Thesis for the Degree of Master of Engineering

Comparison Study on the Degradation of Hazardous Benzene Derivatives by Ferrate(VI)

by

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Interdisciplinary Program of Marine Convergence Design

The Graduate School

Pukyong National University

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Ferrate(VI)를 이용한 유해 벤젠 유도체 분해에 관한 비교 연구

Advisor: Prof. Il-Kyu Kim

by

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Comparison Study on the Degradation of Hazardous Benzene Derivatives by Ferrate(VI)

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Abstract

The degradation of hazardous benzene derivatives by ferrate(VI) have been demonstrated in this experiment. These result prove to be effective in the treatment of selected benzene derivatives such as bromobenzene, chlorobenzene, and toluene in aqueous solutions.

Ferrate (VI) has been studied as an alternative chemical to disinfect water and wastewater in recent years. The Coagulation and oxidation/disinfection effectiveness of two different type of ferrate(VI) (sodium ferrate and potassium ferrate) in wastewater have also been evaluated. Ferrate(VI) is synthesized by addition of ferric oxide and sodium peroxide to the mixture of calcium hypochlorite and sodium hydroxide (refer to U.S. Patent 8961921B2) with some modification steps.

Degradation of chlorobenzene by ferrate(VI) has been demonstrated and several parameters experiment were investigated. Chlorobenzene was removed effectively in the reactor. Complete degradation of chlorobenzene was achieved at molar ratio of 8/1. The degradation of chlorobenzene follows the second order reaction kinetics. The activation energy calculated from the Arrhenius expression is 80.5 KJ/mol. Degradation of chlorobenzene produces 3-methylbut-1-ene and 2,2-dichloroacetic as identified intermediate products. Then further decomposition of chlorobenzene intermediates led to end products like carbon dioxide.

Degradation of bromobenzene by ferrate(VI) has been demonstrated. Bromobenzene were removed rapidly in reactor within 10 minutes of reaction time. The degradation of bromobenzene follows the second order reaction kinetics. The activation energy calculated from the Arrhenius expression are 81.1 KJ/mol. The proposed pathway of bromobenzene degradation resulted product such as isobutyraldehyde and etahane-1,2-diol.

Toluene removal was performed effectively by solid and liquid ferrate(VI). Several parameters experiment were also investigated and both ferrates(VI) showed similar pattern. The degradation of toluene by both ferrates also followed the second order reaction kinetics. The activation energy calculated from the Arrhenius expression are 79.8 KJ/mol (liquid) and 76.8 KJ/mol (solid). Both ferrates produced similar react by-products. The possible pathway for the degradation of toluene can be described by electron transfer, oxygen transfer, and opening of an aromatic ring.

Halogenated benzene, bromobenzene and chlorobenzene were degraded rapidly by ferrate(VI) in aqueous solutions. The degradation efficiency and kinetic rate of chlorobenzene were higher than bromobenzene. The electronegativity of the substituents (-Br and -Cl) play very defined role in the potential degradation by ferrate. The activation energy values are 81.1 KJ/mol and 80.5 KJ/mol for bromobenzene and chlorobenzene, respectively.

Organic pollutants, toluene, chlorobenzene, and bromobenzene were degraded rapidly by ferrate(VI). The degradation efficiency and kinetic rate of toluene were higher than chlorobenzene and bromobenzene. The functional groups (-CH_3, -Cl, and -Br) play very defined role in the potential degradation by ferrate. The activation energy values are 79.4 KJ/mol, 80.5 KJ/mol, and 81.16 KJ/mol for toluene, chlorobenzene, and bromobenzene, respectively.

Based on the investigation for the ferrate reaction of bromobenzene, chlorobenzene, and toluene, the application of ferrate appears to be a promising in both water and wastewater industries in the future.

Ferrate (VI)를 이용한 유해 벤젠 유도체 분해에 관한 비교 연구

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Abstract

본 연구에서는 ferrate(VI) 공정으로 유해 벤젠 유도체가 분해됨을 입증하였다. 이러한 결과는 수용액에서 브로모 벤젠, 클로로 벤젠 및 톨루엔과 같은 선택된 벤젠 유도체의 처리에 효과적이라는 것을 증명한다.

Ferrate(VI)는 최근 몇 년간 물과 폐수를 소독하는 대체 화학 물질로 연구되었으며, 폐수에서 두 가지 유형(고상, 액상) ferrate(VI)의 산화/소독 및 응고 효과에 대해서도 평가된 바 있다. Ferrate(VI)는 일부 수정 단계를 포함하여 칼슘 하이포클로라이트와 수산화 나트륨의 혼합물에 철 산화물과 과산화수소를 첨가하여 합성된다(미국 특허 제 8961921B2 호 참조).

Ferrate (VI)에 의한 클로로 벤젠과 브로모 벤젠의 분해를 증명하기 위해 몇 가지 매개 변수 실험이 수행되었다. 그 결과, 반응기에서 클로로 벤젠을 효과적으로 제거하였으며 몰비 8/1 에서 클로로 벤젠의 완전한 분해가 달성되었다. 클로로 벤젠의 분해는 2 차 반응 속도를 따랐으며 Arrhenius 식에서 계산 된 활성화 에너지는 80.5 KJ/mol 이었다. 브로모 벤젠은 반응 시간 10 분 이내에 반응기에서 제거되었으며, 브로모 벤젠의 분해는 역시 2 차 반응 속도를 따랐다. Arrhenius 식에서 계산 된 활성화 에너지는 81.1 KJ/mol 이었다.

유해 유기 오염물질인 톨루엔도 고상 및 액상 Ferrate (VI)에 의해 효과적으로 제거되었으며, 이에 대한 몇 가지 매개 변수 실험을 수행하였다. 두 가지 유형의 ferrate 에 의한 톨루엔의 분해는 역시 2 차 반응 속도론을 따랐으며, Arrhenius 식에서 계산 된 활성화 에너지는 각각 79.8 KJ/mol (액상) 과 76.8 KJ/mol (고상)이었다. 두 ferrate 는 모두 유사한 반응 부산물을 생성하였으며, 톨루엔 분해는 전자 전달, 산소 전달 및 방향족 고리의 개방에 의해 분해되는 것으로 판단된다.

할로겐화 벤젠, 브로모 벤젠 및 클로로 벤젠은 ferrate(VI)에 의해 빠르게 분해되었다. 클로로 벤젠의 분해 효율 및 반응속도는 브로모 벤젠보다 높았다. 이는

치환체 (-Br 및 -Cl)의 전기 음성도가 ferrate 에 의한 분해에서 매우 중요한 역할을 하기 때문인 것으로 판단된다. 브로모 벤젠 및 클로로 벤젠의 활성화 에너지 값은 각각 81.1 KJ/mol, 80.5 KJ/mol 이었다.

유기오염물질인 톨루엔 및 클로로 벤젠 역시 ferrate (VI)에 의해 빠르게 분해되었다. 특히 톨루엔의 분해 효율 및 반응속도는 클로로 벤젠보다 높았다. 이는 작용기 (-CH_3 및 -Cl)가 Ferrate 에 의한 분해에서 매우 중요한 역할을 하는 것으로 판단된다. 톨루엔 및 클로로 벤젠의 활성화 에너지 값은 각각 79.4 KJ/mol, 80.5 KJ/mol 이었다.

이러한 결과를 바탕으로 향후 물과 폐수 산업분야에서 브로모 벤젠, 클로로 벤젠 및 톨루엔의 제거에 ferrate (VI)을 적용하는 것은 매우 유망할 것으로 판단된다.

Chapter 1

GENERAL INTRODUCTION

A large amount of environmental pollutants released into the ecosystem are usually compounds that are toxic to living organisms (Cao et al. 2009). Among the major environmental pollutants, benzene derivative compounds are of great concern because they have toxicological and environmental implications. Benzene derivatives are frequently employed as solvents, pesticides and other petroleum base industries (Bryant 2014; Clough 2014; Pravasi 2014). Developing a degradation technology for highly toxic substances is an important part of any strategy focusing on water purification. The technologies for hazardous benzene derivatives treatment have improved so far, but these have several disadvantages such as high cost, difficult operation and long operation time (Flores-Chaparro et al. 2017; Musilová-Kebrlová et al. 2009; Wu et al. 2009). Fast, practical, and cost effective technologies should be developed to remediate hazardous benzene derivatives contamination.

Simple and more efficient water treatment, Coagulant and oxidant are two important operations in a wastewater treatment plant. The most common coagulants used include ferric sulphate, aluminium sulphate, and ferric chloride, and the oxidants/disinfectants used are chlorine, sodium hypochlorite, chlorine dioxide, and ozone (Jiang and Lloyd 2002; Licht et al. 2001; Sharma 2002). As water pollution increases and the standards of drinking water supply and wastewater discharge become stringent, water treatment reagents should ideally be able to disinfect microorganisms, partially degrade and oxidize the organic and inorganic impurities, and remove colloidal/suspended particulate materials and heavy metals (Jiang and Lloyd 2002). A potential chemical reagent which meets these criteria may be ferrate(VI).

Ferrate(VI) is the hexavalent form of iron (VI) (FeO_4^{2-}) (Sharma et al. 2015). Ferrate(VI) has shown great potential as an effective coagulant, disinfectant, and oxidant for various water and wastewater treatment processes (Jiang 2014; de Luca et al. 1996; Sharma 2002; Thompson et al. 1951). Recently, in order to investigate the potential of ferrate for effective waste treatment, its reactivity with various pollutants were investigated (Al-Abduly and Sharma 2014; Anquandah and Sharma 2009; Jiang et al. 2016; Pepino Minetti et al. 2017). These pollutants include toluene, cycloalkanes, ketons, hydroquinones, phenols, aminobenzene, estrogens (Jiang et al. 2005), triclosan and benzotriazoles (Yang et al. 2011b). During the oxidation process, ferrate(VI) as a green oxidant will reduced to ferric hydroxide (Fe(III)) and molecular (Anquandah and Sharma 2009; Gombos et al. 2013; Jiang and Lloyd 2002; Lee and Gai 1993; Osathaphan et al. 2014;

Waite and Gilbert 1978). It is well to know that Fe(III) is an excellent scavenger of many anions, such as phosphate, as well as being a coagulant (Waite and Gilbert 1978).

This work studies the degradation of hazardous benzene derivatives in aqueous solutions under controlled laboratory conditions. The effect of relevant parameters on the degradation of benzene derivatives are examined. the reaction intermediates and the reaction pathways were also investigated.

Chapter 2 provides a review of the existing literature on the properties of toluene, chlorobenzene, and bromobenzene. Description of the chemistry, synthesis and applications of ferrate(VI) are also presented.

Chapter 3 demonstrates the degradation of chlorobenzene. Factor that affect the degradation are investigated and the result of intermediate products of chlorobenzene are found. The experiment result show that ferrate(VI) was effective to removed chlorobenzene in the reactor.

Chapter 4 demonstrates the degradation of bromobenzene. Factor that affect the degradation such as pH, molar ratio, and temperature are investigated. The experiment result show that ferrate(VI) was effective to removed bromobenzene in the reactor.

Chapter 5 presents the degradation of toluene by solid and liquid ferrate(VI). Factor that affect the degradation are investigated and the degradation pathways are proposed. The result of intermediate products of toluene oxidation by solid and liquid ferrates(VI) have been investigated and both results have similar byproducts.

Chapter 6 presents the degradation of bromobenzene and chlorobenzene. The electronic effect of the substituent on the degradation and kinetic rate of aromatic halogenated compounds are investigated. The result suggest that carbon-halogen bond also plays an important role in this reaction.

Chapter 7 presents the degradation of toluene and chlorobenzene. The functional group effect on the degradation and kinetic rate of benzene derivatives are investigated. The result suggest that carbon- substituent bond also plays an important role in this reaction.

Chapter 8 presents suggestions and recommendations for future study. Several approaches to understand and improve the existing treatment processes are suggested.

1.1.Objectives

Due to the ever-increasing fluxes of hazardous benzene derivatives into environment, technologies which can effectively remove benzene derivatives must be developed. Recently ferrate process has been reported as powerful, simple and cost-effective methods to remove variety of benzene derivatives.

The research is conducted to investigate the degradation of environmentally important benzene derivatives by ferrate process. Chlorobenzene, bromobenzene and toluene are selected as model benzene derivatives to examine their behavior in aqueous solution when exposed to ferrate(VI). The analyses of intermediates and reaction products provide some important data to investigate the degradation pathways in ferrate reaction. Factors such as the pH, molar ratio, and temperature are investigated in order to find the optimal conditions for ferrate reactions.

Chapter 2

LITERATURE REVIEW

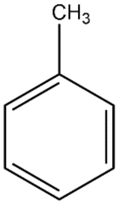
2.1. Contaminant Compounds Overview

2.1.1. Toluene

Toluene is generally produced along with benzene, xylenes and C9 aromatics by the catalytic reforming of C6-C9 naphtas. Most toluene is added to automobile or aviation gasoline as BTX mixtures (benzene, toluene, xylene) to increase octane ratings. Toluene is an excellent organic solvent and is used extensively in the manufacture of benzene derivatives, caprolactam, saccharin, medicines, dyes, perfumes and TNT. (Clough 2014).

After long-term exposure, blood abnormalities, psychomotor disorders, changes in the lens of the eye, immune system changes, kidney effects, menstrual disorders, and birth defects have been observed in some, but not all, studies of workers or abusers, and the possible confounding effect of mixed chemical exposure is mentioned in most cases. Liver effects, which figure prominently in animal studies, have not been observed in occupationally exposed individuals (Clough 2014). The properties of toluene are shown below (Table 1).

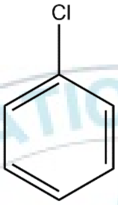
Table 1. Properties of toluene

Parameters	Properties
Molecular Formula	C_7H_8
Chemical structure	
Molecular Weight	92.141 g/mol
Boiling Point	110.7 ^{o}C
Melting Point	-95 ^{o}C
Flash Point	40 F (closed cup)
Vapor Density	3.2 (air = 1)
Vapor Pressure	36.7 mm Hg
Density	0.87 g cm^{-3}
LogP	$\log K_{ow} = 2.73$
solubility	In water, 0.52 g/L. Miscible with alcohol, chloroform.

2.1.2. Chlorobenzene

Chlorobenzene is produced by chlorination of benzene in the presence of a catalyst, and is produced as an end product in the reductive chlorination of di- and trichlorobenzenes. This compound is extensively used in the manufacture of phenol, aniline, and DDT; as a solvent for paints; and as a heat transfer medium. It is also occasionally used in the dry cleaning industry. It is a chemical intermediate in the production of diphenyl oxide, diisocyanates, and nitrochlorobenzene. It has also been used as a fiber-swelling agent and as a dye carrier in textile processing (Pravasi 2014). The properties of chlorobenzene are shown below (Table 2).

Table 2. Properties of chlorobenzene

Parameters	Properties
Molecular Formula	C_7H_5Cl
Chemical structure	
Molecular Weight	112.556 g/mol
Boiling Point	132 °C
Melting Point	-45 °C
Flash Point	27 °C
Vapor Density	3.88 (Air = 1)
Vapor Pressure	9 mmHg
Density	1.11 g cm^{-3}
LogP	log K_{ow} = 2.84
solubility	In water, 499 mg/L at 25^{o}C. Miscible with ethanol, ethyl ether

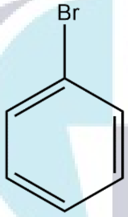
The human literature primarily consists of case reports. In the industrial environment, symptoms including headache, numbness, skin irritation and redness, eye irritation and redness, irritation and redness of the upper respiratory tract, bronchitis, dizziness, somnolence, loss of consciousness, hematopoietic effects, gastritis, hepatitis, and neuromuscular changes have been reported. Lesions of the liver and kidneys have been observed following absorption of toxic doses. The histological changes may progress as exposure becomes more severe or as the period of exposure is lengthened. Liver injury may progress to necrosis and parenchymous degeneration (Pravasi 2014).

2.1.3. Bromobenzene

Bromobenzene is a colorless, flammable liquid with a density greater than water and with an aromatic odor. It is synthesized by the reaction of bromide with benzene in the presence of iron powder. It is used for organic synthesis, particularly in the production of the intermediate phenylmagnesium bromide. Bromobenzene is an additive to motor oils and used as a crystallizing solvent (Bryant 2014). The properties of bromobenzene are shown in Table 3.

The liver and kidney are the only organs affected by longer-term exposure to bromobenzene. Bromobenzene inhalation studies were conducted on rats and mice for 13 weeks with doses ranging from 64.2 to 1926 mgm^{-3} for 6 h per day for 5 days per week. Increased incidence of cytomegaly in the liver was observed in female mice at the highest vapor concentration. Mild renal histopathology was also observed in male rats at the highest concentration. In another study, rats and mice were administered oral doses of bromobenzene by gavage in corn oil at concentrations ranging from 50 to 600 mg kg^{-1} per day for 90 days. Hepatocellular necrosis was observed at oral doses of 400 and 600 mg kg^{-1} in rats and mice (600 mg kg^{-1} in female mice) and hepatocellular cytomegaly was observed at doses of 200 mg kg^{-1} and higher in rats and mice (>400 mg kg^{-1} in female rats) (Bryant 2014).

Table 3. Properties of bromobenzene

Parameters	Properties
Molecular Formula	C_7H_5Br
Chemical structure	
Molecular Weight	157.01 g/mol
Boiling Point	156 °C
Melting Point	-30.8 °C
Flash Point	51 °C
Vapor Density	5.41 (Air = 1)
Vapor Pressure	4.18 mm Hg
Density	1.495 g cm^{-3}
LogP	log K_{ow} = 2.99
solubility	In water, 410 mg/L at 25^{o}C. Miscible with ethanol, ethyl ether, and benzene

2.2. Ferrate(VI)

2.2.1. Synthesis of ferrate(VI)

Ferrate (VI) is a +6 oxidation state of iron that demonstrates useful properties such as oxidizing power and selective reactivity, and decomposes to the more common ion state, ferric (III). There are three general methodologies used to synthesize ferrate (VI); electrolysis, dry oxidation, and wet oxidation (Lee et al. 2004). A review of ferrates and the three methods of preparation of ferrate:

- Dry method - Dry oxidation requires high temperature and pressure when reacting iron oxides with oxidants. To synthesize ferrate (VI) by dry oxidation the following reaction occurs (El Maghraoui et al. 2015) (Eq. 1):

  $$Fe_2O_3 + Na_2O_2 \rightarrow 2Na_2FeO_2 + Na_2O \tag{1}$$

- electrolysis method - Electrolysis uses a pure iron metal electrode anodized in concentrated alkaline solution. The following half-cell reactions occur at an anode (Mácová et al. 2009) (Eq. 2):

  $$Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e^- \tag{2}$$

  and the following half-cell reaction at the cathode (Eq. 3):

  $$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

- Wet method - The wet oxidation procedure for ferrate synthesis uses concentrated hypochlorite in a strong basic solution such as sodium hydroxide (NaOH) to oxidize ferric (III) ion. Additionally, an excess amount of potassium hydroxide is added to the soluble ferrate (VI) to precipitate potassium ferrate salt (K_2FeO_4). The following reactions summarize the wet oxidation synthesis of Fe (VI) (Thompson et al. 1951) (Eqs. 4-5):

$$2Fe(OH)_3 + 3NaClO + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O \quad (4)$$

$$2Na_2FeO_4 + 2KOH \rightarrow K_2FeO_4 + 2NaOH \quad (5)$$

2.2.2. Ferrate(VI) Reactions

Although the use of ferrate has not as yet found wide application in organic synthesis, it seems very promising for oxidation. Under acidic conditions, the redox potential of iron (VI) is greater than ozone and is the strongest of all the oxidants/disinfectants used for water and wastewater treatment, as shown in Table 4 (Jiang and Lloyd 2002).

The ability of Ferrate to act as a coagulant and oxidant make it more attractive than other chemicals used in wastewater treatment such as aluminum sulphate, ferric chloride, potassium permanganate and chromium trioxide (Delaude and Laszlo 1996; Jiang et al. 2001; DE LUCA et al. 1992). De Luca et al. (1983) compared Ferrate to alum coagulation and found that Ferrate removed a higher percentage of trichloroethylene, naphthalene, 1, 2-dichlorobenzene, and bromodichloromethane when coupled with paddle or gas flocculation than alum (De Luca et al. 1983).

Table 4. Redox potential for the oxidant/disinfectant used in water and wastewater treatment

Disinfectant / Oxidant	Reaction	E^o, V
Chlorine	$Cl_2 + 2e \leftrightarrow 2Cl^-$	1.358
	$ClO^- + H_2O + 2e \leftrightarrow Cl^- + 2OH^-$	0.841
Hypochlorite	$HClO + H^+ + 2e \leftrightarrow Cl^- + H_2O$	1.482
Chlorine dioxide	$ClO_2 + e \leftrightarrow ClO_2^-$	0.954
Perchlorate	$ClO_4^- + 8H^+ + 8e \leftrightarrow Cl^- + 4H_2O$	1.389
Ozone	$O_3 + 2H^+ + 2e \leftrightarrow O_2 + H_2O$	2.076
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e \leftrightarrow 2H_2O$	1.776
Dissolved oxygen	$O_2 + 4H^+ + 4e \leftrightarrow 2H_2O$	1.229
Permanganate	$MnO_4^- + 4H^+ + 3e \leftrightarrow MnO_2 + 2H_2O$	1.679
	$MnO_4^- + 8H^+ + 5e \leftrightarrow Mn^{2+} + 4H_2O$	1.507
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e \leftrightarrow Fe^{3+} + 4H_2O^-$	2.20

Ferrate has also been used to oxidize nitrogen-containing compounds. Sharma (2004) found that the reaction between Ferrate and nitrogen or sulfur-containing pollutants follows first order reaction kinetics with the rate of reaction increasing with a decrease in pH. The protonated form of Ferrate, $HFeO_4^-$, reacts more quickly than the non-protonated form, explaining why reactions oxidize faster with a decrease in pH (Sharma 2004). At stoichiometric values, Ferrate was able to oxidize hydrogen sulfide, thiourea, thioacetamide, cyanide, and thiocyanate to non-hazardous products. Ferrate also reduces to Fe^{3+}, another harmless by-product

(Sharma 2007). Goff and Murmann (1971) found that the spontaneous decomposition of Ferrate in water forms molecular oxygen (Goff and K. Murmann 1971).

Ferric hydroxide ($Fe(OH)_3$) is also produced as a by-product of most Ferrate reactions which promotes coagulation (Jiang and Wang 2003; Potts and Churchwell 1994; Stupin and Ozernoi 1995). Ferrate aids in the coagulation process by destroying the organic coating on particles. During coagulation, the floc size is larger when using Ferrate as opposed to alum, suggesting that Ferrate is a better coagulant because of reduced turbidity seen in highly organic waters (Ma and Liu 2002; Sharma et al. 2005b). In addition, Ferrate is advantageous because it can be effective over a wide pH range (Sharma 2007). Using Ferrate as a disinfectant does not produce carcinogenic or mutagenic by-products (De Luca et al. 1983).

2.2.3. Ferrate Chemistry

Ferrate has the molecular formula FeO_4^{2-} in which iron has an oxidation state of +6. Ferrate is an environmentally-friendly oxidant which can oxidize a large number of organic and inorganic pollutants in aquatic environments, substituting for oxidants of environmental concern such as chlorine and chromate (Sharma 2002).

Several researchers who have studied the chemistry of ferrate agree that ferrate has a tetrahedral structure in which four equivalent oxygen atoms are covalently bonded to a central iron atom in +6 oxidation state (Goff and K. Murmann 1971). Lee et al. (2004) proposed that ferrate can have three resonance hybrid structures in aqueous solution as shown in Fig. 1 (Lee et al. 2004).

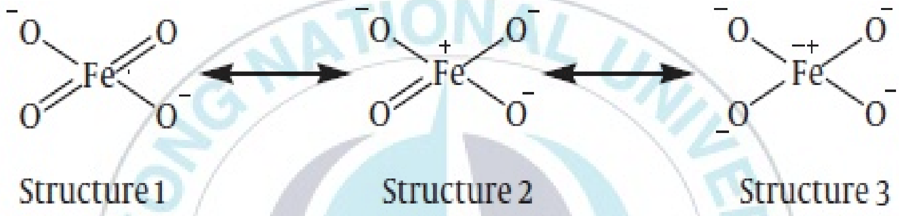


Figure 1. Three resonance hybrid structure of Fe(VI) ion in an aqueous solution

The species distribution of Fe (VI) in aqueous solution is dependent on pH. Recent studies have demonstrated that there exist four Fe (VI) species in aqueous solution via their acid base equilibrium (Rush and Bielski 1994), $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}. Fig. 2 shows these four species and indicates that $HFeO_4^-$, and FeO_4^{2-} are the predominant species in neutral and basic pH conditions respectively; where Fe (VI) is more stable (Lee et al. 2004).

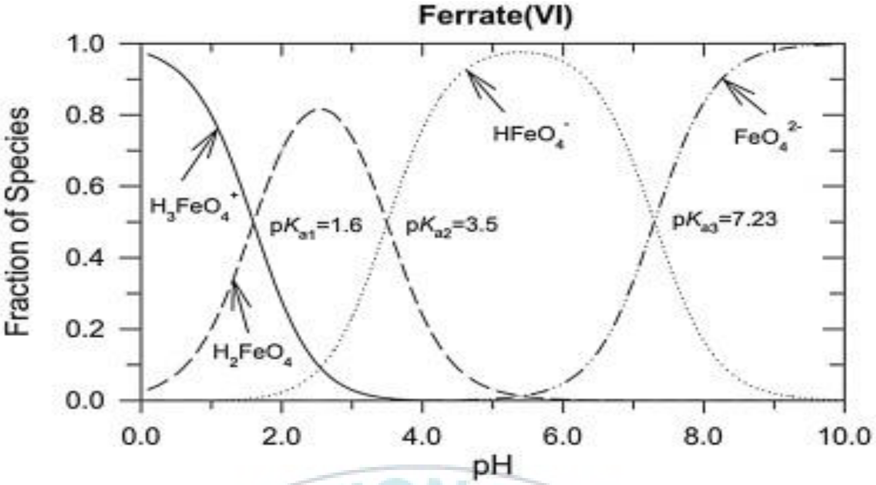


Figure 2. Speciation of ferrate(VI) in solution as a function of pH
(Lee et al. 2004)

Chapter 3

FERRATE(VI) APPLICATION FOR CHLOROBENZENE DEGRADATION

Abstract

Chlorobenzene is frequently detected in the environment and listed as priority pollutants by the U.S. Environmental Protection Agency. Acting as a powerful oxidant, efficient coagulant, and effective disinfectant, ferrate is a good multifunction agent for water treatment. In this study, degradation of chlorobenzene in aqueous solution using Fe(VI) has been examined. The effect of molar ratio ([$(FeO_4)^{2-}$]/ [Chlorobenzene]) (2-8), pH (3-9), and temperature (15-55^{o}C) were investigated. The ferrate(VI) has been successfully produced with a high concentration of 89.000 ppm. In this experiment, the highest chlorobenzene removal was achieved at pH neutral condition (pH = 6.8) with degradation efficiency of 31.125%. For the effect of molar ratio, the degradation efficiency increased as molar ratio increased. Complete degradation of chlorobenzene was achieved at molar ratio of 8/1. The optimal temperature has been observed at 45^{o}C with k_{app} value of 229.76 $M^{-1}s^{-1}$ and activation energy of 80.5 KJ/mol. The intermediate products such as 3-methylbut-1-ene and 2,2-dichloroacetic acid were identified and the possible degradation pathways have been proposed.

3.1. Introduction

Chlorobenzene are halogenated benzene with high toxicity and persistence in the environment (Zhang et al. 2011). Chlorobenzene has vast applications in chemical industry as intermediates in dye and pesticide (Selli et al. 2008). Water contaminated by chlorobenzene is a great concern because of their acute toxicity and has potential to accumulate in the environment (Aelion et al. 1987). Chlorobenzene is also listed as the priority pollutant by the Environmental Protection Agency (USEPA 1988). Therefore, it is necessary to appropriately remove chlorobenzene through various water treatment processes for satisfying the water quality standard. Recently, the most used methods for chlorobenzene removal are electrochemical and biodegradation processes (Monferrán et al. 2005; Musilová-Kebrlová et al. 2009). However, these methods required long operation time and also have low removal efficiency.

In the past decades, ferrate(VI) (Fe(VI)) is found to be a potential and useful oxidant (de Luca et al. 1996; Thompson et al. 1951). Fe(VI), in the form of sodium ferrate (Na_2FeO_4), is a powerful oxidant in a wide pH range (Sharma 2011b) with high oxidation-reduction potential (Sharma 2011b; Yang et al. 2014). Ferrate(VI) has shown great potential as a multi-functional function for coagulation, disinfection, and oxidation (Jiang 2014; Li et al. 2008; Sharma 2002). Morover, ferrate(VI) reportedly produces non-toxic ion, Fe(III) and molecular oxygen (Jiang and Lloyd 2002; Sharma 2002). These facts make Fe(VI) can be a promising candidate for water treatment process.

The superior performance of ferrate(VI) as an oxidant/disenfectant has been extensively investigated for the degradation of water pollutants (Al-Abduly and Sharma 2014; Anquandah and Sharma 2009; Jiang et al. 2016; Pepino Minetti et al. 2017). These pollutants include toluene, cycloalkanes, ketons, hydroquinones, phenols, aminobenzene, estrogens (Jiang et al. 2005), triclosan and benzotriazoles (Yang et al. 2011b). A study (Waite and Gilbert 1978) showed that ferrate could simultaneously remove more than 50% of benzene and alchohol. However, there is very limited information on the application of Fe(VI) for the treatment of halogenated benzene such as chlorobenzene. To answer the above concern, the objective of this work are to synthesize ferrate(VI) and investigate chlorobenzene degradation in various conditions. The parameters experiment such as pH, molar ratio, and temperature were studied.

3.2. Materials and Methods

3.2.1. Materials

The ferrate(VI) was prepared using ferric oxide (Fe_2O_3) and sodium peroxide (Na_2O_2) as the main materials, were purchased from Alfa Aeser.

Chlorobenzene as target compound were purchased from Sigma-Aldrich. The other chemicals such as sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) were purchased from Junsei Company. Buffer solutions for pH adjustment were obtained from Samchun Company.

3.2.2. Methods

3.2.2.1. Synthesis of Ferrate(VI)

The ferrate(VI) was prepared using US Patent method (Sharma 2011b) with some modification steps. The first step to synthesize ferrate(VI) was heating 0.96 g of Fe_2O_3 and 2.36 g of Na_2O_2 at 500°C in a furnace for 30 minutes. Then, 2 g of the mixture was taken, then mixed with 60 mL of NaOCl. And 20 g of NaOH was added gradually. The dark purple solution was produced by mixing of the reagents, indicating that ferrate(VI) in liquid phase was generated. Then it was filtered and ferrate(VI) (Na_2FeO_4) was produced.

3.2.2.2. Degradation Experiment

The degradation experiments were performed in 700mL of closed zero-head space glass reactor with ports for sampling, measuring pH and temperature, and adding ferrate(VI). To control pH, the addition of 5 - 10 mL buffer solution and a few drops of sulfuric acid (0.5 M) were used. The Chlorobenzene solutions with the initial concentration (C_0) of 0.010mM were used in the experiments. The effects of the parameters such as pH (3.7-

9.4), molar ratio (1.05-4.2) and temperature (15°C – 45°C) were investigated within 20 minutes of reaction time. The samples were extracted using liquid-liquid extraction (LLE) method (sample volume = 3mL, vortex mixing time for extraction = 2 minutes, temperature = 25°C, n-hexane volume = 3mL). The concentrations of bromobenzene and chlorobenzene were measured using gas chromatography-electron capture detector (GC-ECD). The temperatures of injection port and detector were 250°C and 300°C, respectively. Initially 40°C was held constant for 5 minutes, followed by 8°C/min ramp until a temperature of 100°C was reached, and followed by 12°C/min ramp until a final temperature of 200°C was reached. In this work, all of the degradation experiments were performed duplicately.

3.2.2.3.Intermediate Study and Degradation Pathway

The gas chromatography-mass spectrometry (GC-MS) technique was used to analyze intermediate products. To stop further degradation reaction, quenching process using sulfuric acid was conducted. GC-MS was performance with Mass Spectrometer System (GC-MS QP2010Plus, Shimadzu, Japan) and an AT-1 capillary column (60 m x 0.32 mm I.d x 1.0 μm film thickness). The temperatures of injection port and detector were 250°C and 300°C, respectively. Initially 40°C was held constant for 5 minutes, followed by 8°C/min ramp until a temperature of 100°C was reached, followed by 12°C/min ramp until a temperature of 200°C was reached, followed by 15°C/min ramp until a final temperature of 250°C was reached.

3.3. Result and Discussion

3.3.1. Synthesis of Ferrate(VI)

In the experiment, Fe_2O_3 was used as the iron(Fe) source in ferrate production. The superior ferrate(VI) (Na_2FeO_4) was successfully generated with high concentration of 89,000ppm. A red-purplish color was formed as a result. The spectral measurement of FeO_4^{2-} in phosphate buffer is given in Fig. 3. It showed that ferrate(VI) has a peak at ~510 nm (Sharma et al. 2001). The molar absorptivity at 510 nm has been determined previously as 150 M^{-1} cm^{-1} by Bielski and Thomas (H. J. Bielski and J. Thomas 1987). Base on the measurements at a wavelength of 510nm, a calibration curve can be established. Furthermore, the ferrate concentration in the experiment can be determined.

Ferrate(VI) was measured right away and used within 1 hour of production to minimize ferrate self-decomposition. The use of ferrate(VI) as oxidant agent is of interest because of its high oxidizing power and because it does not generate hazardous waste after decomposition. In turn, ferrate salts have the ability to act both as a coagulant and oxidant due to formation of $Fe(OH)_3$ as a reaction product, a well-known coagulating-flocculating agent capable of removing a variety of contaminants (Jiang 2007).

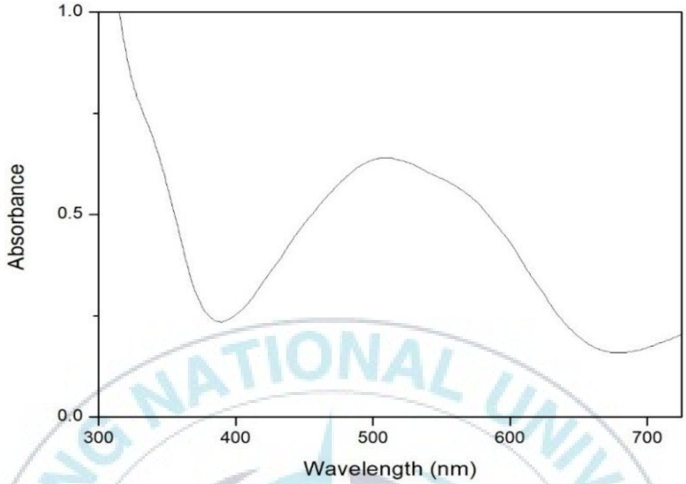


Figure 3. UV-Vis spectrum of ferrate(VI)

The ferrate(VI) formation followed the reaction below (Eqs. 6-7):

$$Fe_2O_3 + Na_2O_2 \rightarrow 2NaFeO_2 + {}^{1}/_{2}\,O_2 \qquad (6)$$

$$2NaFeO_2 + 3NaOCl + 2NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + H_2O \qquad (7)$$

3.3.2. Effect of pH

Ferrate(VI) oxidation power is dependent on pH condition (Thompson et al. 1951). The effect of pH was tested at pH 3.7, 6.8, and 9.7. The pH buffer solution was used for controlling target compound solution. The effect of pH on chlorobenzene degradation is shown in Fig. 4. The chlorobenzene removal efficiency was increased rapidly in the beginning and then slowed down with time. More than 20% of chlorobenzene was degraded within 10 minutes of reaction time. When the initial pH increased from 3.7 to 6.8, the chlorobenzene removal increased obviously from 24.9% to 31.1%. Further initial pH increase to 9.4 reduced the chlorobenzene removal efficiency of 17.9%.

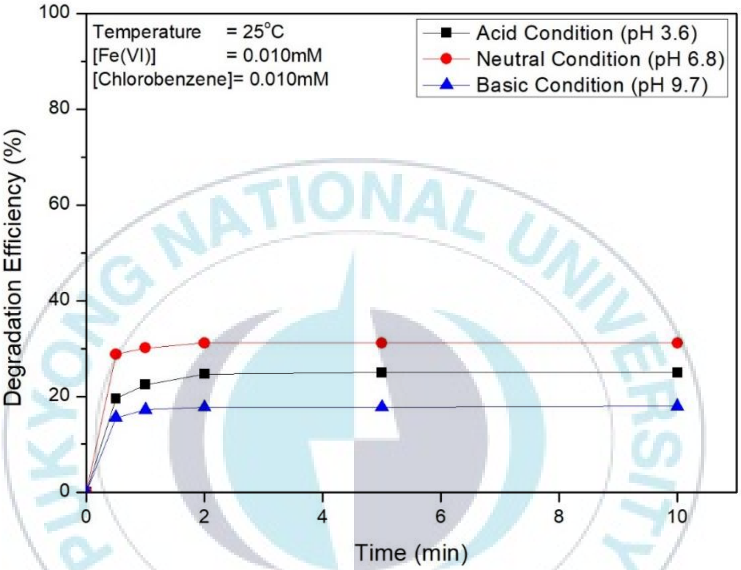


Figure 4. Effect of pH on the removal of chlorobenzene by ferrate(VI)

The number of researchers stated that, the optimum pH range for oxidation of organic substrates by ferrate(VI) on pH 7 to 9.2 (Graham et al. 2004). The highest chlorobenzene degradation was achieved in neutral condition (pH 6.8), while the lowest chlorobenzene degradation was achieved in basic condition (pH 9.4). As can be observed, ferrate has four species ranging from non-protic, monoprotic, diprotic and tri-protic species, the non-protonated species (FeO_4^{-2}) being predominant for alkaline pH, and the monoprotic species ($HFeO_4^-$) for slightly acidic pH (Sharma et al. 2013). According to previous studies, density functional theory (DFT) calculation on the reactivity of Fe(VI) with several compounds showed that the $HFeO_4^-$ (ferrate dominant species at neutral pH condition) has a larger spin density on oxo-ligands, which increases the oxidation ability of protonated Fe(VI) (Anquandah et al. 2011; Kamachi et al. 2008). As the pH increased, the oxidizing power of Fe(VI) decreased with the decrease in the reactive Fe(VI) species ($HFeO_4^-$) (Sharma et al. 2013). Thus, the rapid increase in $HFeO_4^-$ species from pH of 3.7 to 6.8 explains the increased degradation efficiency of chlorobenzene.

The kinetics for the reactions of ferrate (VI) and various compounds have been studied by other researchers and determined to fit very well with the second-order reaction rate law (Yang et al. 2011a). The reaction rate was determined from the k_{app} value using second-order reaction rate equation. The second order reaction rate law can be expressed as Eq. (8).

$$-d\frac{[\text{Chlorobenzene}]}{dt} = k_{app}[Fe(VI)]_{(tot)}[\text{Chlorobenzene}]_{(tot)} \qquad (8)$$

$[Fe(VI)]_{(tot)}$ and $[\text{Chlorobenzene}]_{(tot)}$ are the total concentration of ferrate(VI) species, and the total concentration of chlorobenzene species. Eq. (8) is rearranged and $d\frac{[Chlorobenzene]}{dt}$ is integrated to become Eq. (9):

$$ln\frac{[\text{Chlorobenzene}]}{[\text{Chlorobenzene}]_0} = -k_{app}\int_0^t [Fe(VI)]dt \qquad (9)$$

Where $\int_0^t [Fe(VI)]dt$ is the Fe(VI) exposure, Fe(VI) exposure is a time-integrated concentration of ferrate(VI) due to its instability (Yang et al. 2011a). This equation was used to measure the k_{app} values in other experiments to eximened effects of molar ratio and temperature.

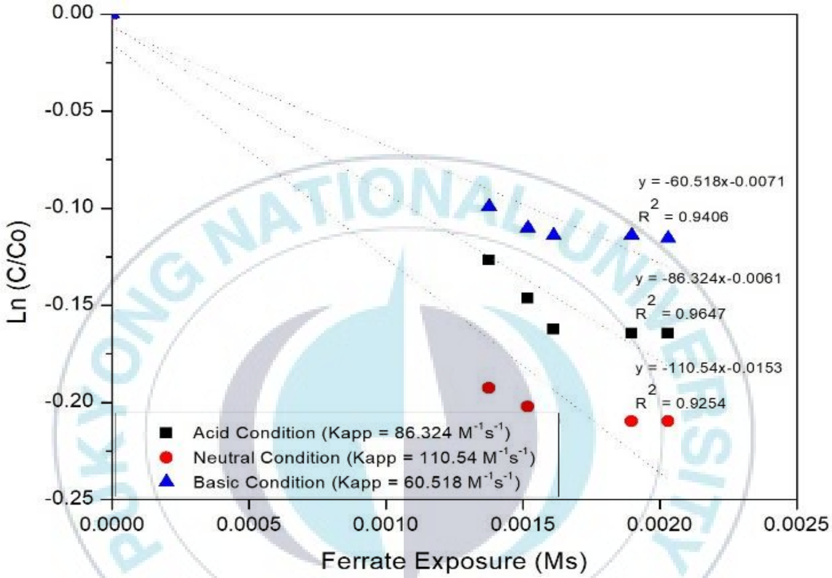


Figure 5. Rate of chlorobenzene removal by ferrate(VI) in various pH levels

From Eq. (11) the values of rate constant (k) for the reaction of ferrate(VI) with chlorobenzene at various pH conditions could be determined and calculated graphically in Fig 5. The k values were obtained from slop of the plots ferrate exposure and ln C/C_0. The R^2 values of rate constant calculation were obtained over than 0.9. The value of k_{app} increased from 86.324 $M^{-1}s^{-1}$ to 110.54 $M^{-1}s^{-1}$ as the pH increased from 3.6, 6,8 then decreased rapidly to 60.518 $M^{-1}s^{-1}$ as the pH increased to 9.7. It was shown that the highest rate constant for degradation of chlorobenzene was achieved at neutral pH condition.

3.3.3. Effect of Molar Ratio

The molar ratio is the important parameter for ferrate(VI) process to remove organic contaminants (Sharma 2013). In order to investigate molar ratio effect, the experiment were carried out at a range of molar ratios ($[FeO4^{2-}]$/[Chlorobenzene]) 2 to 8 with fixed chlorobenzene concentration of 0.010mM. The influence of molar ratio on chlorobenzene removal was studied and the result is summarized in Fig. 6. The degradation of chlorobenzene by ferrate(VI) was a rapid process, with a major removal of chlorobenzene obtained in the initial 2 minutes. The experiment results clearly demonstrated that increasing molar ratios from 2 to 8 apparently increased the removal of chlorobenzene from 44% to 100%. Similar result with other studied, that the degradation efficiency increased with increasing of the molar ratio in a reactor (Sharma and Bielski 1991).

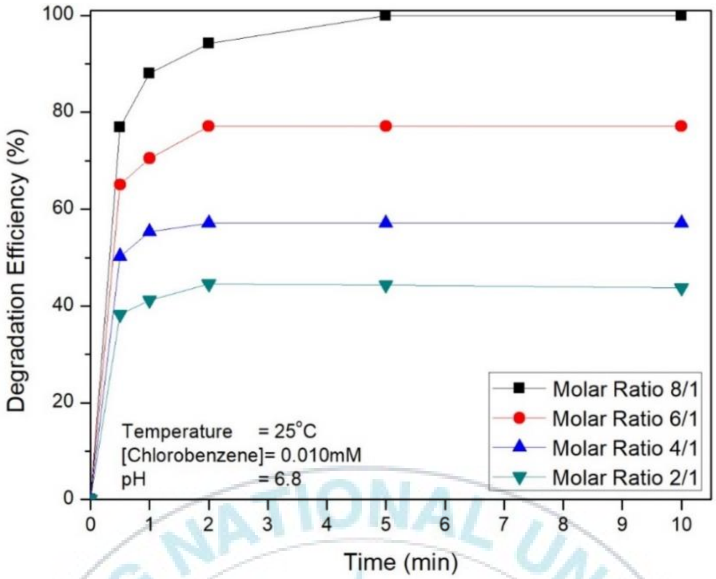


Figure 6. Effect of molar ratio on the removal of chlorobenzene by ferrate(VI)

The increasing of molar ratio on the reactor will definitely affect degradation efficiency. As shown in Fig. 6, complete degradation of chlorobenzene was achieved at molar ratio of 8/1. The degradation of organic pollutants by ferrate(VI) are through two pathways, namely the direct oxidation by ferrate(VI) and the indirect oxidation by the new generated free radicals (as shown in Eqs. 10 - 11) (Zhang et al. 2012). The hydroxyl free radical generated is one of strong oxidizing agent (Han et al. 2013), which is readily decomplex/ degrade the pollutants from aqueous solutions.

$$2FeO_4^{2-} + H_2O \rightarrow 2Fe(OH)_3 + 5[O] \tag{10}$$

$$[O] + H_2O \rightarrow 2HO^{\cdot} \tag{11}$$

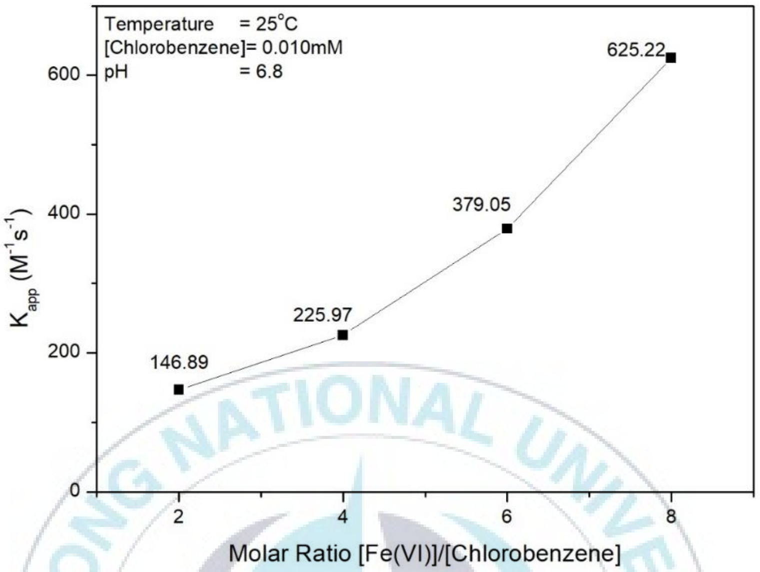


Figure 7. k_{app} of chlorobenzene removal in various molar ratio

The k_{app} values in various molar ratio were calculated and shown in Fig. 7. The second-order rate constant increased from 146.89 $M^{-1}s^{-1}$ to 625.22 $M^{-1}s^{-1}$. The half-life ($t_{1/2}$) for ferrate(VI) to reaction with chlorobenzene ranged from 159.9 to 680.78 s. Indicating this ferrate (VI) oxidizing technology is a promising method for the degradation of chlorobenzene in water.

3.3.4. Effect of Temperature

Temperature is one of the significant parameters for ferrate treatment (Jiang 2014). To determine the effect of temperature on chlorobenzene removal, the temperature experiments were conducted at five different temperature conditions (15, 25, 35, 45, and 55^{o}C). As shown in Fig. 8, the degradation efficiency of chlorobenzene increased in the temperature range from 15 to 45^{o}C, the degradation percentage of chlorobenzene increased significantly from 44.13 % to 54.8 %. Then decreased above 45^{o}C with degradation efficiency of 44.7 %. The optimal temperature condition for removal of chlorobenzene was observed at 45^{o}C.

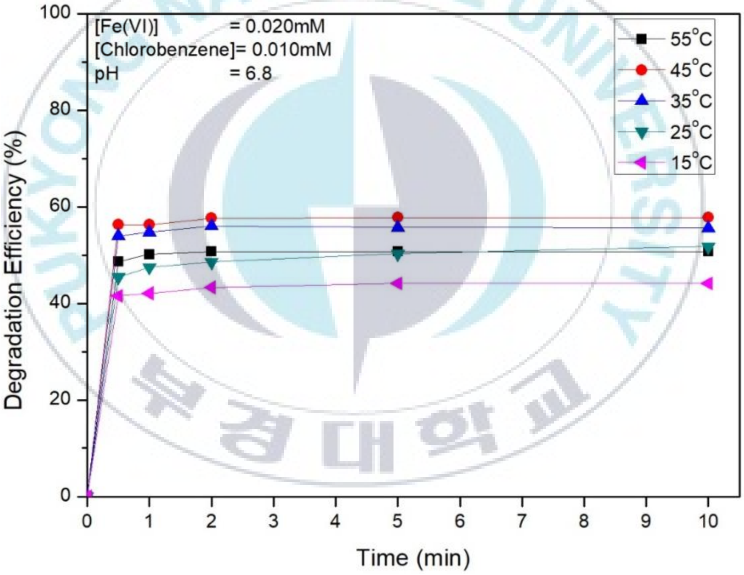


Figure 8. Effect of molar ratio on the removal of chlorobenzene by ferrate(VI)

As shown in Fig. 9, the highest k_{app} values was observed at 45^{o}C. The lowest k_{app} values was observed at 15°C because of the low temperature. The increase in temperature could also increase the effective collision frequencies between ferrate(VI) and target compound, which would promote the oxidation of target compound by ferrate (Han et al. 2015). And reaction kinetics of ferrate(VI) were enhanced when the temperature increased (Sharma et al. 1998a; b). However the k_{app} value decreased upon further increase in the temperature range above 45°C. Several researchers have reported the effect of temperature on the degradation of organic compounds by ferrate(VI). Previous studies have also confirmed the decomposition of ferrate increases rapidly in the range of temperature above 50°C (Deyrup and Mills 1956; Wagner et al. 1952).

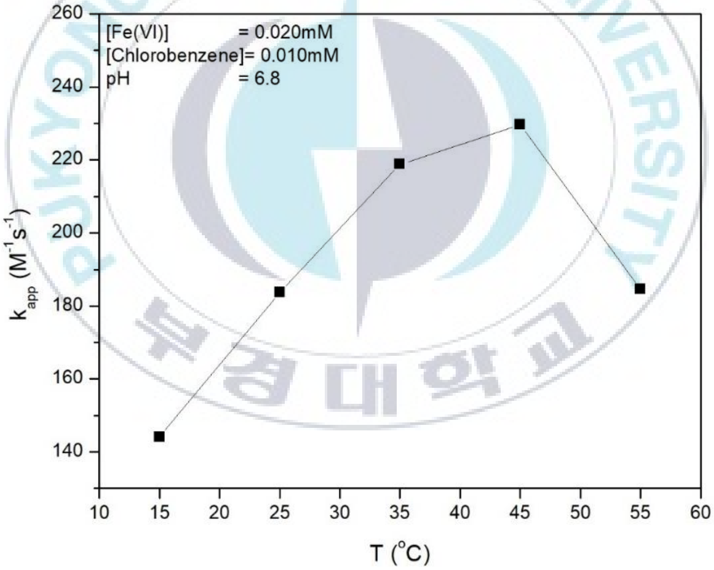


Figure 9. Relationship between T and k_{app} value on chlorobenzene removal

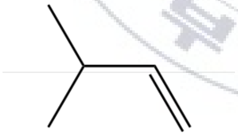
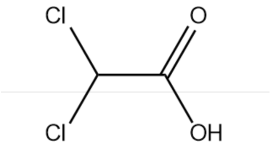
Arrhenius equation of experimental data was used for determining activation energy (Eq. 12), where $E_a$is activation energy; R is the constant value (8.314J K^{-1} mol^{-1}); and T is temperature (K). from the calculation of activation energy for chlorobenzene reaction was 80.5 KJ/mol. Arrhenius equation can be written as:

$$ln\frac{rate_1}{rate_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (12)$$

3.3.5. Intermediate Products

The identity of other intermediate products from chlorobenzene degradation was also evaluated by gas chromatography/mass spectrometry (GC/MS). The mass spectra measurements were examined with the computer database of the National Institute of Science and Technology Mass Spectral Library. Several compounds were evident from the GC/MS–MS chromatogram as summarized in Table 5.

Table 5. Intermediates of chlorobenzene

Chlorobenzene Intermediates	Ret. Time (min)
 3-methylbut-1-ene	4.25
 2,2-dichloroacetic acid	4.75

The degradation pathways of chlorobenzene by ferrate(VI) can be described using reaction product and study literature (Mars et al. 1997; Sedlak and Andren 1991) are proposed in Fig. 10.

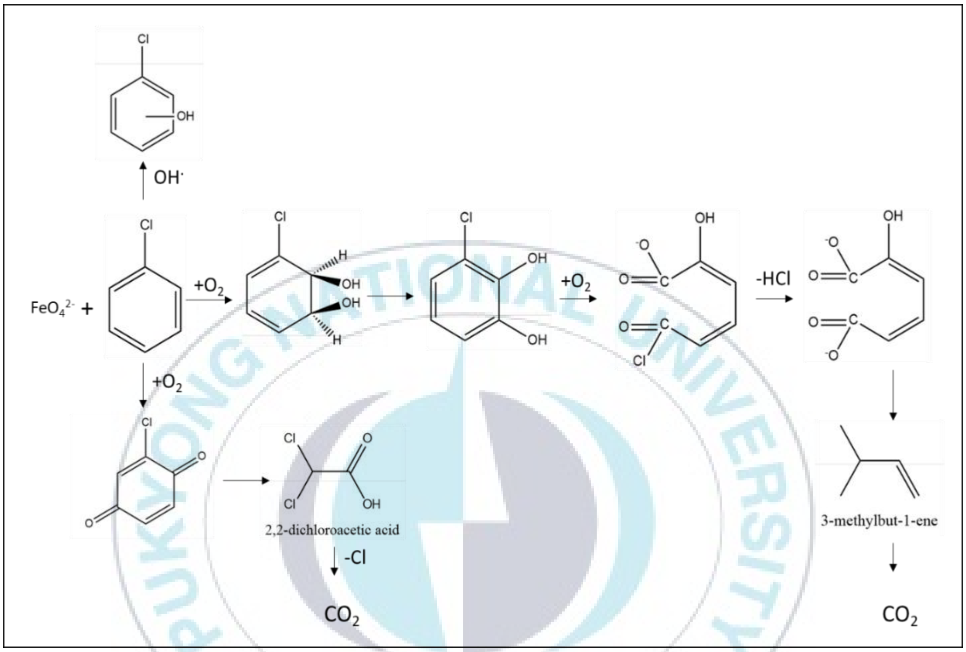


Figure 10. Proposed pathways for chlorobenzene degradation by ferrate(VI)

From the GC-MS analysis, the intermediate compounds that were identified were 3-methylbut-1-ene and 2,2-dichloroacetic acid. The ferrate(VI) reaction during the oxidation of compounds involves, (1) the generation of Fe(V) and Fe(IV) through 1^{e-} and 2^{e-} transfer processes, (2) production of radical species which can also generate Fe(V) and Fe(IV) species, (3) further reactions of Fe(V) and Fe(IV) with contaminants, (4) self-decompositions of Fe(VI), Fe(V), and Fe(IV) species, (5) reactions of ferrates with reactive oxygen species, $O_2^{\cdot-}$, and H_2O_2, produced from self-decompositions (Sharma et al. 2015). The GC/MS detected several compounds substituted with chloride, this chloride from the chlorobenzene and also might be due to chloride from the reagents of ferrate(VI). Then, chlorination also happened in the reactor. Ferrate(VI) were confirmed containing sodium chloride (NaCl), and ferric hydroxide ($Fe(OH)_3$) (Jiang and Lloyd 2002; Ninane et al. 2008). The result is similar to other studies where the intermediate products from degradation of organic compounds by ferrate(VI) also produced several compounds substituted with chloride (Laksono and Kim 2016). On the other hand, for these reasons ferrate(VI) has been investigated as an alternative to chlorine for the disinfection of water and wastewater (Murmann and Robinson 1974).

3.4. Conclusion

This experiment, ferrate(VI) was successfully generated with high concentration of 89,000ppm. Ferrate performance to remove chlorobenzene has been investigated. Like other chemicals oxidants used for the destruction of organic contaminants, the behavior of ferrate is dependent on the pH of the medium, the neutral pH condition has been observed as the best condition for chlorobenzene removal. In effect of molar ratio, the increase of molar ratio was found to be in a linear relationship with degradation efficiency. Whilst under some conditions (e.g. ferrate/

chlorobenzene molar ratio of 8/1) chlorobenzene can be completely degraded in less than 10 min. In effect of temperature, the temperature of 45^{o}C was observed as the optimal temperature with the activation energy of 80.5 KJ/mol. The reaction of chlorobenzene with ferrate was studied in detail in order to identify the formation of intermediate products. The oxidation of chlorobenzene resulted the intermediate product such as 3-methylbut-1-ene and 2,2-dichloroacetic acid.

Chapter 4

FERRATE(VI) APPLICATION FOR BROMOBENZENE DEGRADATION

Abstract

Ferrate [Fe(VI)] was evaluated for the treatment of bromobenzene in aqueous solution. The effect of molar ratio ([$(FeO_4)^{2-}$]/ [Bromobenzene]) (2-8), pH (3-9), and temperature (15-55^{o}C) bromobenzene degradation were investigated. In this experiment, ferrate(VI) was effective to removed bromobenzene in reactor. The highest bromobenzene removal was achieved at pH neutral condition (pH = 6.8), with degradation efficiency of 10.6% within 10 minutes of reaction time. For the effect of molar ratio, the degradation efficiency increased as molar ratio increased. At effect of molar ratio, the highest degradation of bromobenzene was achieved at molar ratio of 8/1. The optimal temperature has been observed at 45^{o}C with k_{app} value of 125.28 $M^{-1}s^{-1}$ and activation energy of 81.16 KJ/mol. The pathway for bromobenzene degradation by ferrate was also discussed.

4.1. Introduction

Bromoaromatic compounds are widely used for the production pesticides, dyes or rubber additives and other chemical products (W. DePierre 2003). Many of these compound are toxic in nature (Bryant 2014;

Puzyn et al. 2010). The widespread use of bromoaromatic compounds have toxicological and environmental implicans(Bryant 2014). One bromoaromatic compounds is bromobenzene (Bryant 2014). Bromobenzene is a poorly soluble, hydrophobic organic compound listed as a priority environmental and marine pollutant and is a known hepatotoxic agent apart from having mutagenic, teratogenic, and carcinogenic effects (Bryant 2014; Darnerud 2003). Developing a dehalogenation and degradation technology for highly toxic substances is an important part of any strategy focusing on water purification. No effective technique has yet been described, although various studies on dehalogenation have been reported (K. Freeman and M. Haugen 1998; Petitto et al. 2006). As a consequence of its wide usage and negative health impacts it is necessary to develop efficient methods to remove bromobenzene from wastewater and freshwater systems.

Over past decades, ferrate (Fe(VI)) has gained lots of attention due to its higher oxidation power (Sharma 2002). Reduction-oxidation (redox) potential of ferrate(VI) has been estimated to be 2.2 under acidic conditions, which is the highest among the practical used water treatment chemicals. Ferrate(VI) has multifunctional functions. When dosed into water, it plays a role of disinfection and oxidation and it is reduced to ferric species including ferric hydroxide which can be served as coagulant/ flocculent

(Jiang and Lloyd 2002), and then it is considered to be a green chemical for water treatment.

Owing to this unique multifunctional properties, ferrate has been used as a disinfectant in place of chlorine for sewage and fresh water (Kazama 1994, 1995; Waite and Gray 1984), in the destruction of toxic organic compounds (Sharma et al. 1998b, 1999), in the removal of toxic metals (Sharma et al. 2005a), as coagulant agent (Jiang et al. 2001), for the removal of organic load (Wei and Yong-Mei 2004), and recently for the removal of emerging pollutants (Ghernaout and Naceur 2011). However, only a few researches have been reported to use ferrate(VI) for bromoaromatic compounds treatment.

In view of the above the present study aims to explore the applicability of ferrate(VI) in the treatment of wastewater contaminated with bromobenzene. The oxidation efficiency, oxidation kinetics and oxidation pattern of bromobenzene using ferrate was investigated at various pH, molar ratio, and temperature.

4.2.Materials and Methods

4.2.1. Materials

The ferrate(VI) was prepared using ferric oxide (Fe_2O_3) and sodium peroxide (Na_2O_2) as the main materials, were purchased from Alfa Aeser.

Bromobenzene as target compound were purchased from Sigma-Aldrich. The other chemicals such as sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) were purchased from Junsei Company. Buffer solutions for pH adjustment were obtained from Samchun Company.

4.2.2. Methods

4.2.2.1. Degradation Experiment

The degradation experiments were performed in 700mL of closed zero-head space glass reactor with ports for sampling, measuring pH and temperature, and adding ferrate(VI). To control pH, the addition of 5 - 10 mL buffer solution and a few drops of sulfuric acid (0.5 M) were used. The bromobenzene solutions with the initial concentration (C_0) of 0.010mM were used in the experiments. The effects of the parameters such as pH (3.7-9.4), molar ratio (1.05-4.2) and temperature (15^{o}C – 45^{o}C) were investigated within 20 minutes of reaction time. The samples were extracted using liquid-liquid extraction (LLE) method (sample volume = 3mL, vortex mixing time for extraction = 2 minutes, temperature = 25^{o}C, n-hexane volume = 3mL). The concentrations of bromobenzene was measured using gas chromatography-electron capture detector (GC-ECD). The temperatures of injection port and detector were 250^{o}C and 300^{o}C, respectively. Initially 40^{o}C was held constant for 5 minutes, followed by 8^{o}C/min ramp until a temperature of 100^{o}C was reached, and followed by

12^{o}C/min ramp until a final temperature of 200^{o}C was reached. In this work, all of the degradation experiments were performed duplicately.

4.3. Result and Discussion

4.3.1. Effect of pH

This experiment was conducted to determine an optimum pH condition for the bromobenzene removal. The effect of pH was tested at pH 3.7, 6.8, and 9.7. The effect of pH on bromobenzene degradation is shown in Fig. 11. When the initial pH increased from 3.7 to 6.8, the bromobenzene removal increased obviously from 8.09% to 10.60%. Further initial pH increase to 9.4 reduced the bromobenzene removal efficiency of 4.89%.

The highest bromobenzene degradation was achieved in neutral condition (pH 6.8), while the lowest bromobenzene degradation was achieved in basic condition (pH 9.4). This can be explained from the species of ferrate(VI) present in the acidic to basic pH range (Licht et al. 2001; Sharma 2002). Triprotonated ($H_3FeO_4^+$), diprotonated (H_2FeO_4), monoprotonated ($HFeO_4^-$), and deprotonated (FeO_4^{2-}) species existed in the acidic to basic pH range (Sharma et al. 2013). According to previous studies, density functional theory (DFT) calculation on the reactivity of Fe(VI) with several compounds showed that the $HFeO_4^-$ (ferrate dominant species at neutral pH condition) has a larger spin density on oxo-ligands, which increases the oxidation ability of protonated Fe(VI) (Anquandah et al. 2011; Kamachi et al. 2008). As the pH increased, the oxidizing power of Fe(VI) decreased with the decrease in the reactive Fe(VI) species ($HFeO_4^-$) (Sharma et al. 2013). Thus, the rapid increase in $HFeO_4^-$ species from pH of 3.7 to 6.8 explains the increased degradation efficiency of bromobenzene.

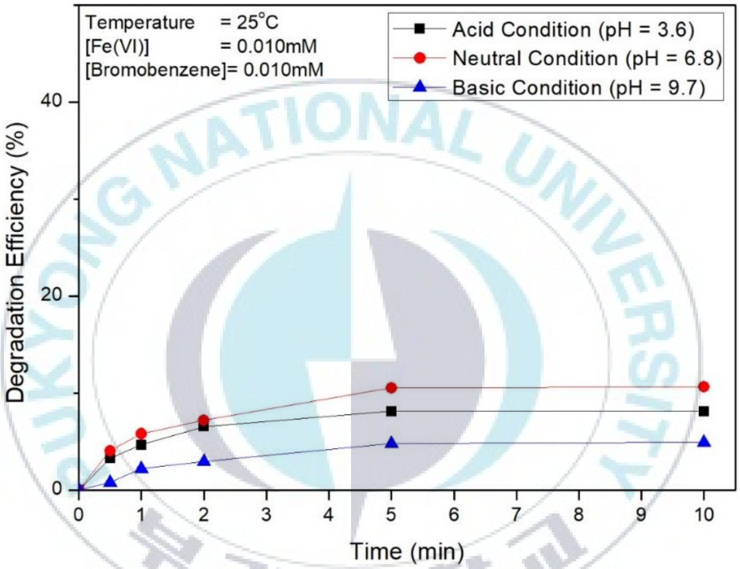


Figure 11. Effect of pH on the removal of bromobenzene by ferrate(VI)

The reaction of ferrate(VI) with the organic compounds is the second order reaction rate (Yang et al. 2011a). The reaction rate was determined from the k_{app} value using second-order reaction rate equation. The second order reaction rate law can be expressed as Eq. (13):

$$-d\frac{[\text{Bromobenzene}]}{dt} = k_{app}[Fe(VI)]_{(tot)}[\text{Bromobenzene }]_{(tot)} \quad (13)$$

$[Fe(VI)]_{(tot)}$ and $[Bromobenzene]_{(tot)}$ are the total concentration of ferrate(VI) species, and the total concentration of bromobenzene species. Eq. (13) is rearranged and $d\frac{[Bromobenzene]}{dt}$ is integrated to become Eq. (14):

$$ln\frac{[\text{Bromobenzene}]}{[\text{Bromobenzene}]_0} = -k_{app}\int_0^t [Fe(VI)]dt \qquad (14)$$

Where $\int_0^t [Fe(VI)]dt$ is the Fe(VI) exposure, Fe(VI) exposure is a time-integrated concentration of ferrate(VI) due to its instability (Yang et al. 2011a). This equation was used to measure the k_{app} values in other experiments to eximened effects of molar ratio and temperature.

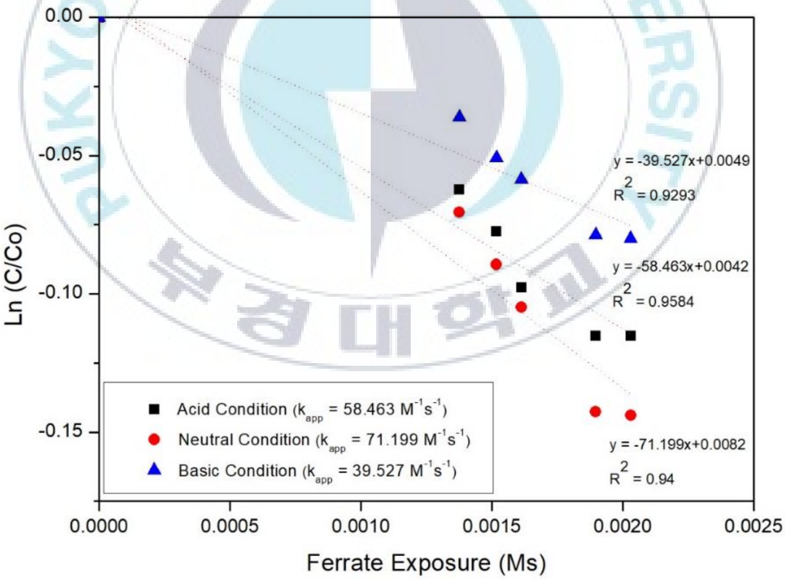


Figure 12. Rate of bromobenzene removal by ferrate(VI) in various pH levels

From Eq. (14) the values of rate constant (k) for the reaction of ferrate(VI) with bromobenzene at various pH conditions could be determined and calculated graphically in Fig 12. The k values were obtained from slop of the plots ferrate exposure and ln C/C_0. The R^2 values of rate constant calculation were obtained over than 0.9. The value of k_{app} increased from 58.46 $M^{-1}s^{-1}$ to 71.19 $M^{-1}s^{-1}$ as the pH increased from 3.6, 6,8 then decreased rapidly to 39.19 $M^{-1}s^{-1}$ as the pH increased to 9.7. It was shown that the highest rate constant for degradation of bromobenzene was achieved at neutral pH condition.

4.3.2. Effect of Molar Ratio

In order to investigate molar ratio effect, the experiments were carried out at a range of molar ratios ([$FeO4^{2-}$]/[Bromobenzene]) 2 to 8 with fixed bromobenzene concentration of 0.010mM. The influence of molar ratio on bromobenzene removal was studied and the result is summarized in Fig. 13. The degradation of bromobenzene by ferrate(VI) was a rapid process, with a major removal of bromobenzene obtained in the initial 5 minutes. The experiment results clearly demonstrated that increasing molar ratios from 2 to 8 apparently increased the removal of bromobenzene from 18% to 39%. Similar result with other studied, that the degradation efficiency increased with increasing of the molar ratio in a reactor (Sharma and Bielski 1991).

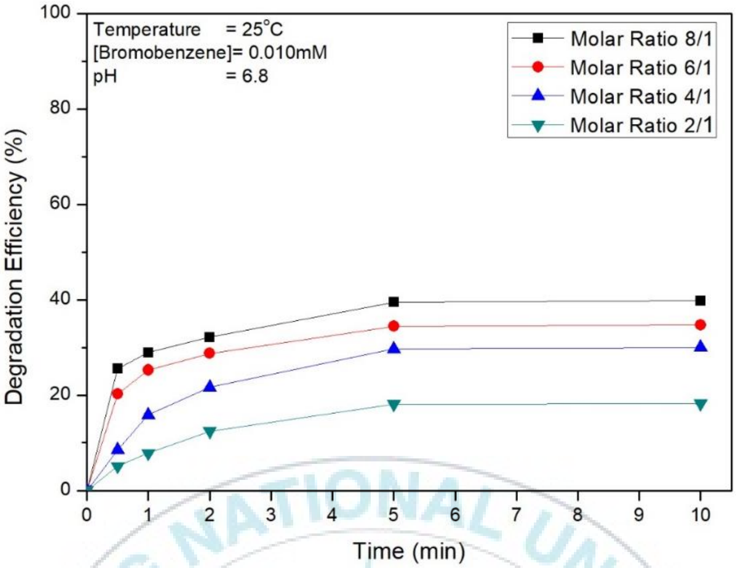


Figure 13. Effect of molar ratio on the removal of bromobenzene by ferrate(VI)

The increasing of molar ratio on the reactor will definitely affect degradation efficiency. As shown in Fig. 14, when the molar ratio increased from 2/1 to 8/1, the degradation percentage of bromobenzene increased significantly from 18% to 39%. Similar result with other studied that the degradation efficiency increased with increasing of the molar ratio in a reactor (Sharma and Bielski 1991). Ferrate will be reduced to iron hydroxide ($Fe(OH)_3$) during its decomposition (Fig. 15). $Fe(OH)_3$ precipitate is considered as a good adsorbent owing to its huge surface dimension and particular chemical surface features (Gu et al. 1994).

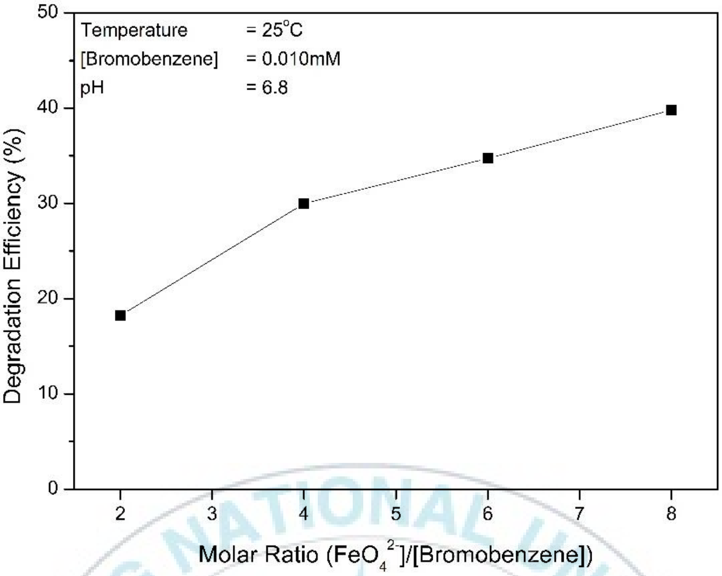


Figure 14. Bromobenzene degraded in various molar ratio

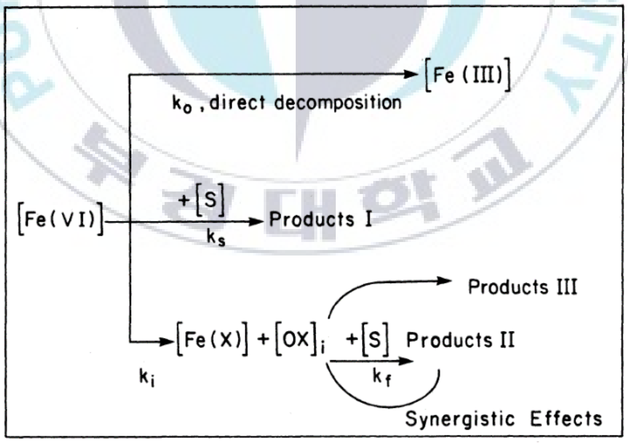


Figure 15. Pathway by which ferrate may decompose to Fe(III) in the presence of substrate where (s) = substrate; Fe(X) = iron(V), (IV), or (III); (OX)$_i$ = intermediate oxidizing species other than Fe(X); k$_s$ = rate of reaction between Fe(VI) and substrate; k$_o$ = normal rate of Fe(VI) under given conditions; k$_i$ = rate of intermediate formation; k$_f$ = rate of reaction between intermediate and substrate (Waite and Gilbert 1978).

4.3.3. Effect of Temperature

The effect of temperature (15 - 55°C) on the bromobenzene degradation and the second-order rate constant, kapp, were investigated, and the result are shown in Fig. 16 and Fig. 17. As shown in Fig. 16, The degradation percentage of bromobenzene increased significantly in the temperature range from 15 to 45°C, then decreased above 45°C. The optimal temperature condition for removal of bromobenzene was observed at 45°C.

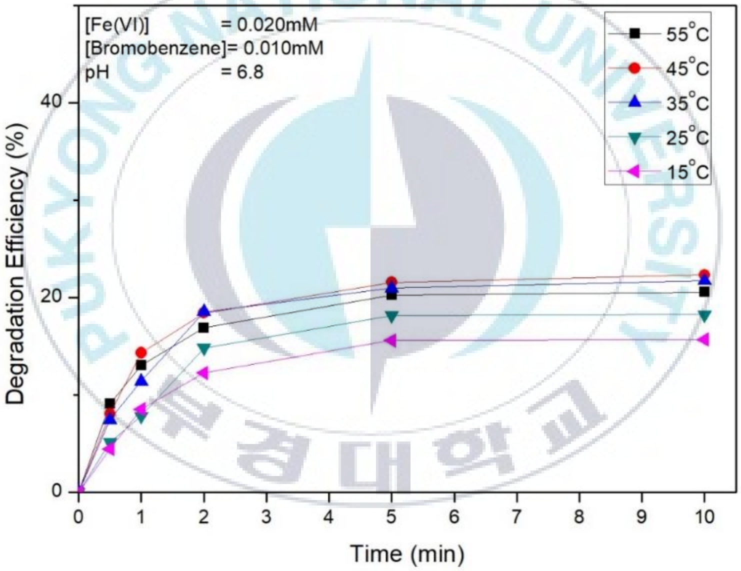


Figure 16. Effect of temperature on the removal of bromobenzene by ferrate(VI)

As shown in Fig. 17, the highest k_{app} values was observed at 45°C. The lowest k_{app} values was observed at 15°C because of the low temperature. The increase in temperature could also increase the effective collision frequencies between ferrate(VI) and bromobenzene, which would promote the oxidation of bromobenzene by ferrate (Han et al. 2015). However the k_{app} value decreased upon further increase in the temperature range above 45°C. Several researchers have reported the effect of temperature on the degradation of organic compounds by ferrate(VI). Previous studies have also confirmed the decomposition of ferrate increases rapidly in the range of temperature above 50°C (Deyrup and Mills 1956; Wagner et al. 1952).

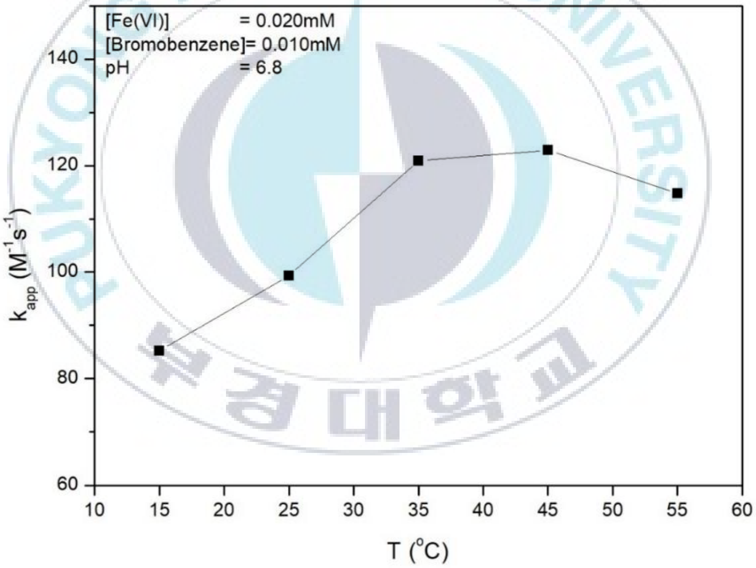


Figure 17. Relationship between T and k_{app} value on bromobenzene removal

Arrhenius equation of experimental data was used for determining activation energy (Eq. 15), where $E_a$is activation energy; R is the constant value (8.314J K^{-1} mol^{-1}); and T is temperature (K). from the calculation of activation energy for bromobenzene reaction was 81.6 KJ/mol. Arrhenius equation can be written as:

$$ln\frac{rate_1}{rate_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (15)$$

4.3.4. Degradation Pathways

The ferrate(VI) reaction during the oxidation of compounds involves, (1) the generation of Fe(V) and Fe(IV) through 1^{e-} and 2^{e-} transfer processes, (2) production of radical species which can also generate Fe(V) and Fe(IV) species, (3) further reactions of Fe(V) and Fe(IV) with contaminants, (4) self-decompositions of Fe(VI), Fe(V), and Fe(IV) species, (5) reactions of ferrates with reactive oxygen species, $O_2^{\cdot-}$, and H_2O_2, produced from self-decompositions (Sharma et al. 2015).

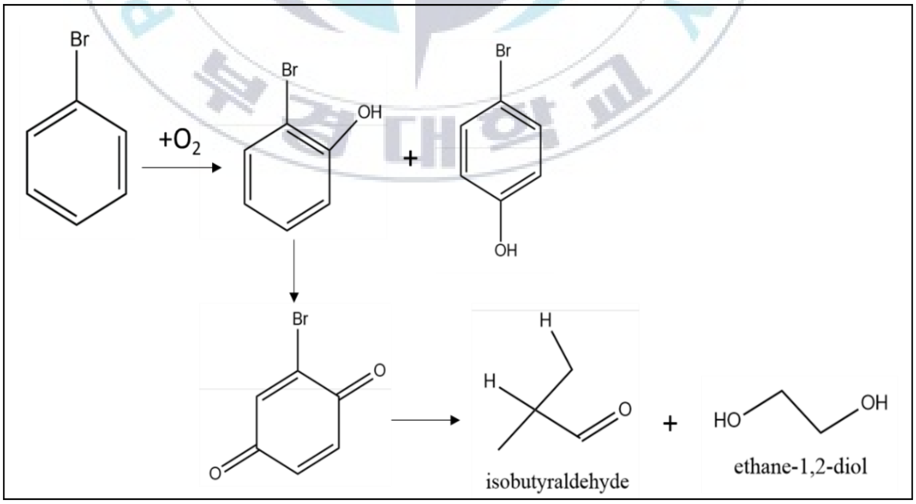


Figure 18. Proposed pathways for bromobenzene degradation by ferrate(VI)

The identification of intermediate product of bromobenzene was not conducted in this experiment. The bromobenzene oxidation pathway was proposed according to other researcher results (Fig. 18). Bromobenzene pathways was proposed from halogenated benzene pathways because the similarity of functional group. Phenol groups is the initial product formed during the benzene derivatives oxidation. As expected the initial attack of ferrate to bromobenzene by reactive oxygen species resulted bromophenol. The bromophenol degradation pathways has been studied by other researcher, the identified intermediate products have also been confirmed during the reaction such as isobutyraldehyde and etahane-1,2-diol (Laksono and Kim 2016). Then further decomposition of intermediates led to end products like carbon dioxide.

4.4.Conclusion

The satisfactory results of bromobenzene degradation by ferrate(VI) had been achieved in this research. In the effect of pH, the neutral pH condition has been observed as the best condition for bromobenzene removal. In agreement with other studies, the oxidation of the bromobenzene was found to be greater for mono-protonated ferrate, HFeO4^{-}, than for non-protonated ferrate, FeO_4^{2-}. In effect of molar ratio, the increase of molar ratio was found to be in a linear relationship with degradation efficiency. In effect of temperature, the temperature of 45^{o}C was observed as the optimal temperature with the activation energy of 81.16 KJ/mol. The proposed of bromobenzene oxidation resulted the intermediate product such as isobutyraldehyde and etahane-1,2-diol. From the investigation of the degradation of bromobenzene by ferrate(VI), it is concluded that ferrate oxidation could be an effective treatment method for the purification of waters containing these particular bromobenzene.

Chapter 5

DEGRADATION OF TOLUENE BY LIQUID FERRATE(VI) AND SOLID FERRATE(VI)

Abstract

Ferrate(VI) ($[FeO_4]^{2-}$) is one of innovative oxidation processes and has strong oxidizing power. In this study, degradation of toluene has been examined using liquid sodium ferrate(VI) and solid potassium ferrate(VI). The effects of pH, molar ratio and temperature on toluene removal by both ferrates(VI) were investigated. The Highest toluene removal efficiency was achieved at neutral pH condition (pH = 6.8) after a reaction period of 20 minutes. For the effect of molar ratio, the degradation efficiency increased as molar ratio increased. The highest toluene degradation was achieved at molar ratio ($[FeO_4^{2-}]$/[Toluene]) of 4.23/1 by both ferrates(VI). The optimal temperature was 45°C with k_{app} value of 389.07 $M^{-1}s^{-1}$ and activation energy of 79.4 KJ/mol for liquid ferrate(VI), and k_{app} value of 567.21 $M^{-1}s^{-1}$ and activation energy of 76.8 KJ/mol for solid ferrate(VI). The intermediate products such as heptanal, 3-methylbutanal, 2-methylhexane, 2-methylbutan-1-ol, 1-chlorobutane, 4-chlorobutane-1-ol, 1-chloro-2-methylpropane were identified and the possible degradation pathways have been proposed.

5.1. Introduction

Many volatile organic compounds (VOCs) are known as harmful contaminants to humans (Hakim et al. 2012). One hazardous VOC is toluene (Neubert et al. 2001). Toluene has high toxicity, carcinogenicity and long persistence in environment (Chu et al. 2017). The World Health Organization guidelines state that the maximum acceptable concentration of toluene is 0.7 mg/L, it becomes more severe issue for the sustainable society (W. H. O. 2004). Therefore, removal of toluene has become serious environmental burden. Various methods have been proposed to remove toluene, including adsorption (Serra et al. 2012), bio-sorption (Flores-Chaparro et al. 2017), photocatalytic (Shinde et al. 2012), and ozone (Huang 2010). However these methods have several disadvantages such as generation of secondary pollutants, high-energy consumption, difficult operation, long operation time and low removal efficiency. More effective and simple operation options are being pursued to remediate toluene contaminations.

For the past decades, ferrate(VI) has been recognized as an effective reagent in water and wastewater treatment (Gombos et al. 2013; de Luca et al. 1996). Ferrate(VI) is the hexavalent form of iron (VI) (FeO_4^{2-}) (Sharma et al. 2015). In the viewpoint of chemical properties, ferrate presents some advantageous characteristics (Murmann and Robinson 1974; Potts and

Churchwell 1994). The oxidation-reduction potential of ferrate(VI) in acidic condition is highest (2.2 V) among oxidants (such as chlorine, hypochlorite, ozone, hydrogen peroxide), and in basic condition it has quite high redox potential of 0.7 V (Sharma et al. 2016). Unlike other alternative oxidants, ferrate(VI) has shown great potential in the process, acting as an oxidant, then a coagulant, and finally as a flocculant (Jiang 2014; Li et al. 2008; Sharma 2002). Moreover ferrate(VI) is safe, least expensive and has high oxidation power (Perfiliev and Sharma 2008).

Currently, ferrate(VI) has been well studied and can degrade wide range of aquatic pollutants (Al-Abduly and Sharma 2014; Anquandah and Sharma 2009; Jiang et al. 2016; Pepino Minetti et al. 2017). Researchers have reported that high performance of ferrate(VI) can be produced as solid ferrate(VI) (K_2FeO_4) (Li et al. 2005; Wei et al. 2015) and liquid ferrate(VI) (Na_2FeO_4) (Batarseh et al. 2007; Sharma 2011b). Liquid and solid ferrates(VI) have been reported as the degradation agents for pollutants including organic contaminants and heavy metals without generating hazardous byproducts (Anquandah and Sharma 2009; Gombos et al. 2013; Osathaphan et al. 2014). Several methods have been successfully developed to generate solid and liquid ferrates(VI) (Jiang and Lloyd 2002). Therefore, solid and liquid ferrates(VI) can be promising oxidants in order to achieve higher water qualities.

Toluene has been the subject of many studies in recent years in the viewpoint of their environmental significance as a persistent and hazardous substance. The uses of solid and liquid ferrates(VI) as oxidizing agents are of interest because of their high oxidizing power and non-hazardous by product. The objective of this research is to evaluate the solid ferrate(VI) and liquid ferrate(VI) for degradation of the selected hazardous contaminant, toluene. Several factors such as pH, molar ratio, and temperature important to both ferrates(VI) were studied. Also the reaction intermediates and the reaction pathways were investigated.

5.2. Materials and Methods

5.2.1. Materials

The chemicals used in the experiments were reagent grade or higher purity. Solid and liquid ferrates(VI) were prepared using ferric oxide (Fe_2O_3) and sodium peroxide (Na_2O_2) as the main materials which were purchased from Alfa Aesar. Toluene was purchased from Sigma-Aldrich and the other chemicals such as sodium hypochlorite (NaOCl), sodium hydroxide (NaOH), and potassium hydroxide (KOH) were obtained from Junsei Company. Buffer solutions for pH adjustment were obtained from Samchun Company. Hexane, n-pentane, and methanol were purchased from B&J ACS/HPLC.

5.2.2. Methods

5.2.2.1. Synthesis of Solid and Liquid Ferrate(VI)

The solid and liquid ferrates(VI) were prepared using US Patent method (Sharma 2011b) with some modification steps. The first step to synthesize these ferrates(VI) were heating 0.96 g of Fe_2O_3 and 2.36 g of Na_2O_2 at 500°C in a furnace for 30 minutes. Then, 2 g of the mixture was taken, then mixed with 60 mL of NaOCl. And 20 g of NaOH was added gradually. The dark purple solution was produced by mixing of the reagents, indicating that ferrate(VI) in liquid phase was generated. Then it was filtered and liquid ferrate(VI) (Na_2FeO_4) was produced. Solid ferrate(VI) was prepared using the procedure as described in the liquid ferrate(VI) method and followed by KOH addition to precipitate K_2FeO_4. Thereafter, ferrate(VI) in solid phase was filtered and washed using n-hexane, n-pentane, and methanol. The dried crystalline ferrate(VI), K_2FeO_4 was produced.

5.2.2.2. Degradation Experiment

The degradation experiments were performed in 700mL of closed zero-head space glass reactor with ports for sampling, measuring pH and temperature, and adding ferrate(VI). To control pH, the addition of 5 - 10 mL buffer solution and a few drops of sulfuric acid (0.5 M) were used. The toluene solution with the initial concentration (C_0) of 0.0775mM was used in the experiments. The effects of the parameters such as pH (3.7-9.4), molar ratio (1.05-4.2) and temperature (15^{o}C-45^{o}C) were investigated within 20 minutes of reaction time. The samples were extracted using liquid-liquid extraction (LLE) method (sample volume = 3mL, vortex mixing time for extraction = 2 minutes, temperature = 25^{o}C, n-hexane volume = 3mL). The concentrations of toluene were measured using gas chromatography-flame ionization detector (GC/FID). The temperatures of injection port and detector were 210^{o}C and 250^{o}C, respectively. The temperature program began at 35^{o}C, followed by 5^{o}C/min ramp until a temperature of 150^{o}C was reached. In this work, all of the degradation experiments were performed duplicately.

5.2.2.3. Intermediate Study and Degradation Pathway

The gas chromatography-mass spectrometry (GC-MS) technique was used to analyze intermediate products. To stop further degradation reaction, quenching process using sulfuric acid was conducted. GC-MS was performance with Mass Spectrometer System (GC-MS QP2010Plus, Shimadzu, Japan) and an AT-1 capillary column (60 m x 0.32 mm I.d x 1.0 µm film thickness). The temperatures of injection port and detector were 250^{o}C and 300^{o}C, respectively. Initially 40^{o}C was held constant for 5 minutes, followed by 8^{o}C/min ramp until a temperature of 100^{o}C was reached, followed by 12^{o}C/min ramp until a temperature of 200^{o}C was reached, followed by 15°C/min ramp until a final temperature of 250°C was reached.

5.3. Results and Discussion

5.3.1. Synthesis of Solid and Liquid Ferrate(VI)

Ferrate(VI) ion has the molecular formula as FeO_4^{2-}. A number of alkali earth salt of ferrates(VI) are known with the molecular formula M_2FeO_4 (M = Li, Na, K, Rb, Cs, and Ag) (Perfiliev and Sharma 2008). In this experiment solid ferrate(VI) (K_2FeO_4) and liquid ferrate(VI) (Na_2FeO_4) were successfully produced. The iron (Fe) source of both ferrates(VI) was Fe_2O_3. The first step was the formation of liquid ferrate(VI) by reacting the mixture of Fe_2O_3 and Na_2O_2 with NaOCl under strong alkaline condition. Solid ferrate(VI) was obtained by adding KOH followed by washing and drying steps. Previous researches reported that there were many methods to characterize ferrate(VI), one of the simple methods was the spectroscopic method (UV-Vis) (Luo et al. 2011). The concentration of liquid ferrate(VI) was measured right away and used within 1 hour of production to minimize ferrate self-decomposition. The dried solid ferrate(VI) must be protected from ambient humidity. Both ferrates(VI) solutions of 20 ppm were prepared separately in phosphate buffer and those aqueous solutions showed red-violet color. The spectral measurements of both ferrates(VI) are given in Fig 19. It was shown that the absorption spectra of solid and liquid ferrates(VI) have a peak at ~510 nm (Sharma et al. 2001). Both ferrates(VI) also show absorption in the UV region with a shoulder between 270 and 305 nm. Base on the measurements at a wavelength of 510nm, a calibration curve can be established. Furthermore, the ferrate concentration in the experiment can be determined. The ferrates(VI) (Fe(VI)) formation followed the reactions below (Eq. 16-18):

Liquid Ferrate(VI)

$$Fe_2O_3 + Na_2O_2 \rightarrow 2NaFeO_2 + {}^{1}/_{2}\,O_2 \tag{16}$$

$$2NaFeO_2 + 3NaOCl + 2NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + H_2O \tag{17}$$

Solid Ferrate(VI)

$$2Na_2FeO_4 + 4KOH \rightarrow 2K_2FeO_4 + 4NaOH \tag{18}$$

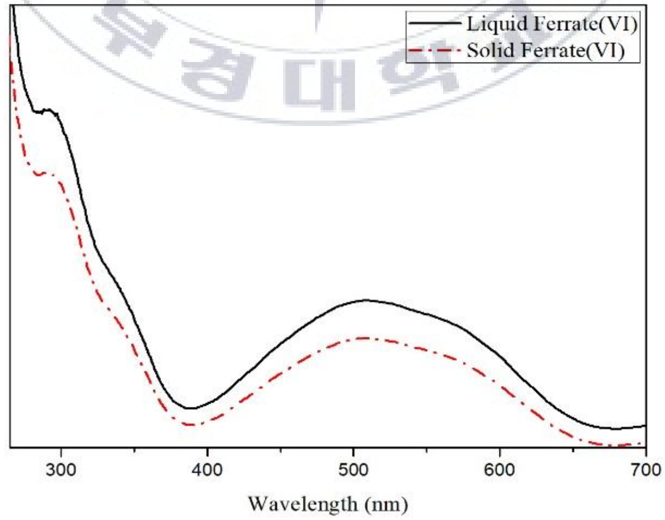


Figure 19. UV-Vis absorption spectrum of solid and liquid ferrate(VI) in phosphate buffer solution

5.3.2. Effect of pH

Ferrate(VI) is a powerful oxidant in the entire pH range (Thompson et al. 1951). The experiments have been carried out at pH 3.7, 6.8, and 9.7. In the degradation experiment, initially the solution in reactor was purple and this rapidly became to yellowish color as ferrate decomposed. Some yellowish particles were observed at the bottom of the reactor, then the solution finally became colorless. The effect of pH on degradation of toluene is shown in Fig. 20. Similar to the results in other studies, ferrate(VI) can complete oxidation reactions in shorter time periods (Sharma 2011b). More than 50% of toluene was degraded within 20 minutes of reaction time. A number of researchers stated that the optimal pH range for oxidation of organic substrates by ferrate(VI) on pH 7 to 9.2 (Graham et al. 2004; Nam et al. 2016). In the experiments, the highest degradation efficiencies of toluene by solid and liquid ferrates(VI) have been achieved at pH 6.8.

The solid ferrate(VI) showed higher oxidation power than liquid ferrate(VI) at various pH values. Because liquid ferrate(VI) contains diverse substances, which causes the ferrate(VI) to be readily decomposed into ferric hydroxides in experiment reactor (Jiang and Lloyd 2002). If ferrate(V) and ferrate(IV) are also generated during toluene oxidation, they will probably reacted with toluene and self-decompose at a faster rate than ferrate(VI) due to its reactivity and instability (Melton and Bielski 1990).

The highest toluene degradation by both ferrates(VI) were achieved in neutral condition, while lowest toluene degradation were achieved in basic condition. This can be explained from the species of ferrate(VI). There are four species of ferrate (Fe(VI)) (equations 23-25) existing in the entire pH range. Density functional theory (DFT) calculation on the reactivity of Fe(VI) with several compounds showed that the $HFeO_4^-$ (ferrate dominant species at neutral pH condition) has a larger spin density on oxo-ligands, which increases the oxidation ability of protonated Fe(VI) (Anquandah et al. 2011; Kamachi et al. 2008). In basic condition (pH>9), FeO_4^{2-} (ferrate dominant species at basic condition) has also been reported to become more chemically stable, then caused the low degradation efficiency (Licht et al. 2001; Sharma 2002).

Ferrate(VI) in aqueous solution presents in four forms that depend on pH as shown below (Eqs. 19 - 21):

$$H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \quad pKa = 1.6 \tag{19}$$

(Licht et al. 2001)

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \quad pKa = 3.5 \tag{20}$$

(Licht et al. 2001; Sharma 2002)

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \quad pKa = 7.3 \tag{21}$$

(Licht et al. 2001; Sharma 2002)

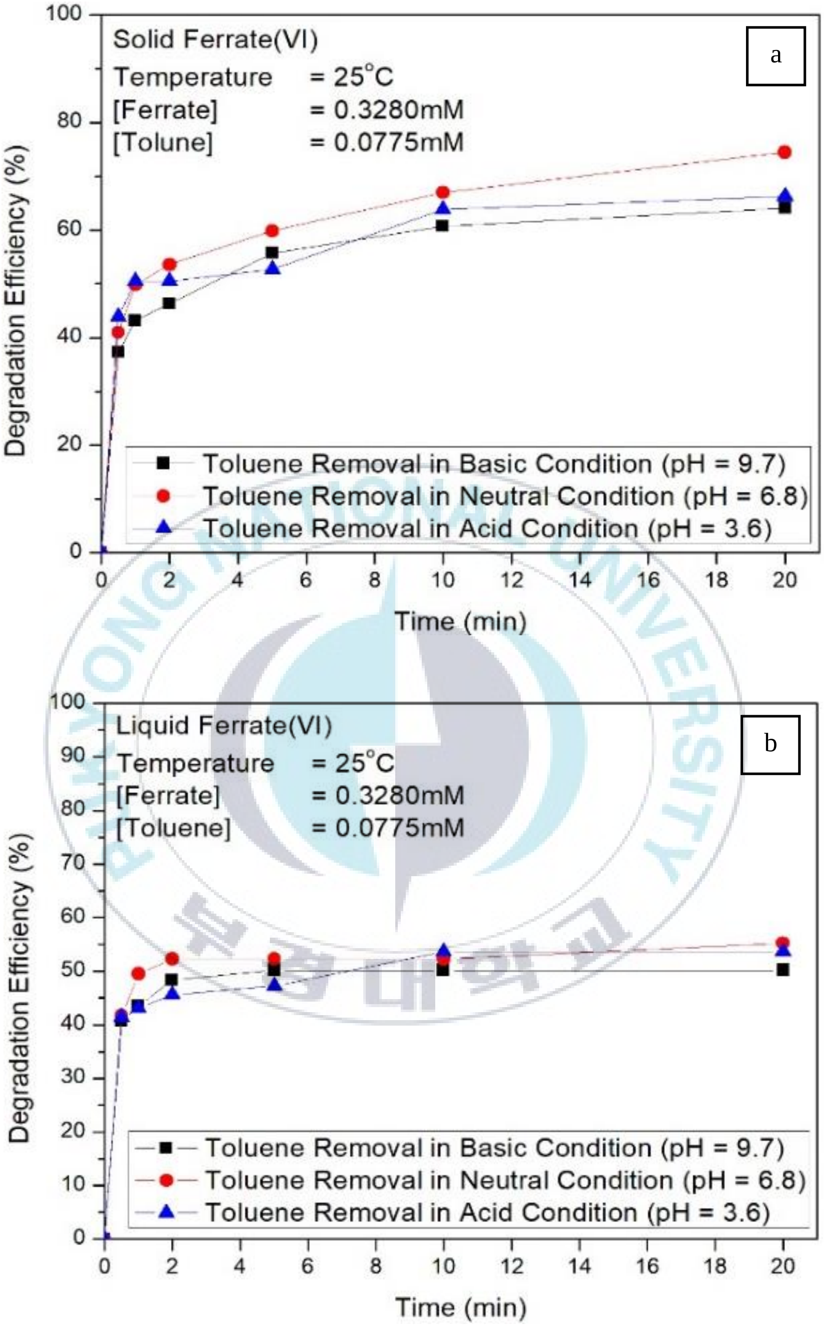


Figure 20. Effect of pH on the removal of Toluene by a. Solid Ferrate(VI) b. Liquid Ferrate(VI)

According to previous studies on ferrate(VI) reaction with organic compounds, the second order reaction rate constants have been obtained (Yang et al. 2011a). The second order reaction rate law can be described by Eq. (22).

$$-d\frac{[Toluene]}{dt} = k_{app}[FeO_4^{2-}]_{(tot)}[Toluene]_{(tot)} \qquad (22)$$

$[FeO_4^{2-}]_{(tot)}$ and $[Toluene]_{(tot)}$ are the total concentration of ferrate(VI) species and the total concentration of toluene species. Eq. (22) is rearranged and $d\frac{[Toluene]}{dt}$ is integrated to become Eq. (23):

$$ln\frac{[Toluene]}{[Toluene]_0} = -k_{app}\int_0^t [FeO_4^{2-}]dt \qquad (23)$$

Where $\int_0^t [FeO_4^{2-}]dt$ is the Fe(VI) exposure, Fe(VI) exposure is a time-integrated concentration of ferrate(VI) due to its instability (Yang et al. 2011a). This equation was used to measure the k_{app} values in other experiments to eximened effects of molar ratio and temperature.

From Eq. (23) the values of rate constant (k) for the reaction of ferrate(VI) with toluene at various pH conditions could be determined and calculated graphically in Fig 21. The k values were obtained from slop of the plots ferrate exposure and ln C/C_0. The R^2 values of rate constant calculation were obtained over than 0.9. The second order reaction rate values in various pH conditions are shown in Table 6. It was shown that the highest rate constant for degradation of toluene was achieved by solid ferrate(VI) at neutral pH condition.

Table 6. k_{app} Value in various of pH

Ferrate(VI) type	pH	k_{app} ($M^{-1}s^{-1}$)
Liquid Ferrate(VI)	3.6	367.80
	6.8	389.07
	9.7	346.16
Solid Ferrate(VI)	3.6	467.45
	6.8	579.41
	9.7	451.36

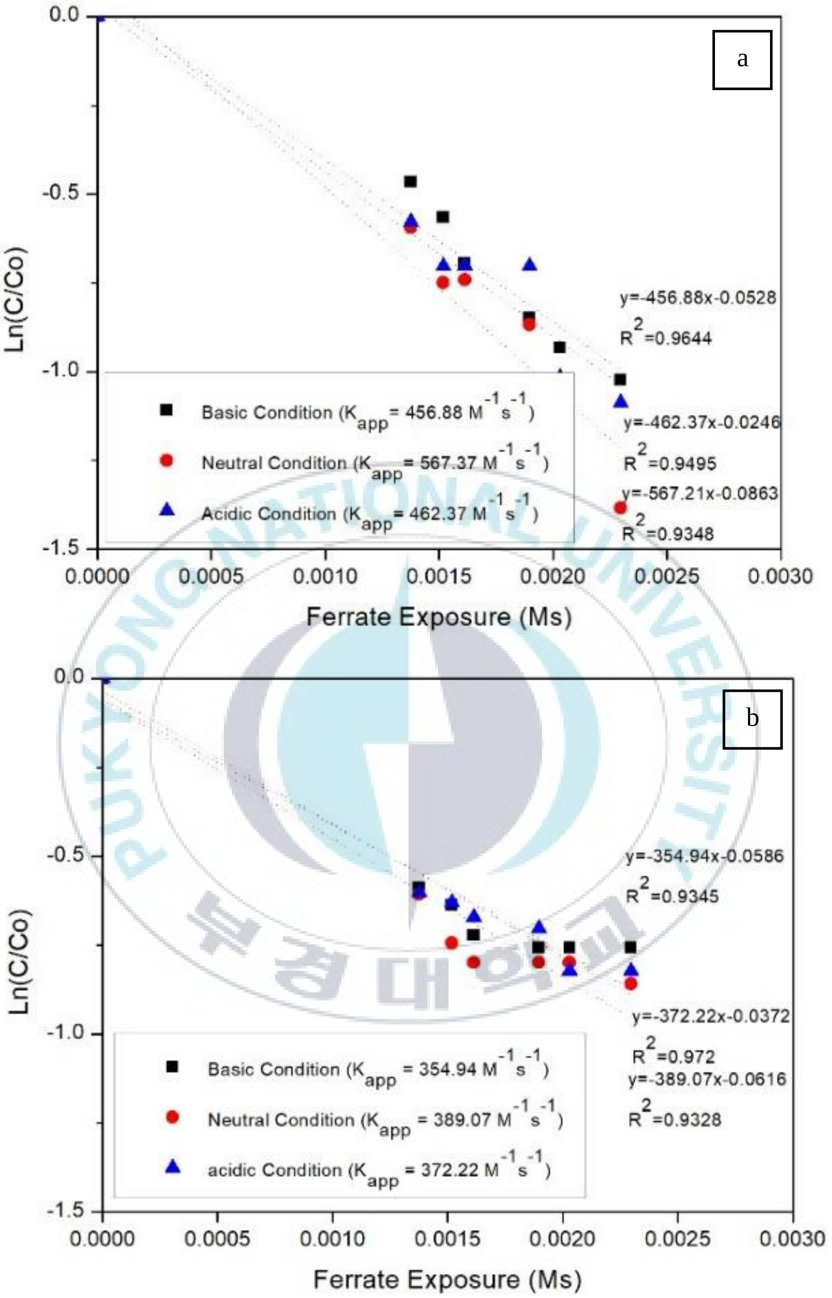


Figure 21. Rate of toluene removal by a. Solid ferrate(VI) b. Liquid ferrate(VI)

5.3.3. Effect of Molar Ratio

Molar ratio is one of the important parameters that affect the degradation efficiency (Sharma 2013). In order to investigate the effect of molar ratio, several ratios ($[FeO_4^{2-}]/[Toluene]$) (1.05, 2.11, 3.17, and 4.23) were used to remove toluene in the reactor. When ferrate(VI) is add to the reactor, it oxidizes organic compound and will not produce any harmful by-products in the treatment process (Graham et al. 2004). The influence of molar ratio on toluene degradation was studied and the result was summarized in Fig. 22. It was shown that fast degradation of toluene by both ferrates occurred within 20 minutes.

The degradation efficiency of toluene was strongly dependent on the molar ratio in the reactor. The highest toluene degradation by both ferrates were achieved at a molar ratio ($[FeO_4^{2-}]/[Toluene]$) of 4.23. The removal of toluene was only 46.6% when the molar ratio was 1.05, while the molar ratio increased to 4.23 leading to a rapid increase up to 74.4% of removal for solid ferrate(VI). The removal of toluene was 43.7% when the molar ratio was 1.05, while the molar ratio increased to 4.23 leading to a rapid increase up to 55.2% of removal for liquid ferrate(VI). Similar to the results in other studies, the degradation efficiency increased with the increasing of the molar ratio in a reactor (Sharma and Bielski 1991). The toluene degradation by solid and liquid ferrates(VI) increased as molar ratio increased, but the oxidation power of solid ferrate(VI) was higher than that of liquid ferrate(VI). Ferrate(VI) oxidizes compounds by electron transfer, hydrogen atom transfer, hydride ion transfer, or covalently bonded ferrate intermediates (Lee and Gai 1993). One or more of the above-mentioned mechanisms can be involved in the oxidation of toluene.

The k_{app} values in the various molar ratios were calculated and shown in Fig. 23. The optimal k_{app} values obtained from the experiments were 567.98 $M^{-1}s^{-1}$ for solid ferrate(VI) and 389.07 $M^{-1}s^{-1}$ for liquid ferrate(VI). The k_{app} values increased gradually with increasing of the molar ratio. A higher molar ratio was required in order to achieve complete removal of toluene.

The oxidation equations of toluene by ferrate are presented (Pepino Minetti et al. 2017), which give the stoichiometric ratio to achieved the complete removal of toluene:

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 28H^+ + 28e^- \tag{24}$$

$$10(FeO_4^{2-} + 3e^- + 5H^+ \rightarrow Fe(OH)_3 + H_2O) \tag{25}$$

$$C_7H_8 + 10FeO_4^{2-} + 4H_2O + 22H^+ \rightarrow 7CO_2 + 10Fe(OH)_3 \tag{26}$$

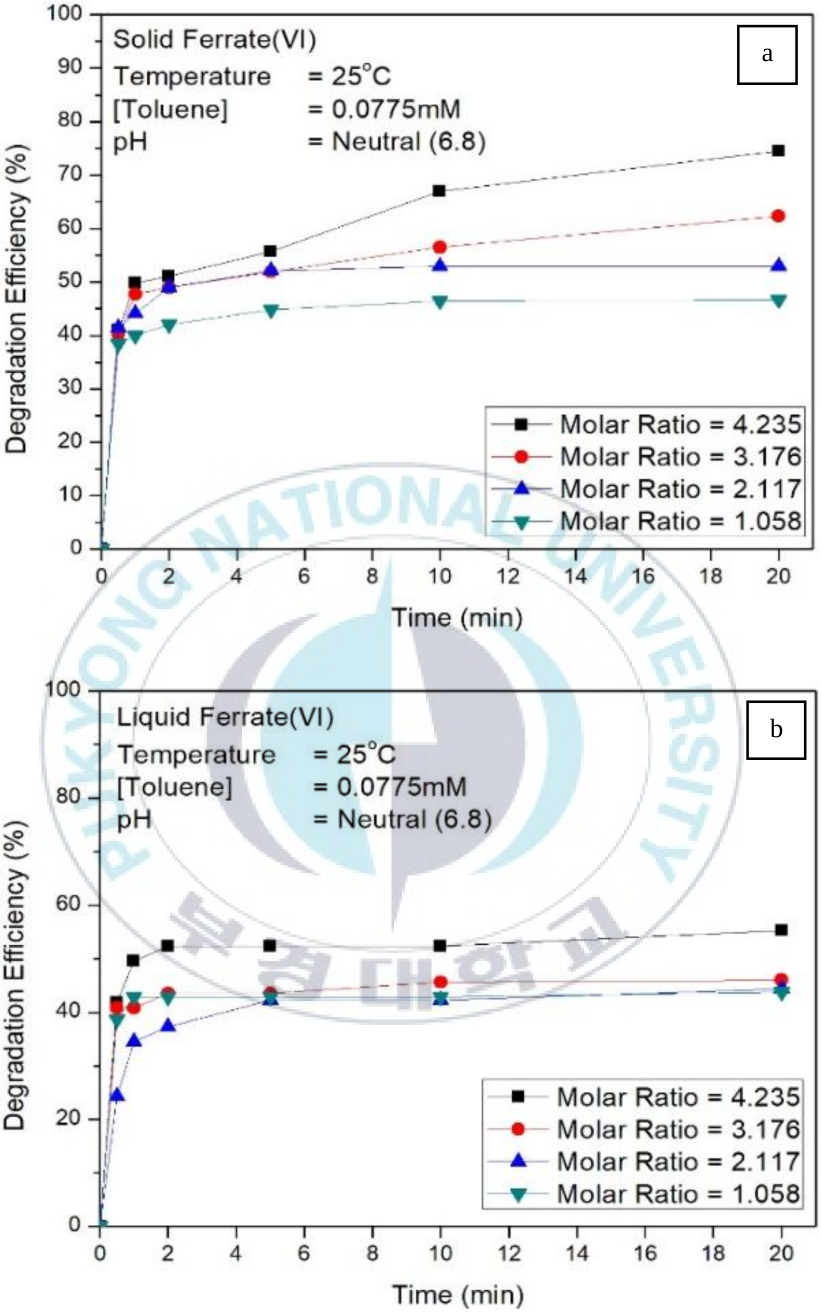


Figure 22. Effect of molar ratio on the removal of toluene by a. Solid ferrate(VI) b. Liquid ferrate(VI)

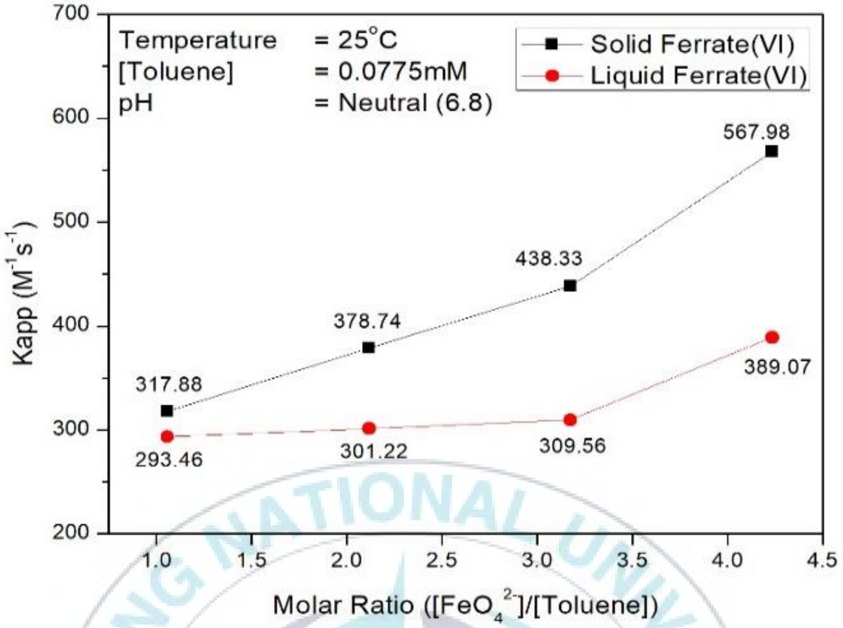


Figure 23. k_{app} of Toluene degradation in the various molar ratio

According to the equations (24-26) the stoichiometric relationships are in the order 10/1 [FeO_4^{2-}]/[Toluene] ratio, 10 moles of ferrate(VI) consumed/ 1 mole of toluene. Therefore, the ratio of 10/1 was proposed for complete toluene degradation by ferrate(VI).

5.3.4. Effect of Temperature

The effect of temperature was examined at five different temperature conditions (15, 25, 35, 45, and 55°C). The degradation efficiency of toluene increased in the temperature range from 15 to 45°C, then decreased above 45°C, as shown in Fig. 24. The optimal temperature condition for toluene degradation by both ferrates(VI) were observed at 45°C. The degradation efficiencies of toluene at 45^{o}C by solid ferrate(VI) and liquid ferrate(VI) were 57% and 33%, respectively.

As shown in Fig. 25, both ferrates(VI) showed similar pattern where the highest k_{app} values were observed at 45^{o}C. The lowest k_{app} values were observed at 15°C because of the low temperature. The collision frequencies between ferrate(VI) and target compound are enhanced with increasing temperature, then increasing the degradation rate of toluene (Han et al. 2015). And reaction kinetics of ferrate(VI) were enhanced when the temperature increased (Sharma et al. 1998a; b). However the k_{app} value decreased upon further increase in the temperature range above 45^{o}C. Several researchers have reported the effect of temperature on the degradation of organic compounds by ferrate(VI). Previous studies have also confirmed the decomposition of ferrate increases rapidly in the range of temperature above 50^{o}C (Deyrup and Mills 1956; Wagner et al. 1952).

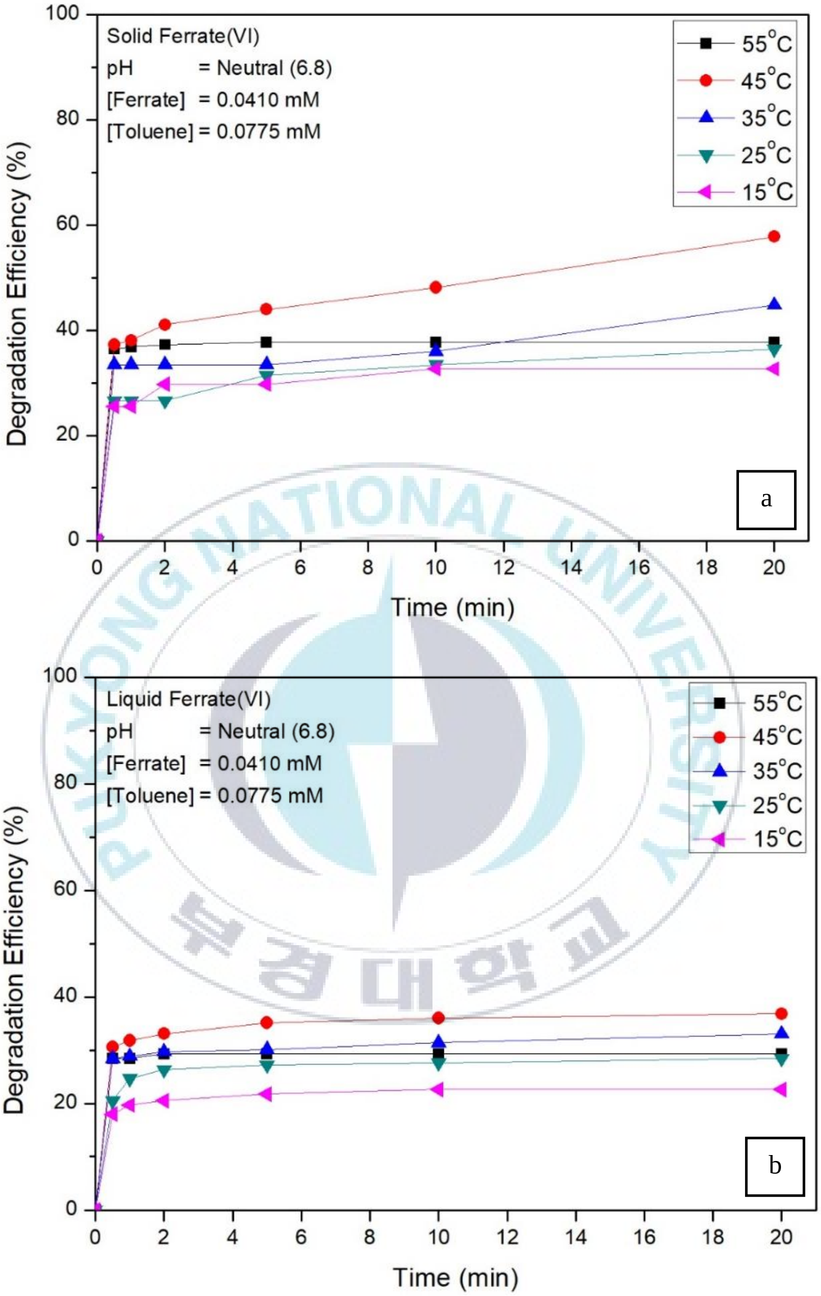


Figure 24. Effect of molar ratio on the removal of toluene by a. Solid ferrate(VI) b. Liquid ferrate(VI)

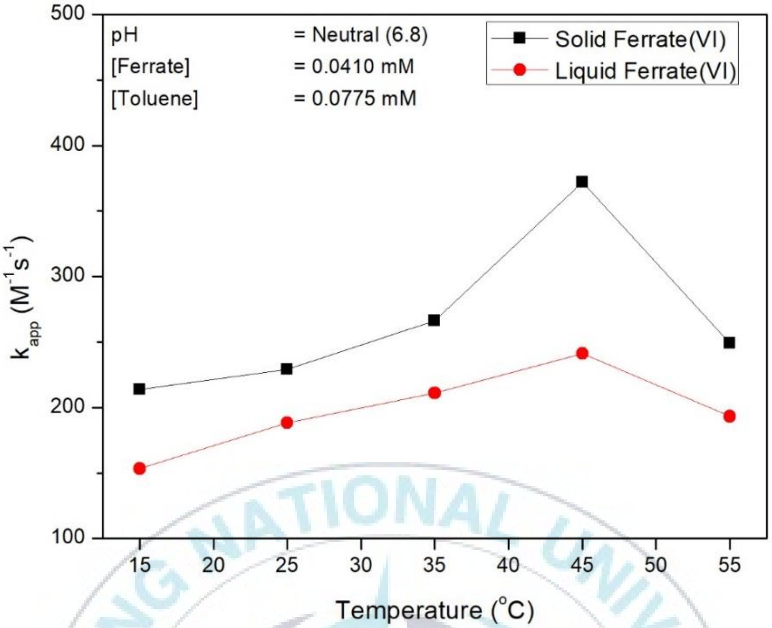


Figure 25. Relationship between T and k_{app} value on toluene degradation

The Arrhenius equation can be used to determine activation energy. Arrhenius equation can be written as (Eq. 27):

$$ln\frac{rate_1}{rate_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{27}$$

Where E_a is activation energy; R is a constant value (8.314 JK^{-1} mol^{-1}); and T is temperature (K). The calculated E_a values were 76.8 KJ/mol and 79.4 KJ/mol for solid ferrate(VI) and liquid ferrate(VI), respectively.

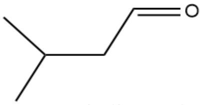
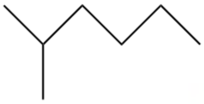
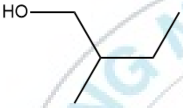
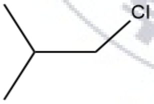
5.3.5. Intermediate Products Study and Degradation Pathways

The intermediate products of toluene oxidation were identified using gas chromatography/mass spectrometry (GC/MS). The mass spectra measurements were examined with the computer database of the National Institute of Science and Technology Mass Spectral Library. The degradation of benzene derivatives by ferrate(VI) usually started from oxygen transfer and proton addition (Arnold and Roberts 2000). The intermediate products of toluene oxidation by solid and liquid ferrates(VI) have been investigated and both results have similar byproducts as shown in Table 7. The basic oxidation-reduction reaction involved can be written as (Eq. 28):

$$C_7H_8(toluene) + FeO_4^{-2}(ferrate(VI)) \rightarrow Intermediates \rightarrow Products + Fe(III) \qquad (28)$$

The degradation pathways of toluene by ferrate(VI) can be described using the distribution and differentiation between primary and non-primary reaction products of the GCMS results. The degradation pathways for toluene by ferrate are proposed in Fig. 26.

Table 7. Intermediates of toluene

Toluene Intermediate	Ret. Time (min)
 heptanal	6.10
 3-methylbutanal	8.35
 2-methylhexane	9.50
 2-methylbutan-1-ol	10.05
 1-chlorobutane	10.32
 4-chlorobutan-1-ol	13.10
 1-chloro-2-methylpropane	13.28

The ferrate(VI) reaction during the oxidation of compounds involves, (1) the generation of Fe(V) and Fe(IV) through 1^{e-} and 2^{e-} transfer processes, (2) production of radical species which can also generate Fe(V) and Fe(IV) species, (3) further reactions of Fe(V) and Fe(IV) with contaminants, (4) self-decompositions of Fe(VI), Fe(V), and Fe(IV) species, (5) reactions of ferrates with reactive oxygen species, $O_2^{\cdot -}$, and H_2O_2, produced from self-decompositions (Sharma et al. 2015). The GC/MS detected several compounds substituted with chloride, this chloride might be due to chloride from the reagents of both ferrates(VI). Then, chlorination also happened in the reactor. Liquid ferrate(VI) (Na_2FeO_4) and solid ferrate(VI) (K_2FeO_4) were confirmed containing potassium chloride (KCl), potassium chlorate ($KClO_3$), sodium chloride (NaCl), and ferric hydroxide ($Fe(OH)_3$) (Jiang and Lloyd 2002; Ninane et al. 2008). The result is similar to other studies where the intermediate products from degradation of organic compounds by ferrate(VI) also produced several compounds substituted with chloride (Laksono and Kim 2016). On the other hand, for these reasons ferrate(VI) has been investigated as an alternative to chlorine for the disinfection of water and wastewater (Murmann and Robinson 1974).

The previous studies have reported the initial oxidation steps of toluene which generally started with oxygen transfer and ring opening (Irokawa et al. 2006). The oxidation of toluene also resulted in transition state compound caused by oxygen and electron transfer (Chu et al. 2017). Some studies have also confirmed the ferrate reaction mechanisms where the ring opening oxidation step of benzene ring happened by attacking the double bond of aromatic (Anquandah et al. 2013; Li et al. 2008), or the formation of aldehyde groups was observed (Feng et al. 2016). It was shown in proposed pathways (Fig. 26). Initially, ferrate(VI) oxidizes the methyl group of toluene by one electron transfer, then generating radical toluene. The radical toluene is stabilized and forms aldehyde group. In second pathway, ferrate(VI) reacts with the double bond of the aromatic ring, resulting in the opening of an aromatic ring. Similar result was observed in previous work that ring opening products and aldehyde group are generated from oxidation of aromatic hydrocarbon by ferrate(VI) (Guan et al. 2014). Then it was proposed that further decomposition of toluene intermediates led to end products like carbon dioxide (Chu et al. 2017; Irokawa et al. 2006).

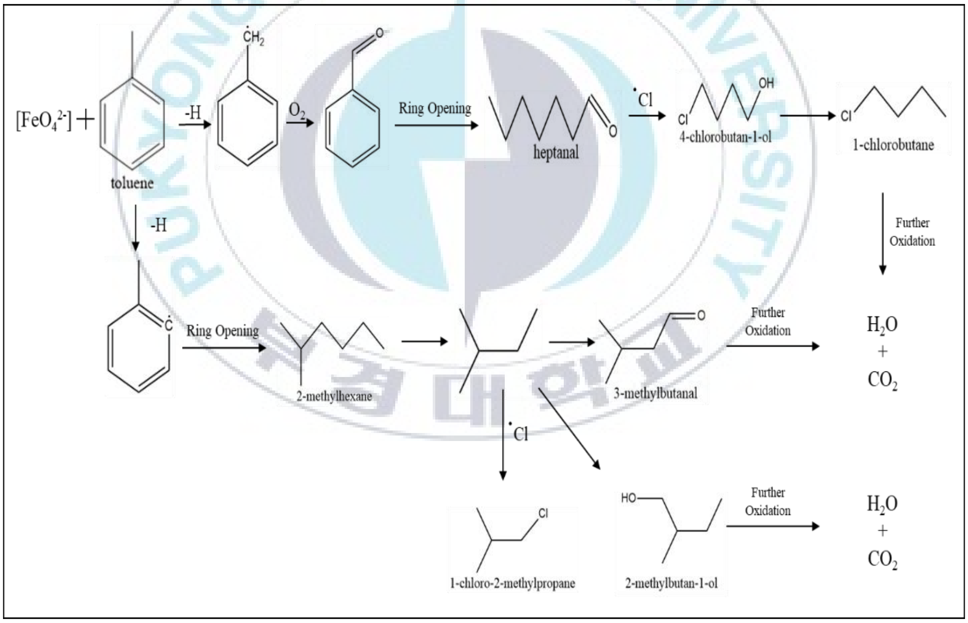


Figure 26. Proposed pathways for toluene degradation by ferrate(VI)

5.4. Conclusion

The ferrates(VI) were successfully synthesized in two different phases which were solid ferrate (K_2FeO_4) and liquid ferrate (Na_2FeO_4). The ability of solid and liquid ferrates(VI) to remove toluene have been investigated. In the effect of pH, the neutral condition has been observed as the best condition for both ferrates(VI). In the effect of molar ratio, the increase of molar ratio was found to be in a linear relationship with removal efficiency (%). In the effect of temperature, the temperature of 45°C was observed as the optimal temperature with the activation energy values, 76.8 KJ/mol for solid ferrate and 79.4 KJ/mol for liquid ferrate. The experimental data showed that oxidation power of solid ferrate(VI) was more powerful than liquid ferrate(VI). The oxidation of toluene by solid and liquid ferrates(VI) have similar intermediate products. Toluene degradation pathways were proposed based on intermediate products. The reaction with toluene resulted in the opening of an aromatic ring and the formation of aldehyde group. Based on the experimental data, it can be stated that the Fe(VI) process is a promising solution in wastewater treatment including organic contaminants.

Chapter 6

BROMOBENZENE AND CHLOROBENZENE DEGRADATION BY FERRATE(VI)

Abstract

The objective of this research was to investigate the functional groups effect on the degradation and kinetic rate of aromatic halogenated compounds. In this study, degradation of selected aromatic halogenated compound, bromobenzene and chlorobenzene in aqueous solution using Fe(VI) have been examined. The effect of molar ratio ($[(FeO_4)^{2-}]/[Compound]$) (2-8), pH (3-9), and temperature (15-55°C) were conducted. In this experiment, ferrate(VI) was effective to removed bromobenzene and chlorobenzene in reactor. The highest bromobenzene and chlorobenzene removal were achieved at pH neutral condition (pH = 6.8) with degradation efficiency of 10.6% for bromobenzene and 31.125% for chlorobenzene within 10 minutes reaction time. For the effect of molar ratio, the degradation efficiency increased as molar ratio increased. The highest degradation efficiency of bromobenzene and chlorobenzene were achieved at molar ratio of 8/1. The optimal temperature was 45°C with k_{app} value of 125.28 $M^{-1}s^{-1}$ and activation energy of 81.1 KJ/mol for bromobenzene removal, and k_{app} value of 229.76 $M^{-1}s^{-1}$ and activation energy of 80.5 KJ/mol chlorobenzene removal.

6.1. Introduction

Aromatic halogenated compounds are frequently employed as solvents, pesticides and refrigerants (Bryant 2014; Pravasi 2014; Selli et al. 2008). Bromobenzene and chlorobenzene are aromatic halogenated compounds with high toxicity and persistence in the environment (Zhang et al. 2011). The widespread use of halogenated organic compounds has toxicological and environmental implications (Tomasi et al. 1983). Water contaminated by bromobenzene and chlorobenzene are a great concern because of their acute toxicity and has potential to accumulate in the environment (Aelion et al. 1987; Bryant 2014; Pravasi 2014). Bromobenzene and chlorobenzene also listed as the priority pollutant by the Environmental Protection Agency (USEPA 1988). Therefore, it is necessary to appropriately remove the organic pollutant through various water treatment processes for satisfying the water quality standard. Recently, the most used methods for chlorobenzene removal are electrochemical, electron beam irradiation and biodegradation processes (Monferrán et al. 2005; Musilová-Kebrlová et al. 2009; Wu et al. 2009). However, these methods required long operation time and also has low removal efficiency.

In the past decades, ferrate(VI) (Fe(VI)) is found to be a potential and useful oxidant (de Luca et al. 1996; Thompson et al. 1951). Fe(VI), in the form of sodium ferrate (Na_2FeO_4), is a powerful oxidant in a wide pH range

(Sharma 2011b) with high oxidation-reduction potential (Sharma 2011b; Yang et al. 2014). Ferrate(VI) has shown great potential as a multi-functional function for coagulation, disinfection, and oxidation (Jiang 2014; Li et al. 2008; Sharma 2002). Morover, ferrate(VI) reportedly produces non-toxic ion, Fe(III) and molecular oxygen (Jiang and Lloyd 2002; Sharma 2002). These facts make Fe(VI) can be a promising candidate for water treatment process.

The superior performance of ferrate(VI) as an oxidant/disenfectant has been extensively investigated for the degradation of water pollutants (Al-Abduly and Sharma 2014; Anquandah and Sharma 2009; Jiang et al. 2016; Pepino Minetti et al. 2017). These pollutants include toluene, cycloalkanes, ketons, hydroquinones, phenols, aminobenzene, estrogens (Jiang et al. 2005), triclosan and benzotriazoles (Yang et al. 2011b). A study (Waite and Gilbert 1978) showed that ferrate could simultaneously remove more than 50% of benzene and alchohol. However, there is very limited information on the application of Fe(VI) for the treatment of halogenated benzene such as bromobenzene and chlorobenzene. To answer the above concern, the objective of this work are to synthesize ferrate(VI) and investigate bromobenzene and chlorobenzene degradation in various conditions. The parameters experiment such as pH, molar ratio, and temperature were studied.

6.2.Materials and Methods

6.2.1. Materials

Chlorobenzene and bromobenzene as target compound were purchased from Sigma-Aldrich. The other chemicals such as sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) were purchased from Junsei Company. Buffer solutions for pH adjustment were obtained from Samchun Company.

6.2.2. Methods

6.2.2.1.Degradation Experiment

The degradation experiments were performed in 700mL of closed zero-head space glass reactor with ports for sampling, measuring pH and temperature, and adding ferrate(VI). To control pH, the addition of 5 - 10 mL buffer solution and a few drops of sulfuric acid (0.5 M) were used. The bromobenzene and chlorobenzene solutions with the initial concentration (C_0) of 0.010mM were used in the experiments. The effects of the parameters such as pH (3.7-9.4), molar ratio (2-8) and temperature (15^{o}C – 45^{o}C) were investigated within 20 minutes of reaction time. The samples were extracted using liquid-liquid extraction (LLE) method (sample volume = 3mL, vortex mixing time for extraction = 2 minutes, temperature = 25^{o}C, n-hexane volume = 3mL). The concentrations of bromobenzene and chlorobenzene were measured using gas chromatography-electron capture detector (GC-ECD). The temperatures of injection port and detector were 250^{o}C and 300^{o}C, respectively. Initially 40^{o}C was held constant for 5 minutes, followed by 8^{o}C/min ramp until a temperature of 100^{o}C was reached, and followed by 12^{o}C/min ramp until a final temperature of 200^{o}C was reached. In this work, all of the degradation experiments were performed duplicately.

6.3. Result and Discussion

6.3.1. Effect of pH

The impact of pH on the chemical oxidation of toluene and chlorobenzene in aqueous solution by ferrate has been studied. Sharma (2011), has determined the speciation of ferrate according to the pH variation considering pKa values (Sharma 2011a). The study further extended to observe the pH effect (i.e. from pH 3.7 - 9.4) for a molar ratio of (Ferrate)/(Target Compound) = 1/1. The data were collected as the change of percent target compounds reduction as a function of time for different pH condition and are returned in Fig. 27. Fig. 27 clearly demonstrated that high bromobenzene and chlorobenzene removal efficiency were observed at pH 6.8 (neutral pH). When the initial pH increased from 3.7 to 6.8, the chlorobenzene removal increased obviously from 24.9% to 31.1%. Further initial pH increase to 9.4 reduced the chlorobenzene removal efficiency of 17.9%. When the initial pH increased from 3.7 to 6.8, the bromobenzene removal increased obviously from 8.09% to 10.6%. Further initial pH increase to 9.4 reduced the bromobenzene removal efficiency of 4.8%.

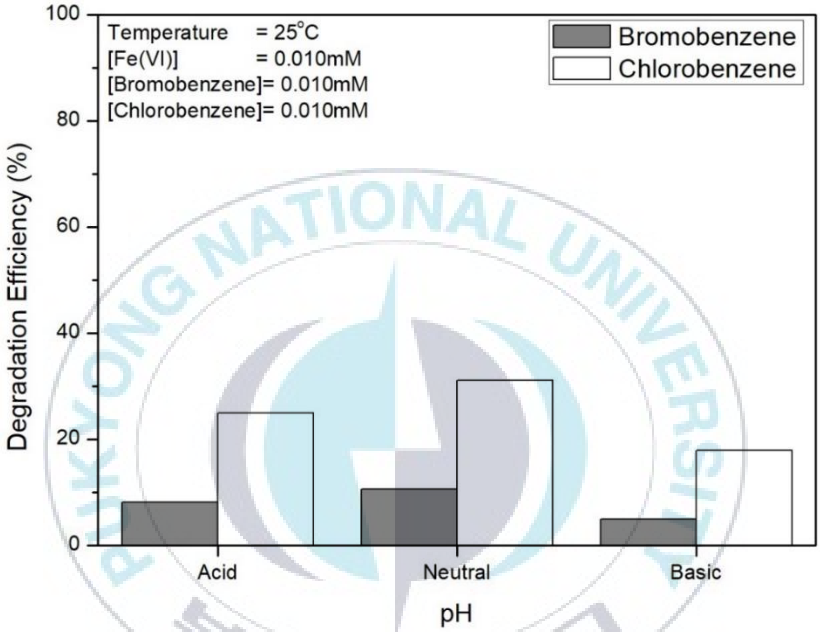


Figure 27. Bromobenzene and chlorobenzene degradation by ferrate(VI) in various of pH levels

The reaction between ferrate and; bromobenzene and chlorobenzene, the highest degradation were achieved in neutral condition (pH 6.8), while the lowest degradation were achieved in basic condition (pH 9.4). Compared to chlorobenzene degradation, the minor degree of bromobenzene degradation obtained in entire pH indicates that the rate of aqueous decomposition is much greater than the rate of ferrate reaction with bromobenzene.

The reaction of ferrate(VI) with an organic compound is second order reaction rate (Yang et al. 2014). The values of rate constant (k) for the reaction of ferrate(VI) with bromobenzene and chlorobenzene at various pH conditions have been determined and calculated. The value of second-order rate constant values (k, $M^{-1}s^{-1}$) in various pH conditions are given in Table 8. It was shown that the highest rate constant for degradation of bromobenzene and chlorobenzene were achieved at neutral pH condition.

Table 8. k_{app} values of bromobenzene and chlorobenzene removal in various pH levels

Compound	pH, k_{app} ($M^{-1}s^{-1}$)		
	3.6	6.8	9.7
Bromobenzene	58.463	71.199	39.527
Chlorobenzene	86.324	110.54	60.518

6.3.2. Effect of Molar Ratio

The molar ratio is the important parameter for ferrate(VI) process to remove organic contaminants (Sharma 2013). In order to investigate molar ratio effect, the experiments were carried out at range of molar ratios ($[FeO_4^{2-}]/[Compound]$) 2 to 8 with fixed bromobenzene and chlorobenzene concentration of 0.010mM. The influence of molar ratio on bromobenzene and chlorobenzene removal was studied and the result are summarized in Fig. 28. The degradation of bromobenzene and chlorobenzene by ferrate(VI) were a rapid process, with a major removal of bromobenzene and chlorobenzene obtained in the initial 5 minutes.

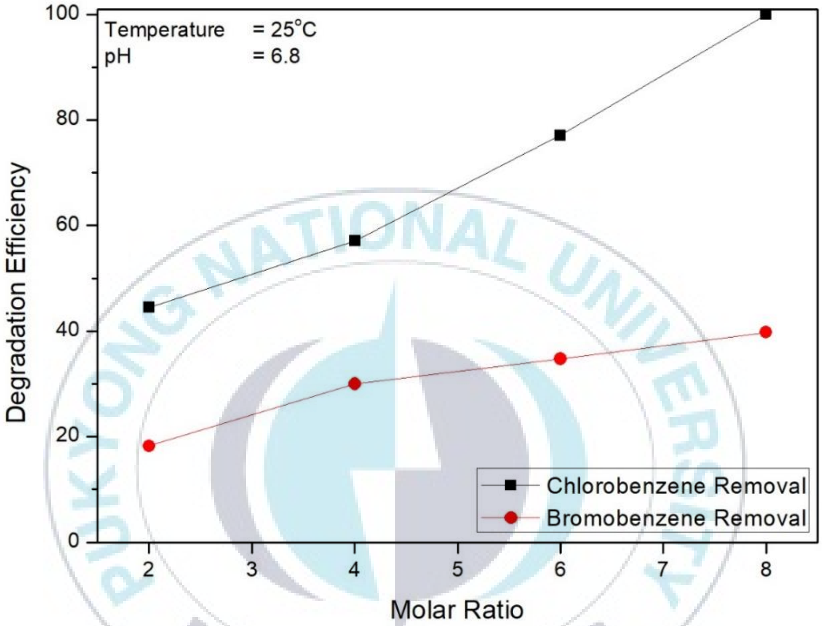


Figure 28. Bromobenzene and chlorobenzene degradation by ferrate(VI) in various molar ratio

The increasing of molar ratio on the reactor will definitely affect degradation efficiency. The removal of chlorobenzene was only 44.5% when the molar ratio was 2, while the molar ratio increased to 8 leading to a rapid increase up to 100% of removal. The removal of bromobenzene was 18.2% when the molar ratio was 2, while the molar ratio increased to 8 leading to a rapid increase up to 39.7% of removal. The observed removal efficiency increased gradually as molar ratio increased (Sharma and Bielski 1991).

Degradation of chlorobenzene was faster than bromobenzene. It can be seen that functional groups play very defined role in the potential degradation by ferrate. The electronegativity of carbon-halogen bond increased follow the order: F-C> Cl-C> Br-C> I-C (Freitas Dos Santos et al. 1999). The electronegativity provides a greater oxidation (Graham et al. 2004). Therefore, chlorobenzene degradation by ferrate is became easier and has higher degradation efficiency than bromobenzene degradation.

6.3.3. Effect of Temperature

Temperature is one of the significant parameters for ferrate treatment (Jiang 2014). As shown in Fig. 29, degradation of bromobenzene and chlorobenzene showed similar pattern where the efficiency increased in the temperature range from 15 to 45°C, then decreased above 45°C. The optimal temperature condition for removal of chlorobenzene bromobenzene were observed at 45°C. The degradation efficiencies of bromobenzene and chlorobenzene at 45°C were 22.3% and 57.7%, respectively.

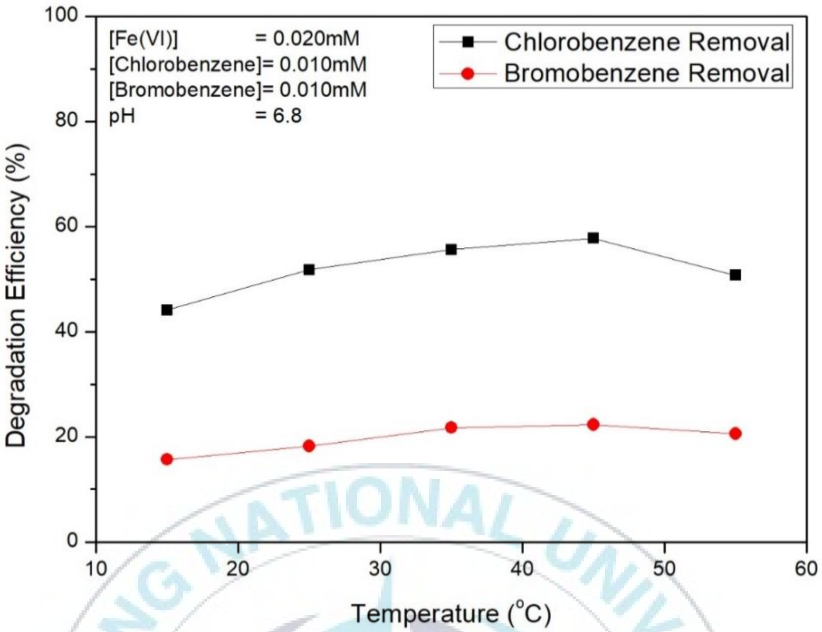


Figure 29. Bromobenzene and chlorobenzene degradation by ferrate(VI) in various temperature

The highest k_{app} values were observed at 45°C (Table 9). The lowest k_{app} values were observed at 15°C because of the low temperature. The collision frequencies between ferrate(VI) and target compound are enhanced with increasing temperature, then increasing the degradation rate of toluene (Han et al. 2015). And reaction kinetics of ferrate(VI) were enhanced when the temperature increased (Sharma et al. 1998a; b). However the k_{app} value decreased upon further increase in the temperature range above 45°C (Fig. 30). Several researchers have reported the effect of temperature on the degradation of organic compounds by ferrate(VI).

Previous studies have also confirmed the decomposition of ferrate increases rapidly in the range of temperature above 50°C (Deyrup and Mills 1956; Wagner et al. 1952).

Table 9. k_{app} values of bromobenzene and chlorobenzene removal in various molar ratio

Compound	Temperature, k_{app} ($M^{-1}s^{-1}$)				
	15°C	25°C	35°C	45°C	55°C
Bromobenzene	85.242	99.34	120.93	122.87	114.81
Chlorobenzene	144.89	183.75	218.80	229.76	216.50

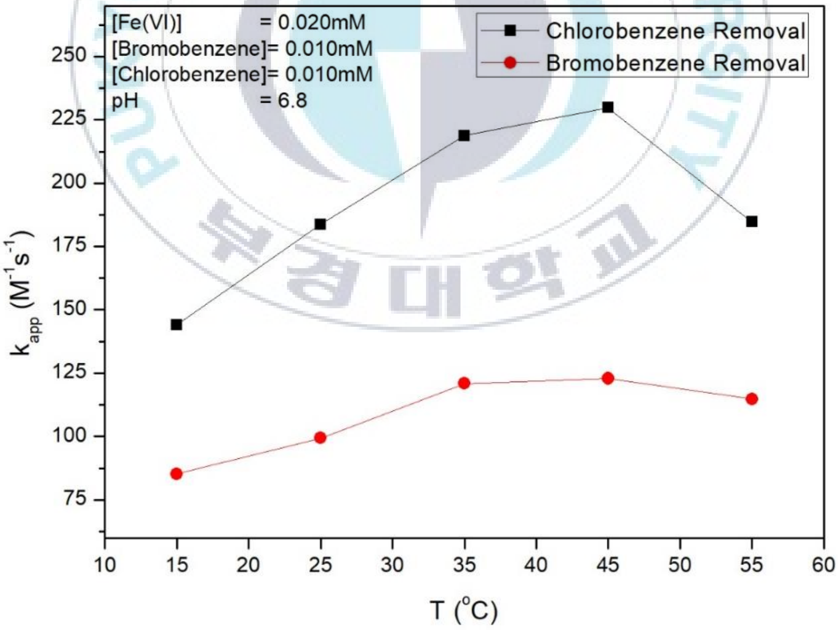


Figure 30. Relationship between T and k_{app} value on bromobenzene and chlorobenzene degradation

6.4.Conclusion

This study, have shown that potassium ferrate is a highly oxidative. For the reaction of ferrate with bromobenzene and chlorobenzene, the overall extent of compound degradation by ferrate was found to be highly pH, molar ratio and temperature dependent. In the effect of pH, the neutral condition has been observed as the best condition for both compounds. In effect of molar ratio, the increase of molar ratio was found to be in a linear relationship with degradation efficiency. In effect of temperature, the temperature of 45°C was observed as the optimal temperature with the activation energy of 81.1 KJ/mol for bromobenzene and 80.5 KJ/mol for chlorobenzene. It was found that degree of electronegativity (-Br and -Cl) also play very defined role, corresponds to an increasing reactivity and a decreasing reactivity of compound.

Chapter 7

TOLUENE, CHLOROBENZENE AND BROMOBENZENE DEGRADATION BY FERRATE(VI)

Abstract

The objective of this research was to investigate the functional groups effect on the degradation and kinetic rate of benzene derivatives. In this study, degradation of selected benzene derivatives, toluene, chlorobenzene and bromobenzene by ferrate(VI) have been examined. The effect of molar ratio ([$(FeO_4)^{2-}$]/ [Compound]) (1-6), pH (3-9), and temperature (15-55^{o}C) on the degradation of benzene derivatives were investigated. In this experiment, ferrate(VI) was effective to removed toluene, chlorobenzene and bromobenzene in reactor. The highest toluene, chlorobenzene, and bromobenzene removal were achieved at pH neutral condition (pH = 6.8) with degradation efficiency of 55.23%, 31.12%, 10.60%, respectively. For the effect of molar ratio, the degradation efficiency increased as molar ratio increased. The highest degradation efficiency of toluene, chlorobenzene and bromobenzene were achieved at molar ratio of 6/1. The optimal temperature was 45^{o}C with k_{app} value of 241.12 $M^{-1}s^{-1}$ and activation energy of 79.4 KJ/mol for toluene removal, k_{app} value of 229.76 $M^{-1}s^{-1}$ and activation energy of 80.5 KJ/mol chlorobenzene removal, and k_{app} value of 125.28 $M^{-1}s^{-1}$ and activation energy of 81.1 KJ/mol for bromobenzene. The

degradation pathway of toluene, chlorobenzene and bromobenzene are also studied.

7.1. Introduction

The presence of benzene derivatives in the water supply has increased in the last few years because their high stability in solution and their extensive use as pesticides and herbicides (Bryant 2014; Clough 2014; Pravasi 2014). Their elimination is necessary, especially if the water is destined for household consumption. Hence there is a continuing interest in the application of more efficient water treatment chemical reagents to achieve higher water quality.

Ferrate(VI) (Fe(VI)) has been found to be a powerful oxidant over a wide pH range and many studies have considered its role as an oxidant in water and wastewater treatment (Jiang and Lloyd 2002). The standard half-cell reduction potential of ferrate has been estimated to be from +2.20 V to +0.72 V in acidic and basic solution, respectively (H. Wood 1958). Thus the oxidation potential of potassium ferrate is the strongest of all the oxidants/disinfectants used in water and wastewater treatment, including chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, dissolved oxygen, and permanganate (Jiang and Lloyd 2002).

The use of ferrate(VI) in the wastewater treatment technologies shows multifunctional applicability since during initial stage of treatment, ferrate(VI) serves to oxidize the degradable impurities and in the latter stages the reduced ferric(III) coagulates or even adsorbs the non-degradable metallic impurities (Jiang 2007; Li et al. 2005; Sharma 2002; Tiwari and Lee 2011). Previous investigations have considered aspects of Fe(VI) treatment such as the inactivation of micro-organisms (Kazama 1995), its reactivity with a wide range of aqueous contaminants, such as ammonia and heavy metals (Murmann and Robinson 1974) and the treatment of industrial and municipal wastewaters (D. Johnson and F. Read 1996; Delaude and Laszlo 1996; Sharma et al. 1999). Recently we reported on the degradation of phenol and chlorophenols by potassium ferrate (Graham et al. 2004). These facts make Fe(VI) can be a promising candidate for water treatment process.

The aim of this study is to determine the electronic effect of the substituent on the degradation and kinetic rate of benzene derivatives. Toluene, chlorobenzene and bromobenzene were selected as hazardous benzene derivatives. The parameters experiment such as pH, molar ratio, and temperature were studied.

7.2.Materials and Methods

7.2.1. Materials

The ferrate(VI) was prepared using ferric oxide (Fe_2O_3) and sodium peroxide (Na_2O_2) as the main materials, were purchased from Alfa Aeser.

Chlorobenzene, bromobenzene and toluene as target compound were purchased from Sigma-Aldrich. The other chemicals such as sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) were purchased from Junsei Company. Buffer solutions for pH adjustment were obtained from Samchun Company.

7.2.2. Methods

7.2.2.1.Degradation Experiment

The degradation experiments were performed in 700mL of closed zero-head space glass reactor with ports for sampling, measuring pH and temperature, and adding ferrate(VI). To control pH, the addition of 5 - 10 mL buffer solution and a few drops of sulfuric acid (0.5 M) were used. Each toluene, chlorobenzene, bromobenzene solutions with the initial concentration (C_0) of 0.010mM were used in the experiments. The effects of the parameters such as pH (3.7-9.4), molar ratio (1-6) and temperature (15^{o}C – 45^{o}C) were investigated within 20 minutes of reaction time. The samples were extracted using liquid-liquid extraction (LLE) method (sample volume = 3mL, vortex mixing time for extraction = 2 minutes, temperature = 25^{o}C, n-hexane volume = 3mL). The concentrations chlorobenzene and bromobenzene were measured using gas chromatography-electron capture detector (GC-ECD). The temperatures of injection port and detector were 250^{o}C and 300^{o}C, respectively. Initially 40^{o}C was held constant for 5 minutes, followed by 8^{o}C/min ramp until a temperature of 100^{o}C was reached, and followed by 12^{o}C/min ramp until a final temperature of 200^{o}C was reached. The concentration of toluene was determined using GC-FID. The temperatures of injection port and detector were 210^{o}C and 250^{o}C, respectively. The temperature program began at 35^{o}C, followed by 5^{o}C/min ramp until a temperature of 150^{o}C was reached. In this work, all of the degradation experiments were performed duplicately.

7.3. Result and Discussion

7.3.1. Effect of pH

The impact of pH on the chemical oxidation of toluene, chlorobenzene and bromobenzene in aqueous solution by ferrate has been studied. Sharma (2011), has determined the speciation of ferrate according to the pH variation considering pKa values (Sharma 2011a). The study further extended to observe the pH effect (i.e. from pH 3.7 - 9.4) for a molar ratio of (Ferrate)/(Target Compound) = 1/1. The data were collected as the change of percent target compounds reduction as a function of time for different pH condition and are returned in Fig. 31. It is clearly showed that high toluene and chlorobenzene removal efficiency were observed at pH 6.8 (neutral pH). When the initial pH increased from 3.7 to 6.8, the toluene removal increased obviously from 8.09% to 10.6%. Further initial pH increase to 9.4 reduced the toluene removal efficiency of 4.8%. When the initial pH increased from 3.7 to 6.8, the chlorobenzene removal increased obviously from 24.9% to 31.1%. Further initial pH increase to 9.4 reduced the chlorobenzene removal efficiency of 17.9%. When the initial pH increased from 3.7 to 6.8, the bromobenzene removal increased obviously from 8.09% to 10.6%. Further initial pH increase to 9.4 reduced the bromobenzene removal efficiency of 4.8%.

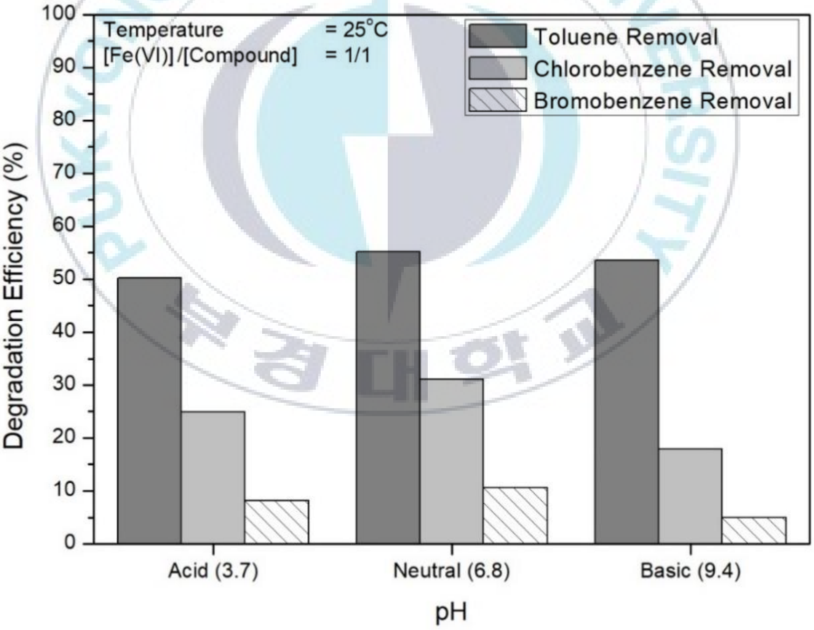


Figure 31. Toluene, chlorobenzene, and bromobenzene degradation by ferrate(VI) in various of pH levels

The results showed that the highest degradation were achieved in neutral condition (pH 6.8), while the lowest degradation were achieved in basic condition (pH 9.4). Toluene degradation has higher efficiency compared to chlorobenzene and bromobenzene degradation. Toluene has been found to be readily oxidisable owing to the presence of the $-CH_3$ electron donor group, leading to electrophilic attack at reactive carbons (in the *ortho* and *para* positions) on the aromatic ring (Bellany Chapman and Shorter 2018). Thus, the electron attracting effect of the substituent halogen atoms is believed to make the compounds (chlorobenzene and bromobenzene) more electronically stable (Graham et al. 2004).

The reaction of ferrate(VI) with an organic compound is second order reaction rate (Yang et al. 2014). The values of rate constant (k, $M^{-1}s^{-1}$) for the reaction of ferrate(VI) with toluene and chlorobenzene at various pH conditions have been determined and presented in Table 10. It was shown that the highest rate constant for degradation of toluene and chlorobenzene were achieved at neutral pH condition.

Table 10. k_{app} values of toluene, chlorobenzene, and bromobenzene removal in various pH levels

Compound	pH, k_{app} ($M^{-1}s^{-1}$)		
	3.6	6.8	9.7
Toluene	372.22	389.07	354.94
Chlorobenzene	86.324	110.54	60.518
Bromobenzene	58.46	71.19	39.52

7.3.2. Effect of Molar Ratio

The molar ratio is the important parameter for ferrate(VI) process to remove organic contaminants (Sharma 2013). In order to investigate molar ratio effect, the experiment were carried out at range of molar ratios ([FeO_4^{2-}]/[Compound]) 1 to 6 with fixed toluene and chlorobenzene concentration of 0.010mM. The influence of molar ratio on toluene and chlorobenzene removal was studied and the result are summarized in Fig. 32. The degradation of toluene, chlorobenzene, and bromobenzene by ferrate(VI) were a rapid process, with a major removal obtained in the initial 5 minutes.

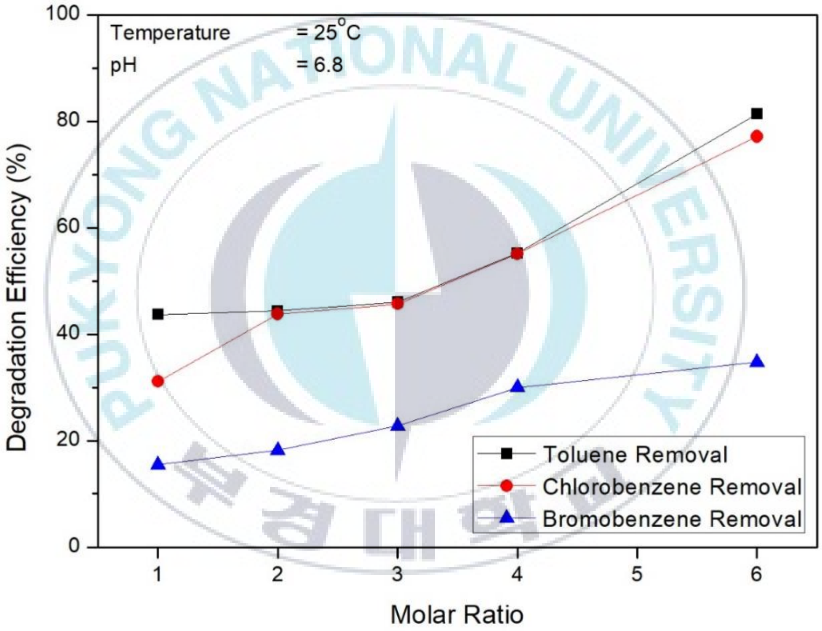


Figure 32. Toluene, chlorobenzene and bromobenzene degradation by ferrate(VI) in various molar ratio

The increasing of molar ratio on the reactor will definitely affect degradation efficiency. The removal of toluene was 43.70% when the molar ratio was 1, while the molar ratio increased to 6 leading to a rapid increase up to 81.34% of removal. The removal of chlorobenzene was only 31.12% when the molar ratio was 1, while the molar ratio increased to 6 leading to a rapid increase up to 77.11% of removal. The removal of bromobenzene was 15.42% when the molar ratio was 1, while the molar ratio increased to 6 leading to a rapid increase up to 34.73% of removal. The observed removal efficiency increased gradually as molar ratio increased (Sharma and Bielski 1991).

Lower degradation of compounds substituted with electron-withdrawing radicals (-Cl and -Br) is observed comparatively to compounds substituted with electron-donating one ($-CH_3$). These experiments agree with other study that degradation of aromatic compounds is faster with electron-donating radicals (alkyl group) than with strongly electron-withdrawing radicals (Cl or Br) (Bougheloum and Messalhi 2009).

A small number of previous studies (Graham et al. 2004) have been considered the electronegativity effect of carbon-halogen bond also plays very defined role in the degradation of target compounds by ferrate. The electronegativity of carbon-halogen bond increased follow the order: Cl-C>

Br-C> I-C (Freitas Dos Santos et al. 1999). It is believed that the electronegativity also provides a greater susceptibility to oxidation (Graham et al. 2004). Therefore, the degradation efficiency of chlorobenzene is slightly different than toluene degradation efficiency.

7.3.3. Effect of Temperature

Temperature is one of the significant parameters for ferrate treatment (Jiang 2014). As shown in Fig. 33, degradation of toluene and chlorobenzene showed similar pattern where the efficiency increased in the temperature range from 15 to 45°C, then decreased above 45°C. The optimal temperature condition for removal of toluene, chlorobenzene and bromobenzene were observed at 45°C. The degradation efficiencies of toluene, chlorobenzene and bromobenzene at 45°C were 29.28%, 44.77%, and 22.30%, respectively.

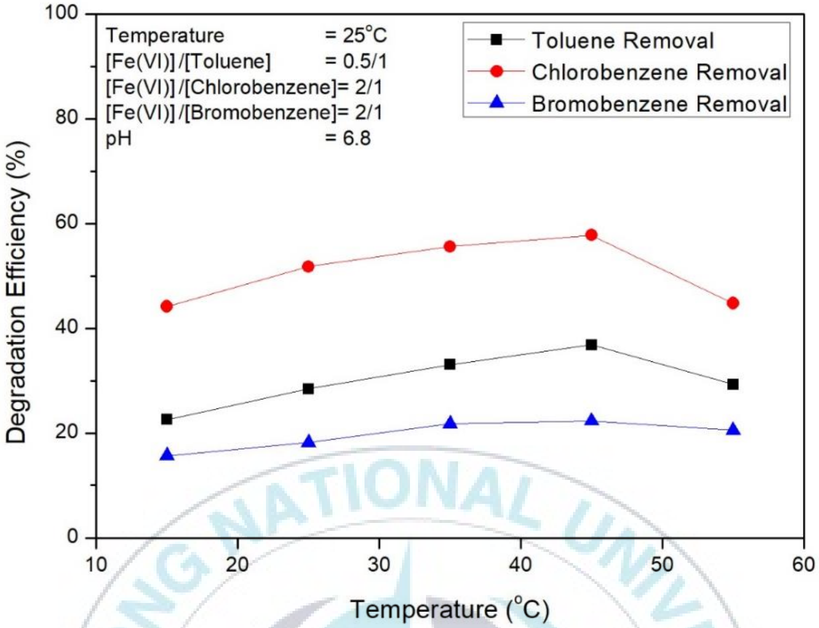


Figure 33. Toluene, chlorobenzene and bromobenzene degradation by ferrate(VI) in various temperature

The highest k_{app} values were observed at 45°C (Table 11). The lowest k_{app} values were observed at 15°C because of the low temperature. The collision frequencies between ferrate(VI) and target compound are enhanced with increasing temperature, then increasing the degradation rate of target compound (Han et al. 2015). And reaction kinetics of ferrate(VI) were enhanced when the temperature increased (Sharma et al. 1998a; b). However the k_{app} value decreased upon further increase in the temperature range above 45°C (Fig. 34). Several researchers have reported the effect of temperature on the degradation of organic compounds by ferrate(VI).

Previous studies have also confirmed the decomposition of ferrate increases rapidly in the range of temperature above 50°C (Deyrup and Mills 1956; Wagner et al. 1952).

Table 11. k_{app} values of toluene, chlorobenzene, bromobenzene removal in various temperature

Compound	Temperature, k_{app} ($M^{-1}s^{-1}$)				
	15°C	25°C	35°C	45°C	55°C
Toluene	153.41	188.19	210.94	241.12	193.17
Chlorobenzene	144.06	183.75	218.80	229.76	216.50
Bromobenzene	85.24	99.34	120.93	122.87	114.81

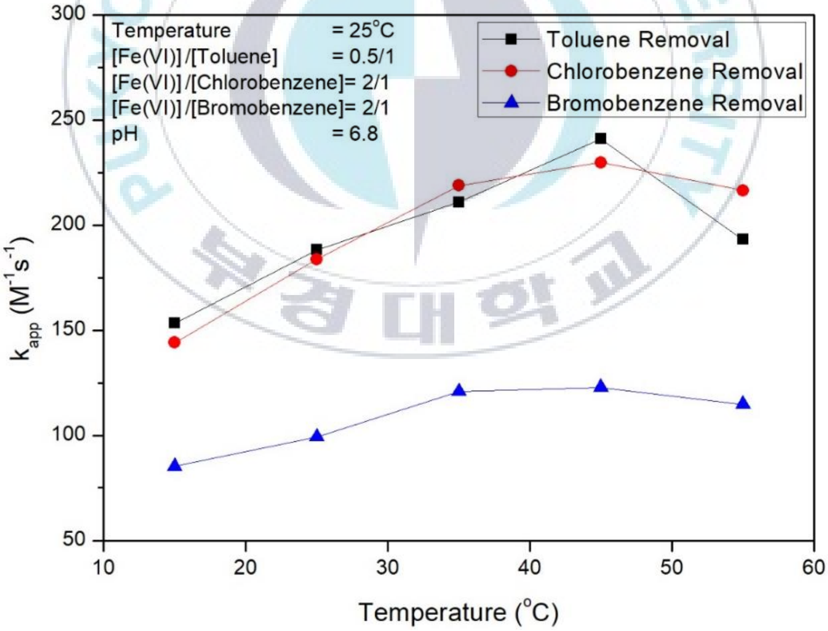


Figure 34. Relationship between T and k_{app} value on toluene, chlorobenzene, and bromobenzene degradation

7.3.4. Degradation Pathways of Toluene and Halogenated Benzene

In this work the comparison of degradation pathways of toluene and chlorobenzene were studied. Ferrate(VI) oxidizes compounds by electron transfer, hydrogen atom transfer, hydride ion transfer, or reactions of ferrates with reactive oxygen species, $O_2^{\cdot -}$, and H_2O_2, produced from self-decompositions,(Lee and Gai 1993; Sharma et al. 2015) one or more of the above-mentioned mechanisms can be involved in the oxidation of toluene and chlorobenzene. The Gas Chromatography-Mass Spectrometry (GC-MS) analysis of toluene and chlorobenzene degradation by ferrate showed the formation of several by products. The formation of different by-products of toluene degradation such as heptanal, 3-methylbutanal, 2-methylhexane, 2-methylbutan-1-ol, 1-chlorobutane, 4-chlorobutan-1-ol, 1-chloro-2-methylpropane are proposed in Fig. 35. And the formation of different by-products of chlorobenzene degradation such as 3-methylbut-1-ene, 2,2-dichloroacetic acid are proposed in Fig. 35.

The previous studies have reported the initial oxidation steps of organic pollutant which generally started with oxygen transfer and ring opening (Irokawa et al. 2006). It was shown in proposed pathways (Fig. 35). Initially, ferrate(VI) oxidizes the methyl group of toluene by one electron transfer, then generating radical toluene. The radical toluene is stabilized and forms aldehyde group. In second pathway, ferrate(VI) reacts with the double bond of the aromatic ring, resulting in the opening of an aromatic ring. Similar result was observed in previous work that ring opening products and aldehyde group are generated from oxidation of aromatic hydrocarbon by ferrate(VI) (Guan et al. 2014).

Ferrate(VI) oxidizes the chlorobenzene by oxygen transfer, then generating phenol and aldehyde groups. Ferrate(VI) also reacts with the aromatic of benzene ring, resulting in the opening of an aromatic ring. Then it was proposed that further decomposition of organic pollutants intermediate led to end products like carbon dioxide (Chu et al. 2017; Irokawa et al. 2006). Agree with other researcher that the degradation of benzene derivatives by ferrate(VI) usually started from oxygen transfer and proton addition (Arnold and Roberts 2000).

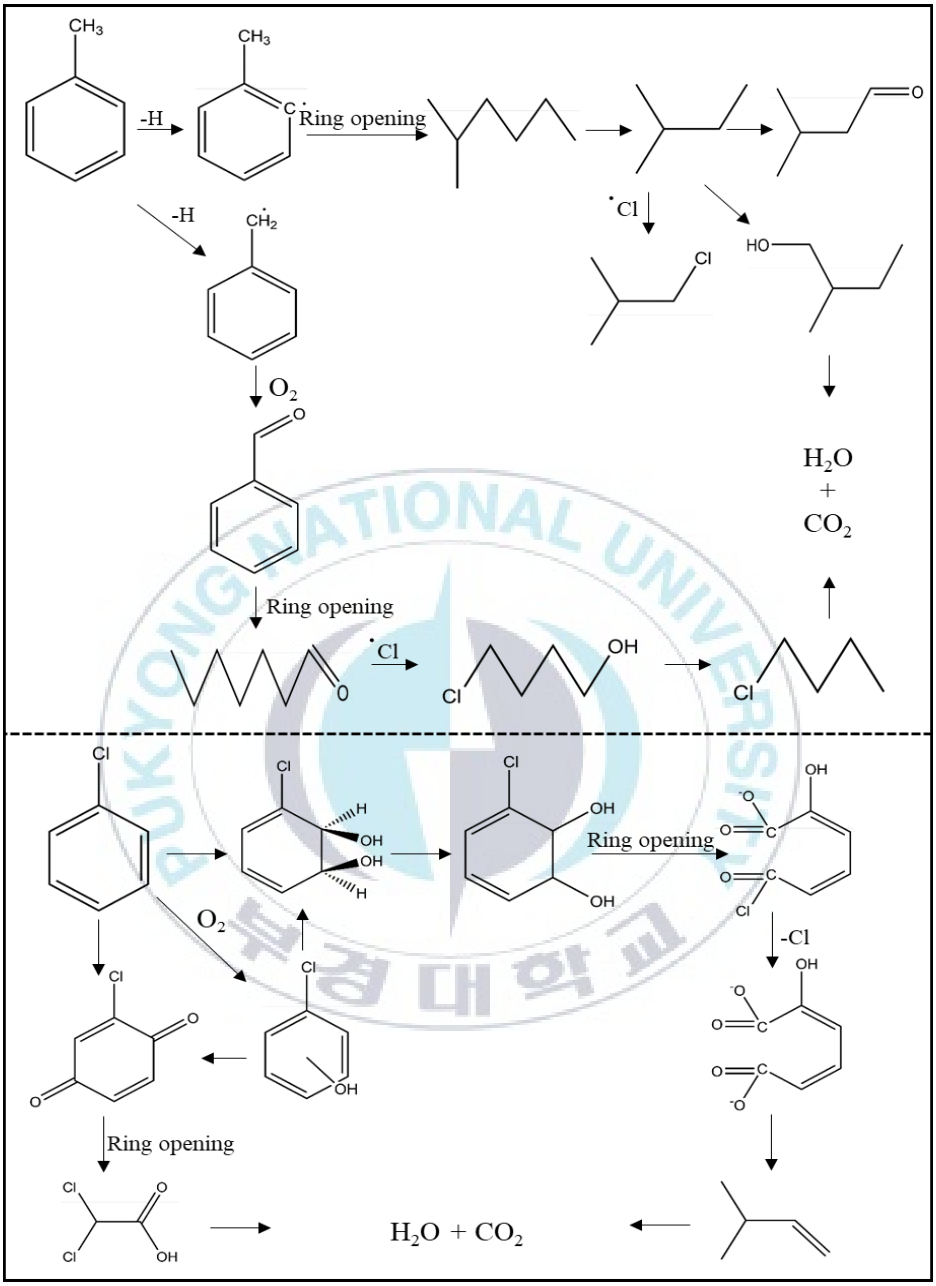


Figure 35. Degradation pathways of toluene, and halogenated benzene

7.4.Conclusion

This study, have shown that potassium ferrate is a highly oxidative. For the reaction of ferrate with toluene and chlorobenzene, the overall extent of compound degradation by ferrate was found to be highly pH, molar ratio and temperature dependent. In the effect of pH, the neutral condition has been observed as the best condition for both compounds. In effect of molar ratio, the increase of molar ratio was found to be in a linear relationship with degradation efficiency. In effect of temperature, the temperature of 45°C was observed as the optimal temperature with the activation energy of 79.4 KJ/mol for toluene, 80.5 KJ/mol for chlorobenzene, and 81.1 KJ/mol for bromobenzene. It was found that the functional groups ($-CH_3$, -Cl, and -Br) also play very defined role, corresponds to an increasing reactivity and a decreasing reactivity of compound.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1. Conclusions

The degradation of hazardous benzene derivatives by ferrate(VI) have been demonstrated in this experiment. This process was found to be an effective method for the treatment of toluene, chlorobenzene, and bromobenzene in aqueous solutions.

Working as oxidant and coagulant, ferrate can readily degrade chlorobenzene in aqueous solution. The second order reaction rate provided a good fit of the experiment data. Degradation of chlorobenzene produces more bio-degradable organic byproduct such as 3-methylbut-1-ene and 2,2-dichloroacetic.

The bromobenzene was degraded rapidly by ferrate in aqueous solution. Neutral condition has been observed as the best condition for bromobenzene removal. The degradation of bromobenzene greatly depended on the pH, molar ratio and temperature. The degradation of bromobenzene followed the second order reaction. The temperature of 45^{o}C was observed as the optimal temperature with the activation energy of 81.16 KJ/mol. Degradation of chlorobenzene produces more bio-degradable organic such as isobutyraldehyde and ethane-1,2-diol.

On degradation of toluene, liquid and solid ferrates(VI) showed similar pattern. the optimal condition of toluene degradation was found at neutral pH, molar ratio of 4/1 and temperature experiment of 45^{o}C. The intermediate products such as heptanal, 3-methylbutanal, 2-methylhexane, 2-methylbutan-1-ol, 1-chlorobutane, 4-chlorobutane-1-ol, 1-chloro-2-methylpropane were identified. The possible pathway for the degradation of toluene can be described by electron transfer, oxygen transfer and opening of an aromatic ring. The degradation of toluene followed the second order reaction.

The halogenated benzene, chlorobenzene and bromobenzene were degraded rapidly by ferrate in aqueous solution. The optimal condition of chlorobenzene and bromobenzene degradation were found at neutral pH, molar ratio of 8/1 and temperature of 45^{o}C. The degradation of chlorobenzene and bromobenzene follows the second order reaction kinetics. The electronegativity of carbon-halogen bond (C-Cl and C-Br) play very defined role. Degradation of chlorobenzene was faster than bromobenzene.

Organic pollutant such as toluene chlorobenzene and bromobenzene were degraded rapidly by ferrate in aqueous solution. The optimal condition of toluene, chlorobenzene, and bromobenzene degradation were found at neutral pH, molar ratio of 6/1 and temperature of 45^{o}C. The degradation of toluene, chlorobenzene, bromobenzene follows the second order reaction kinetics. The functional groups (-CH_3, -Cl, and -Br) play very defined role. Degradation of aromatic compounds is faster with electron-donating radical (alkyl group) than with strongly electron-withdrawing radicals (Cl or Br). Degradation efficiency follows the order: Toluene > chlorobenzene > bromobenzene. Degradation of toluene and halogenated benzene by ferrate(VI) produced more bio-degradable organic byproduct.

Based on the investigation for the ferrate reaction of chlorobenzene, bromobenzene, and toluene, the application of ferrate process appears to be a promising in both water and wastewater industries.

8.2. Further Recommendations

Future studies should involve evaluating the effectiveness of ferrate on effluent from industrial wastewater streams containing range of organics and other microorganisms. It is important that an economic method of synthesizing ferrate in large quantities has to be investigated, if ferrate should be used in water and wastewater industry successfully. HPLC should be used as a more definitive means of quantifying the by-products, since in such a complex wastewater, many compounds will be competing for oxidation by Ferrate. To avoid chlorine substitution on the by-products, a different formula for Ferrate synthesis could be used. A formula with submolar sodium hypochlorite dosages for the dissolution phase of the reaction to synthesize ferrate would be less likely to cause chlorine substitution and high chlorine residual. The by-products may be less harmful to the environment if chlorine is not present, and could also be less toxic. For the safety issue, the risk of the formation of some highly toxic byproduct should be evaluated carefully. This research can provide a basis of study for more complex reactions of Ferrate with substrates and can also be applicable to large-scale engineering uses, such as industrial wastewater treatment. Furthermore, this research supports the conclusion of others, that ferrate is a strong oxidizer which can be used in water and wastewater treatment.

REFERENCES

Aelion, C. M., Swindoll, C. M., and Pfaender, F. K. (1987). "Adaptation to and biodegradation of xenobiotic compounds by microbial communities from a pristine aquifer." *Applied and Environmental Microbiology*, 53(9), 2212–2217.

Al-Abduly, A., and Sharma, V. K. (2014). "Oxidation of benzothiophene, dibenzothiophene, and methyl-dibenzothiophene by ferrate(VI)." *Journal of Hazardous Materials*, 279, 296–301.

Anquandah, G. A. K., and Sharma, V. K. (2009). "Oxidation of octylphenol by ferrate(VI)." *Journal of Environmental Science and Health, Part A,* Taylor & Francis, 44(1), 62–66.

Anquandah, G. A. K., Sharma, V. K., Knight, D. A., Batchu, S. R., and Gardinali, P. R. (2011). "Oxidation of Trimethoprim by Ferrate(VI): Kinetics, Products, and Antibacterial Activity." *Environmental Science & Technology*, American Chemical Society, 45(24), 10575–10581.

Anquandah, G. A. K., Sharma, V. K., Panditi, V. R., Gardinali, P. R., Kim, H., and Oturan, M. A. (2013). "Ferrate(VI) oxidation of propranolol: Kinetics and products." *Chemosphere*, 91(1), 105–109.

Arnold, W. A., and Roberts, A. L. (2000). "Pathways and Kinetics of

Chlorinated Ethylene and Chlorinated Acetylene Reaction with Fe(0) Particles." *Environmental Science & Technology*, American Chemical Society, 34(9), 1794–1805.

Batarseh, E. S., Reinhart, D. R., and Daly, L. (2007). "Liquid Sodium Ferrate and Fenton ' s Reagent for Treatment of Mature Landfill Leachate." *Journal of Environtmental Engineering (ASCE),* 133(November), 1042–1050.

Bellany Chapman, N., and Shorter, J. (2018). *Correlation analysis in chemistry : recent advances / edited by N. B. Chapman and J. Shorter*. *SERBIULA (sistema Librum 2.0).*

Bougheloum, C., and Messalhi, A. (2009). "Photocatalytic Degradation of Benzene Derivatives on TiO2 Catalyst." *Physics Procedia*, 2(3), 1055–1058.

Bryant, M. A. (2014). "Bromobenzene A2 - Wexler, Philip BT - Encyclopedia of Toxicology (Third Edition)." Academic Press, Oxford, 559–560.

Cao, B., Nagarajan, K., and Loh, K.-C. (2009). *Biodegradation of aromatic compounds: Current status and opportunities for biomolecular approaches*. *Applied Microbiology and Biotechnology*.

Chu, H., Lin, Y. H., and Lin, Y. C. (2017). "Characterization, Degradation, and Reaction Pathways of Indoor Toluene over Visible-light-driven S, Zn Co-doped TiO 2." *IOP Conference Series: Earth and Environmental Science*, 51(1), 12001.

Clough, S. R. (2014). "Toluene A2 - Wexler, Philip BT - Encyclopedia of Toxicology (Third Edition)." Academic Press, Oxford, 595–598.

D. Johnson, M., and F. Read, J. (1996). *Kinetics and Mechanism of the Ferrate Oxidation of Thiosulfate and Other Sulfur-Containing Species. Inorganic chemistry*.

Darnerud, P. O. (2003). "Toxic effects of brominated flame retardants in man and in wildlife." *Environment International*, 29(6), 841–853.

Delaude, L., and Laszlo, P. (1996). "A Novel Oxidizing Reagent Based on Potassium Ferrate(VI)1." *The Journal of Organic Chemistry*, American Chemical Society, 61(18), 6360–6370.

Deyrup, A. J., and Mills, J. R. (1956). "Water purification process." Google Patents.

Feng, M., Wang, X., Chen, J., Qu, R., Sui, Y., Cizmas, L., Wang, Z., and Sharma, V. K. (2016). "Degradation of fluoroquinolone antibiotics by ferrate(VI): Effects of water constituents and oxidized products." *Water Research*, 103, 48–57.

Flores-Chaparro, C. E., Chazaro Ruiz, L. F., Alfaro de la Torre, M. C., Huerta-Diaz, M. A., and Rangel-Mendez, J. R. (2017). "Biosorption removal of benzene and toluene by three dried macroalgae at different ionic strength and temperatures: Algae biochemical composition and kinetics." *Journal of Environmental Management*, 193, 126–135.

Freitas Dos Santos, L. M., Lamarca, D., Gilges, M., and New, A. (1999). "Biodegradation of Bromobenzene, Chlorobenzene, Iodobenzene and Fluorobenzene: Batch and Continuous Experiments." *Process Safety and Environmental Protection*, 77(1), 43–48.

Ghernaout, D., and Naceur, M. W. (2011). "Ferrate(VI): In situ generation and water treatment – A review." *Desalination and Water Treatment*, Taylor & Francis, 30(1–3), 319–332.

Goff, H., and K. Murmann, R. (1971). *Studies on the mechanism of isotopic oxygen exchange and reduction of ferrate(VI) ion (FeO42-). Journal of the American Chemical Society*.

Gombos, E., Barkács, K., Felföldi, T., Vértes, C., Makó, M., Palkó, G., and Záray, G. (2013). "Removal of organic matters in wastewater treatment by ferrate (VI)-technology." *Microchemical Journal*, 107(Supplement C), 115–120.

Graham, N., Jiang, C., Li, X.-Z., Jiang, J.-Q., and Ma, J. (2004). "The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate." *Chemosphere*, 56(10), 949–956.

Gu, B., Schmitt, J., Chen, Z., Liang, L., and McCarthy, J. F. (1994). "Adsorption and desorption of natural organic matter on iron oxide:

mechanisms and models.” *Environmental Science & Technology*, American Chemical Society, 28(1), 38–46.

Guan, W., Xie, Z., and Zhang, J. (2014). *Preparation and Aromatic Hydrocarbon Removal Performance of Potassium Ferrate*. *Journal of Spectroscopy*.

H. J. Bielski, B., and J. Thomas, M. (1987). *Studies of hypervalent iron in aqueous solutions. 1. Radiation-induced reduction of iron(VI) to iron(V) by CO2-*. *Journal of The American Chemical Society - J AM CHEM SOC*.

H. Wood, R. (1958). *The Heat, Free Energy and Entropy of the Ferrate(VI) Ion*. *Journal of the American Chemical Society (U.S.)*.

Hakim, M., Broza, Y. Y., Barash, O., Peled, N., Phillips, M., Amann, A., and Haick, H. (2012). “Volatile Organic Compounds of Lung Cancer and Possible Biochemical Pathways.” *Chemical Reviews*, American Chemical Society, 112(11), 5949–5966.

Han, Q., Wang, H., Dong, W., Liu, T., Yin, Y., and Fan, H. (2015). “Degradation of bisphenol A by ferrate(VI) oxidation: Kinetics, products and toxicity assessment.” *Chemical Engineering Journal*, 262, 34–40.

Han, Z., Chang, V.-W., Wang, X., Lim, T.-T., and Hildemann, L. (2013). “Experimental study on visible-light induced photocatalytic oxidation of gaseous formaldehyde by polyester fiber supported photocatalysts." *Chemical Engineering Journal*, 218, 9–18.

Huang, H. (2010). "Removal of Air Pollutants by Photocatalysis with Ozone in a Continuous-Flow Reactor."

Irokawa, Y., Morikawa, T., Aoki, K., Kosaka, S., Ohwaki, T., and Taga, Y. (2006). "Photodegradation of toluene over TiO2-xNx under visible light irradiation." *Phys. Chem. Chem. Phys.*, The Royal Society of Chemistry, 8(9), 1116–1121.

Jiang, J.-Q. (2014). "Advances in the development and application of ferrate(VI) for water and wastewater treatment." *Journal of Chemical Technology & Biotechnology*, John Wiley & Sons, Ltd, 89(2), 165–177.

Jiang, J.-Q., and Lloyd, B. (2002). "Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment." *Water Research*, 36(6), 1397–1408.

Jiang, J.-Q., Lloyd, B., and Grigore, L. (2001). *Preparation and Evaluation of Potassium Ferrate as an Oxidant and Coagulant for Potable Water Treatment*. *Environmental Engineering Science - ENVIRON ENG SCI*.

Jiang, J.-Q., and Wang, S. (2003). *Enhanced Coagulation with Potassium Ferrate(VI) for Removing Humic Substances*. *Environmental Engineering Science - ENVIRON ENG SCI*.

Jiang, J. Q. (2007). “Research progress in the use of ferrate(VI) for the environmental remediation.” *Journal of Hazardous Materials*, 146(3), 617–623.

Jiang, J. Q., Yin, Q., Zhou, J. L., and Pearce, P. (2005). “Occurrence and treatment trials of endocrine disrupting chemicals (EDCs) in wastewaters.” *Chemosphere*, 61(4), 544–550.

Jiang, Y., Goodwill, J. E., Tobiason, J. E., and Reckhow, D. A. (2016). “Impacts of ferrate oxidation on natural organic matter and disinfection byproduct precursors.” *Water Research*, 96, 114–125.

K. Freeman, P., and M. Haugen, C. (1998). *Differential photohydrodehalogenation reactivity of bromobenzenes (1,2,4-tribromobenzene, 1,2,3,5-tetrabromobenzene) and pentachlorobenzene: Sunlight-based remediation*. *Journal of chemical technology and biotechnology (Oxford, Oxfordshire : 1986)*.

Kamachi, T., Nakayama, T., and Yoshizawa, K. (2008). *Mechanism and Kinetics of Cyanide Decomposition by Ferrate*. *Bulletin of The Chemical Society of Japan - BULL CHEM SOC JPN*.

Kazama, F. (1994). *Inactivation of coliphage Qβ by potassium ferrate*. *FEMS microbiology letters*.

Kazama, F. (1995). “Viral inactivation by potassium ferrate.” *Water Science and Technology*, 31(5), 165–168.

Laksono, F. B., and Kim, I. (2016). "Removal of 2-Bromophenol by Advanced Oxidation Process with In- situ Liquid Ferrate (VI)." 128–135.

Lee, D. G., and Gai, H. (1993). "Kinetics and mechanism of the oxidation of alcohols by ferrate ion." *Canadian Journal of Chemistry*, NRC Research Press, 71(9), 1394–1400.

Lee, Y., Cho, M., Kim, J. Y., and Yoon, J. (2004). *Chemistry of ferrate (fe(vi)) in aqueous solution and its applications as a green chemical*. *Journal of Industrial and Engineering Chemistry*.

Li, C., Li, X. Z., and Graham, N. (2005). "A study of the preparation and reactivity of potassium ferrate." *Chemosphere*, 61(4), 537–543.

Li, C., Li, X. Z., Graham, N., and Gao, N. Y. (2008). "The aqueous degradation of bisphenol A and steroid estrogens by ferrate." *Water Research*, 42(1), 109–120.

Licht, S., Naschitz, V., Halperin, L., Halperin, N., Lin, L., Chen, J., Ghosh, S., and Liu, B. (2001). "Analysis of ferrate(VI) compounds and super-iron Fe(VI) battery cathodes: FTIR, ICP, titrimetric, XRD, UV/VIS, and electrochemical characterization." *Journal of Power Sources*, 101(2), 167–176.

De Luca, S., Allen, C., and Smallwood. (1983). "Removal of Organic Priority Pollutants by Oxidation-Coagulation." *Journal of*

Environmental Engineering, American Society of Civil Engineers, 109(1), 36–46.

DE LUCA, S. J., CANTELLI, M., and DELUCA, M. A. (1992). *FERRATE VS TRADITIONAL COAGULANTS IN THE TREATMENT OF COMBINED INDUSTRIAL-WASTES*.

de Luca, S. J., Idle, C. N., and Chao, A. C. (1996). “Quality improvement of biosolids by ferrate(VI) oxidation of offensive odour compounds.” *Water Science and Technology*, 33(3), 119–130.

Luo, Z., Strouse, M., Jiang, J.-Q., and Sharma, V. K. (2011). “Methodologies for the analytical determination of ferrate(VI): A Review.” *Journal of Environmental Science and Health, Part A*, Taylor & Francis, 46(5), 453–460.

Ma, J., and Liu, W. (2002). “Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation.” *Water Research*, 36(4), 871–878.

Mácová, Z., Bouzek, K., Híveš, J., Sharma, V. K., Terryn, R. J., and Baum, J. C. (2009). “Research progress in the electrochemical synthesis of ferrate(VI).” *Electrochimica Acta*, 54(10), 2673–2683.

El Maghraoui, A., Zerouale, A., and Ijjaali, M. (2015). *Process for the Synthesis of Ferrate (VI) Alkali Metal Dry*. *Advances in Materials Physics and Chemistry*.

Mars, A. E., Kasberg, T., Kaschabek, S. R., Martin, H., Janssen, D. B., and Reineke, W. (1997). "Microbial Degradation of Chloroaromatics : Use of the meta - Cleavage Pathway for Mineralization of Chlorobenzene." 179(14), 4530–4537.

Melton, J. D., and Bielski, B. H. J. (1990). "Studies of the kinetic, spectral and chemical properties of Fe(IV) pyrophosphate by pulse radiolysis." *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry*, 36(6), 725–733.

Monferrán, M. V, Echenique, J. R., and Wunderlin, D. A. (2005). "Degradation of chlorobenzenes by a strain of Acidovorax avenae isolated from a polluted aquifer." *Chemosphere*, 61(1), 98–106.

Murmann, R. K., and Robinson, P. R. (1974). "Experiments utilizing FeO42− for purifying water." *Water Research*, 8(8), 543–547.

Musilová-Kebrlová, N., Janderka, P., and Trnková, L. (2009). "Electrochemical processes of adsorbed chlorobenzene and fluorobenzene on a platinum polycrystalline electrode." *Collection of Czechoslovak Chemical Communications*, 74, 611–625.

Nam, J.-H., Kim, I.-K., Kwon, J., and Kim, Y. Do. (2016). "Applications of electrochemical ferrate(VI) for degradation of trichloroethylene in the aqueous phase." *Desalination and Water Treatment*, Taylor & Francis, 57(11), 5138–5145.

Neubert, D., Gericke, C., Hanke, B., Beckmann, G., Baltes, M. M., Kühl, K.-P., Bochert, G., and Hartmann, J. (2001). "Multicenter field trial on possible health effects of toluene. II. Cross-sectional evaluation of acute low-level exposure." *Toxicology*, 168(2), 159–183.

Ninane, L., Kanari, N., Criado, C., Jeannot, C., Evrard, O., and Neveux, N. (2008). "New Processes for Alkali Ferrate Synthesis." *Ferrates*, ACS Symposium Series, American Chemical Society, 102-111 SE–6.

Osathaphan, K., Kittisarn, W., Chatchaitanawat, P., Yngard, R. A., Kim, H., and Sharma, V. K. (2014). "Oxidation of Ni(II)-cyano and Co(III)-cyano complexes by Ferrate(VI): Effect of pH." *Journal of Environmental Science and Health, Part A*, Taylor & Francis, 49(12), 1380–1384.

Pepino Minetti, R. C., Macaño, H. R., Britch, J., and Allende, M. C. (2017). "In situ chemical oxidation of BTEX and MTBE by ferrate: pH dependence and stability." *Journal of Hazardous Materials*, 324, 448–456.

Perfiliev, Y. D., and Sharma, V. K. (2008). "Higher Oxidation States of Iron in Solid State: Synthesis and Their Mössbauer Characterization." *Ferrates*, ACS Symposium Series, American Chemical Society, 112-123 SE–7.

Petitto, S., M Marsh, E., and A Langell, M. (2006). *Adsorption of*

Bromobenzene on Periodically Stepped and Nonstepped NiO(100). The journal of physical chemistry. B.

Potts, M. E., and Churchwell, D. R. (1994). “Removal of radionuclides in wastewaters utilizing potassium ferrate (VI).” 66(April), 107–109.

Pravasi, S. D. (2014). “Chlorobenzene A2 - Wexler, Philip BT - Encyclopedia of Toxicology (Third Edition).” Academic Press, Oxford, 870–873.

Puzyn, T., Haranczyk, M., Suzuki, N., and Sakurai, T. (2010). *Estimating persistence of brominated and chlorinated organic pollutants in air, water, soil, and sediments with the QSPR-based classification scheme. Molecular diversity*.

Rush, J. D., and Bielski, B. H. J. (1994). “Decay of Ferrate(V) in Neutral and Acidic Solutions. A Premix Pulse Radiolysis Study.” *Inorganic Chemistry,* American Chemical Society, 33(24), 5499–5502.

Sedlak, D. L., and Andren, A. W. (1991). “Oxidation of chlorobenzene with Fenton’s reagent.” *Environmental Science & Technology*, American Chemical Society, 25(4), 777–782.

Selli, E., Bianchi, C. L., Pirola, C., Cappelletti, G., and Ragaini, V. (2008). “Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO2 and sonolysis.” *Journal of Hazardous Materials,* 153(3), 1136–1141.

Serra, R. M., Miró, E. E., Bolcatto, P., and Boix, A. V. (2012). "Experimental and theoretical studies about the adsorption of toluene on ZSM5 and mordenite zeolites modified with Cs." *Microporous and Mesoporous Materials*, 147(1), 17–29.

Sharma, V. (2004). *Use of iron(VI) and iron(V) in water and wastewater treatment. Water science and technology : a journal of the International Association on Water Pollution Research*.

Sharma, V. (2007). *Disinfection performance of Fe(VI) in water and wastewater: A review. Water science and technology : a journal of the International Association on Water Pollution Research*.

Sharma, V. K. (2002). "Potassium ferrate(VI): an environmentally friendly oxidant." *Advances in Environmental Research*, 6(2), 143–156.

Sharma, V. K. (2011a). "Oxidation of inorganic contaminants by ferrates (VI, V, and IV)–kinetics and mechanisms: A review." *Journal of Environmental Management*, 92(4), 1051–1073.

Sharma, V. K. (2011b). "Apparatus and Method For Producing Liquid Ferrate." Google Patents.

Sharma, V. K. (2013). "Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism." *Coordination Chemistry Reviews*, 257(2), 495–510.

Sharma, V. K., and Bielski, B. H. J. (1991). "Reactivity of ferrate(VI) and ferrate(V) with amino acids." *Inorganic Chemistry*, American Chemical Society, 30(23), 4306–4310.

Sharma, V. K., Bloom, J. T., and Joshi, V. N. (1998a). "Oxidation of ammonia by ferrate(vi)." *Journal of Environmental Science and Health, Part A*, Taylor & Francis, 33(4), 635–650.

Sharma, V. K., Burnett, C. R., Yngard, R. A., and Cabelli, D. E. (2005a). "Iron(VI) and Iron(V) Oxidation of Copper(I) Cyanide." *Environmental Science & Technology*, American Chemical Society, 39(10), 3849–3854.

Sharma, V. K., Chen, L., and Zboril, R. (2016). "Review on High Valent FeVI (Ferrate): A Sustainable Green Oxidant in Organic Chemistry and Transformation of Pharmaceuticals." *ACS Sustainable Chemistry & Engineering*, American Chemical Society, 4(1), 18–34.

Sharma, V. K., Liu, F., Tolan, S., Sohn, M., Kim, H., and Oturan, M. A. (2013). "Oxidation of β-lactam antibiotics by ferrate(VI)." *Chemical Engineering Journal*, 221, 446–451.

Sharma, V. K., Rivera, W., Joshi, V. N., Millero, F. J., and O'Connor, D. (1999). "Ferrate(VI) Oxidation of Thiourea." *Environmental Science & Technology*, American Chemical Society, 33(15), 2645–2650.

Sharma, V. K., Rivera, W., Smith, J. O., and O'Brien, B. (1998b). "Ferrate(VI) Oxidation of Aqueous Cyanide." *Environmental Science*

& Technology, American Chemical Society, 32(17), 2608–2613.

Sharma, V. K., Zboril, R., and Varma, R. S. (2015). “Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies.” *Accounts of Chemical Research*, American Chemical Society, 48(2), 182–191.

Sharma, V., Kazama, F., Hu, J., and Ray, A. (2005b). *Ferrates (iron(VI) and iron(V)): Environmentally friendly oxidants and disinfectants*. *Journal of water and health*.

Sharma, V., R. Burnett, C., and Millero, F. (2001). *Dissociation constants of the monoprotic ferrate(VI) ion in NaCl media*. *Physical Chemistry Chemical Physics - PHYS CHEM CHEM PHYS*.

Shinde, S. S., Bhosale, C. H., and Rajpure, K. Y. (2012). “Photocatalytic degradation of toluene using sprayed N-doped ZnO thin films in aqueous suspension.” *Journal of Photochemistry and Photobiology B: Biology*, 113, 70–77.

Stupin, D. Y., and Ozernoi, M. I. (1995). *Coprecipitation of {sup 152}Eu with Iron(III) hydroxide formed upon reduction of sodium ferrate(VI) in aqueous medium*. *Radiochemistry*.

Thompson, G. W., Ockerman, L. T., and Schreyer, J. M. (1951). “Preparation and Purification of Potassium Ferrate. VI.” *Journal of the American Chemical Society*, American Chemical Society, 73(3), 1379–1381.

Tiwari, D., and Lee, S.-M. (2011). *Ferrate(VI) in the Treatment of Wastewaters: A New Generation Green Chemical*.

Tomasi, A., Billing, S., Garner, A., Slater, T. F., and Albano, E. (1983). “The metabolism of halothane by hepatocytes: A comparison between free radical spin trapping and lipid peroxidation in relation to cell damage.” *Chemico-Biological Interactions*, 46(3), 353–368.

USEPA. (1988). “National pollutant discharge elimination system.” *Code of Federal Regulations*, (1988).

W. DePierre, J. (2003). *Mammalian Toxicity of Organic Compounds of Bromine and Iodine*. *The Handbook of Environmental Chemistry*.

W. H. O. (2004). *Guidelines for Drinking-water Quality*. Geneva.

Wagner, W. F., Gump, J. R., and Hart, E. N. (1952). “Factors Affecting Stability of Aqueous Potassium Ferrate(VI) Solutions.” *Analytical Chemistry,* American Chemical Society, 24(9), 1497–1498.

Waite, T. D., and Gilbert, M. (1978). “Oxidative destruction of phenol and other organic water residuals by iron (VI) ferrate.” *Journal (Water Pollution Control Federation),* JSTOR, 543–551.

Waite, T. D., and Gray, K. A. (1984). “Oxidation and Coagulation of Wastewater Effluent Utilizing Ferrate (VI) ion.” *Chemistry for Protection of The Environment*, L. Pawlowski, A. J. Verdier, and W. J.

B. T.-S. in E. S. Lacy, eds., Elsevier, 407–420.

Wei, L., and Yong-Mei, L. (2004). “Use of ferrate pre-oxidation in enhancing the treatment of NOM-rich lake waters.” *Water Science and Technology: Water Supply*, 4(4), 121 LP-128.

Wei, Y.-L., Wang, Y.-S., and Liu, C.-H. (2015). “Preparation of Potassium Ferrate from Spent Steel Pickling Liquid.” *Metals*, 5(4), 1770–1787.

Wu, M., Shi, W., Wang, Y., Jiao, Z., Wang, J., Ding, G., and Fu, J. (2009). “Degradation of halogenated benzenes in solution by electron beam irradiation method.” *Environmental Technology*, Taylor & Francis, 30(2), 191–197.

Yang, B., Ying, G.-G., Chen, Z.-F., Zhao, J.-L., Peng, F.-Q., and Chen, X.-W. (2014). “Ferrate(VI) oxidation of tetrabromobisphenol A in comparison with bisphenol A.” *Water Research*, 62, 211–219.

Yang, B., Ying, G.-G., Zhang, L.-J., Zhou, L.-J., Liu, S., and Fang, Y.-X. (2011a). “Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles.” *Water Research*, 45(6), 2261–2269.

Yang, B., Ying, G.-G., Zhao, J.-L., Zhang, L.-J., Fang, Y.-X., and Nghiem, L. D. (2011b). “Oxidation of triclosan by ferrate: Reaction kinetics, products identification and toxicity evaluation.” *Journal of Hazardous Materials*, 186(1), 227–235.

Zhang, L. L., Leng, S. Q., Zhu, R. Y., and Chen, J. M. (2011). “Degradation of chlorobenzene by strain Ralstonia pickettii L2 isolated from a biotrickling filter treating a chlorobenzene-contaminated gas stream." *Applied Microbiology and Biotechnology*, 91(2), 407–415.

Zhang, P., Zhang, G., Dong, J., Fan, M., and Zeng, G. (2012). "Bisphenol A oxidative removal by ferrate (Fe(VI)) under a weak acidic condition." *Separation and Purification Technology*, 84, 46–51.