and food samples, Talanta, 89 (2012) 1-11

J. Huff, Long-term toxicology and carcinogenicity of 2,4,6-trichlorophenol, Chemosphere, 89 (2012) 521-525.

Z. Pei, L. Li, L. Sun, S. Zhang, X.-q. Shan, S. Yang, B. Wen, Adsorption characteristics of 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, 2-naphthol and naphthalene on graphene and grapheneoxide, Carbon, 51 (2013) 156-163.

Y. Zhang, R.G. Mancke, M. Sabelfeld, S.-U. Geißen, Adsorption of trichlorophenol on zeolite and adsorbent regeneration with ozone, J. Hazard. Mater., 271 (2014) 178-184.

P. Arora, H. Bae, Bacterial degradation of chlorophenols and their derivatives, Microb. Cell Fact., 13 (2014) 31-1−31-17.

S.-G. Chung, Y.-S. Chang, J.-W. Choi, K.-Y. Baek, S.-W. Hong,S.-T. Yun, S.-H. Lee, Photocatalytic degradation of chlorophenols using star block copolymers: Removalefficiency, by-products and toxicity of catalyst, Chem. Eng. J., 215–216 (2013) 921-928.

M. Munoz, Z.M. de Pedro, J.A. Casas, J.J. Rodriguez, Chlorophenols breakdown by a sequential hydrodechlorination-oxidation treatment with a magnetic Pd–Fe/-Al2O3catalyst, Water Res., 47 (2013) 3070-3080.

2,4,6 Trichlorophenol. United States Environmental Protection Agency. Jan 2000. Retrieved 2007-11-16.

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