การเพิ่มประสิทธิภาพการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์และการย่อยสลายทางชีวภาพของสารอันตรายอินทรีย์โดยใช้เฟนตันแบบดั้งเดิมและแบบประยุกต์

นางสาว นวรัตน์ เสริมสัย

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MINERALIZATION AND BIODEGRADABILITY ENHANCEMENT OF HAZARDOUS ORGANIC COMPOUNDS USING CONVENTIONAL AND MODIFIED FENTON'S REAGENTS

Miss Nawarat Sermsai

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นวรัตน์ เสริมสัย : การเพิ่มประสิทธิภาพการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์และการย่อยสลายทางชีวภาพของสารอันตรายอินทรีย์โดยใช้เฟนตันแบบดั้งเดิมและแบบประยุกต์. (MINERALIZATION AND BIODEGRADABILITY ENHANCEMENT OF HAZARDOUS ORGANIC COMPOUNDS USING CONVENTIONAL AND MODIFIED FENTON'S REAGENTS) อ. ที่ปรึกษา: ร ศ.ดร.วันเพ็ญ วิโรจนกูฏ, อ.ที่ปรึกษาร่วม: ผศ.ดร.เอกลักษณ์ คาน 159 หน้า. ISBN 974-17-4193-6.

งานวิจัยนี้ทำการศึกษาการเพิ่มประสิทธิภาพของเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์ และการย่อยสลายทางชีวภาพ ของสารอันตรายอินทรีย์ด้วยปฏิกิริยาเฟนตันแบบดั้งเดิมและแบบประยุกต์ ดัชนีบ่งชี้ความสามารถในการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์ คือ สารอินทรีย์ละลายน้ำ (DOC) และความสามารถในการย่อยสลายทางชีวภาพ คือ อัตราส่วนระหว่างสารอินทรีย์ละลายน้ำที่สามารถย่อยสลายทางชีวภาพต่อสารอินทรีย์ละลายน้ำ (BDOC/DOC) โดยทำการทดลองกับสารอันตรายอินทรีย์ 4 ชนิด ได้แก่ trichloroethene (TCE), 2,4-dichlorophenol (2,4-DCP), 1,4-dioxane (1,4-D) และ 1,2,3-trichloropropane (TCP) ซึ่งสารแต่ละชนิดที่ใช้ในการทดลองทำการศึกษาหาสภาวะที่เหมาะสม ของชนิดของตัวเร่งปฏิกิริยาเหล็ก 3 ชนิด (Fe^{+2}, Fe^{+3} และ Fe^0) อัตราส่วนโดยน้ำหนักของเหล็ก:ไฮโดรเจนเปอร์ออกไซด์ (H_2O_2):DOC และพีเอช เริ่มต้นของการทดลอง ผลการทดลองแสดงให้เห็นว่าสภาวะที่เหมาะสมในการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์ และการย่อยสลายทางชีวภาพของสารชนิดเดียวกัน ไม่จำเป็นต้องเป็นสภาวะเดียวกัน และสารที่ต่างชนิดกันย่อมมีสภาวะที่เหมาะสมต่างกัน อัตราส่วนที่เหมาะสมสำหรับการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์และการย่อยสลายทางชีวภาพ คือ 10:20:1 (Fe^{+2} และ Fe^0) ยกเว้น TCP ซึ่งอัตราส่วนที่เหมาะสม คือ 10:10:1 (Fe^{+2}) พีเอชเริ่มต้นของสารละลายมีผลเล็กน้อยต่อความสามารถในการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์ และความสามารถในการย่อยสลายทางชีวภาพ ระยะเวลาที่ใช้ในการเปลี่ยนสารละลายอินทรีย์ และ การเพิ่มความสามารถในการย่อยสลายทางชีวภาพทั้งหมด ให้ได้มากกว่าร้อยละ 90 คือ 120 นาที และ 60 นาที ตามลำดับ ปฏิกิริยาการเปลี่ยนสารอินทรีย์เป็นสารอนินทรีย์เป็นแบบอันดับที่ 1 (pseudo-first order) และแบบอันดับที่ 2 (second order) ส่วนปฏิกิริยาการย่อยสลายทางชีวภาพ เป็นแบบอันดับศูนย์ (zero order) นอกจากนี้ผลการวิเคราะห์ชนิดสารที่คงเหลืออยู่ในสารละลายที่ผ่านกระบวนการเฟนตันโดยใช้เครื่องวิเคราะห์ GC/MS พบว่า ชนิดของสารที่คงเหลืออยู่ในสารละลายโดยใช้ Fe^0 เป็นตัวเร่งปฏิกิริยาแตกต่างจากใช้ Fe^{+2} และ Fe^{+3} เนื่องจากกลไกการเกิดปฏิกิริยาของเหล็กแต่ละชนิดแตกต่างกัน โดยปฏิกิริยาที่เกิดเมื่อใช้ Fe^0 คือปฏิกิริยารีดักชั่นและออกซิเดชั่น ขณะที่ Fe^{+2} และ Fe^{+3} เกิดปฏิกิริยาออกซิเดชั่นเพียงอย่างเดียว

สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)	ลายมือชื่อนิสิต..............................
ปีการศึกษา 2548	ลายมือชื่ออาจารย์ที่ปรึกษา..............................
	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..............................

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KEY WORD: FENTON/ MINERALIZATION/ BIODEGRADABILITY

NAWARAT SERMSAI: MINERALIZATION AND BIODEGRADABILITY ENHANCEMENT OF HAZARDOUS ORGANIC COMPOUNDS USING CONVENTIONAL AND MODIFIED FENTON'S REAGENTS. THESIS ADVISOR: ASSOC. PROF. WANPEN WIROJANAGUD, Ph.D., THESIS COADVISOR: ASST. PROF. EAKALAK KHAN, Ph.D., 159 pp. ISBN 974-17-4193-6.

Enhancement on mineralization and biodegradability of hazardous organic compounds could be performed by conventional or modified Fenton's reaction. The degree of mineralization was measured by dissolved organic carbon (DOC) while the biodegradability was quantified by biodegradable DOC (BDOC)/DOC ratio. Four hazardous organic compounds were tested including trichloroethene (TCE), 2,4-dichlorophenol (2,4-DCP), 1,4-dioxane (1,4-D) and 1,2,3-trichloropropane (TCP) solutions. Three types of iron catalyst of ferrous ion (Fe^{+2}), ferric ion (Fe^{+3}) and zero-valence iron (Fe^0) were investigated. Three different types of iron:H_2O_2:DOC of 5:10:1, 10:10:1 and 10:20:1 on mass basis and pH of 2, 3 and 4 were tested to identify the conditions that maximized DOC elimination, biodegradability increase and DOC elimination plus the biodegradability increase of water samples. The results showed that the conditions for the highest DOC reduction were not necessary to be the same as the conditions of the largest biodegradability increase. Similarly, the optimum conditions for different compounds solution on mineralization and biodegradability enhancement were not necessary to be the same. Generally, the optimum conditions for combination of DOC elimination and biodegradability increase observed as the ratio of iron (Fe^{+2} and Fe^0): H_2O_2:DOC were10:20:1, except Fe^{+2}:H_2O_2:DOC for TCP as 10:10:1. Initial pH exerted small effect on mineralization and biodegradability of 4 compounds. More than 90% of total DOC reduction and biodegradability increase were almost found in 120 and 60 minutes, respectively. The pseudo-first order and second order were found the best fit for mineralization reaction rate while zero order was considered as the biodegradability reaction rate. The oxidation by-products for each organic compound were identified by GC/MS analysis. The results show that the by-products of Fe^0 in Fenton's reaction were not similar to the by-products of Fe^{+2} and Fe^{+3} according to the different mechanisms as for reduction and oxidation for Fe^0 while only oxidation for Fe^{+2} and Fe^{+3}, respectively.

Field of study Environmental Management (Inter-Department)

Academic year 2005

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Advisor's signature.....W. Wirojanagud.....

Co-advisor's signature.............................

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NOMENCLATURES

AOPs = Advanced oxidation processes

ATSDR = Agency for Toxic Substances and Disease Registry

2,4-DCP= 2,4-Dichlorophenol

BDOC = Biodegradable dissolved organic carbon

COD = Chemical oxygen demand

1,4-D = 1,4-Dioxane

DI = Deionized

DOC = Dissolved organic carbon

Fe^{+2} = Ferrous ion

Fe^{+3} = Ferric ion

Fe^0 = Zero-valent iron/ iron powder

H_2O_2 = Hydrogen peroxide

Mg/l = Milligram/liter

O_3 = Ozone

$OH^\bullet$ = Hydroxyl radical

TCE = Trichloroethene

TCP = 1,2,3-Trichloropropane

TOC = Total organic carbon

US.EPA = United States Environmental Protection Agency

UV = Ultraviolet

WHO = World Health Organization

CHAPTER I
INTRODUCTION

1.1 Background

Advanced oxidation processes (AOPs) have been used to degrade many biorefractory organic pollutants. They are considered an effective method for wastewater treatment due to generation of hydroxyl radical ($OH^{\bullet}$), a powerful and nonselective oxidant, which acts rapidly with most organic compounds. Various advanced oxidation processes, such as O_3/UV, O_3/H_2O_2, UV/H_2O_2, Fenton and photo-Fenton, have been applied successfully in wastewater treatment to degrade TCE, 2,4-DCP, 1,4-D and TCP (Adams *et al.,* 1994; Weeks *et al.*, 2000; Viocu *et al.,* 2001; Pera-Titus *et al.*, 2003).

Conventional Fenton reagent, a mixture of hydrogen peroxide and ferrous iron salts, is an attractive AOP method due to the facts that: (1) iron is a highly abundant and non-toxic element, and (2) hydrogen peroxide is easy to handle. Fenton's reagent has been used to degrade many hazardous organic compounds in water such as phenol, chlorinated organic compounds and herbicides (Pignatello, 1992; Teel *et al.,* 2001; Momani *et al.,* 2004). Furthermore, it has been used to reduce the chemical oxygen demand (COD) and total organic carbon (TOC) in wastewater (Lipczynska-Kochany *et al.,* 1995; Safarzadeh *et al.,* 1996; Kang and Hwang, 2000). Fenton has the highest efficiency when the pH is acidic (Kitis *et al.,* 1999; Lu *et al.,* 2001; Yoon *et al.,* 2001). Moreover, Fenton process produces the large amount of iron sludge, which must be disposed. These are limitations of the process.

Modified Fenton reagent is effective in contaminants degradation. Ferric ion (Fe^{+3}) and zero valent iron (Fe^0) employed as the catalysts had been intensively studied (Watts et al., 1993; Khan et al., 1996; Tang and Chen, 1996; and Pignatello 1997) for degrading hazardous organic compounds contaminated in soil. Such processes are based on the standard Fenton's reaction.

Degradation of organic contaminants by Fenton's reaction results in mineralization and biodegradability enhancement. Traditionally, the ratio of biochemical oxygen demand and chemical oxygen demand (BOD/COD) has been used to represent the biodegradability. Several researchers were able to successfully use the ratio to indicate biodegradability increase promoted by AOPs (Gilbert *et al.*, 1987; Chamarro *et al.*, 2000). But the ratio of BOD/COD has some limitations, such as poor precision and low sensitivity for low organic concentration water samples. Khan *et al.* (2005) applied Fenton reagent to degrade low level *p*-nitrophenol. The parameters used to indicate the mineralization and biodegradability are dissolved organic carbon (DOC) and biodegradable DOC (BDOC)/DOC, respectively. BDOC analysis measures the portion of organic carbon that can be mineralized by heterotrophic flora (Huck, 1990) or the portion of DOC that is biodegradable (Khan *et al.*, 1998).

1.2 Motivation/Statement of research problems

Generally, the performance of wastewater treatment is evaluated by the reduction of the contaminants concentration. However, the mineralization and biodegradability increase are considered as for the better indicators than the contaminant concentration as the reaction’s results will present the actual performance of the treatment. In addition, the analysis of mineralization and biodegradability are economical and easier. BOD_5/COD has been used as a parameter to indicate biodegradability for many decades. An alternative novel indicator, BDOC/DOC, which is more accurate and sensitive than BOD_5/COD. Thus, BDOC/DOC has been commonly used in the fields of drinking water and wastewater reclamation.

Volatile organic carbon including Trichloroethene (TCE), 2,4-dichlorophenol (2,4-DCP) 1,4-dioxane (1,4-D) and 1,2,3-trichloropropane (TCP) have been widely used in several industrial processes. Some of these compounds are intermediates in the production of other chemicals. For example, 2,4-DCP and TCP are key intermediates in the production of pesticides and herbicides (WHO, 2003). 1,4-D is formed as a by-product of the chemical processes such as ethylene glycol or ethylene oxide (Popoola, 1992). Moreover, all of these compounds cause adverse health effects. TCE, 2,4-DCP, 1,4-D and TCP are classified by the United States Environmental Protection Agency (US.EPA) as potential human carcinogens.

TCE, 2,4-DCP, 1,4-D and 1,2,3-TCP were the model compounds studied in this resaech. TCE and 2,4-DCP are traditional organic contaminants which have been researched for degradation using different types of Fenton, but no comparison on mineralization and biodegradability enhancement. For 1,4-D and TCP are emerging contaminants, the Fenton study on these two compounds is not yet known. Therefore, this study focused on mineralization and biodegradability enhancement of such four compounds using conventional and modified Fenton's reagent.

1.3 Objectives

The main objective of this study is to compare the mineralization and biodegradability enhancement performances of traditional and modified Fenton's reagent for the degradation TCE, 2,4-DCP, 1,4-D, and TCP. The specific objectives are:

1. To examine the optimal iron and hydrogen peroxide doses, pH, and reaction time for each type of Fenton's reagent for the comparison of the performances.
2. To identify the oxidation by products.

1.4 Hypotheses

1. Fenton reagents with different types of iron provide different efficiencies in mineralizing and enhancing biodegradability of TCE, 2,4-DCP, 1,4-D and TCP.
2. The degrees of mineralization and biodegradability enhancement of TCE, 2,4-DCP, 1,4-D and TCP by Fenton reagents depend on either an initial pH or the amounts of H_2O_2 and iron.

1.5 Scopes of study

1. Properties and previous studies on the Fenton process and/or other AOPs of the four compounds are reviewed. The information is gathered from related publications.
2. A batch laboratory-scale experimental setup is constructed.
3. The optimum iron concentration, hydrogen peroxide dose, pH and reaction time are examined.
4. The by-products from oxidation process for each contaminant are investigated.
5. The experimental results are analyzed to determine the mineralization and biodegradability enhancement of the contaminants and degradation by-products.

CHAPTER II
LITERATURE REVIEW

2.1 General description on the compounds studied

2.1.1 Trichloroethene or -ethylene

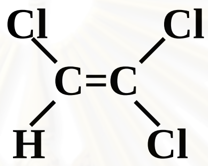


Figure 2.1 Chemical structure of TCE

Trichloroethene or -ethylene is a man made chemical that does not occur naturally in the environment. It is now used as an industrial cleaner (solvent) to remove grease from metal parts and also often used in making other chemicals. TCE can be found in many consumer products, including typewriter correction fluid, paint removers, adhesives, and spot removers. TCE is a non-flammable and colorless liquid at room temperature with somewhat sweet odor and sweet burning taste. It is carcinogenic and often recalcitrant in the environment because of low water solubility and higher density than water. As a result, it is normally found as dense non-aqueous phase liquids in aquifers of contaminated sites. Moreover, it partitions to the atmosphere from surface water rapidly. Although TCE evaporates easily, it can persist in soil and in groundwater. It can break down under high heat and alkaline conditions and forms dichloroacetylene and phosgene.

TCE enters to the human body not only by inhalation and ingestion but also dermal contact. In the body, it may break down into dichloroacetic acid, trichloroacetic acid, chloral hydrate and 2-chloroacetaldehyde. These products have been shown to be toxic to animals and probably toxic to humans (ATSDR, 1997; CLU-IN, 2005)

2.1.2 2,4-Dichlorophenol

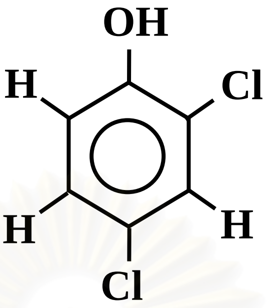


Figure 2.2 Chemical structure of 2,4-DCP

22,4-Dichlorophenol is a key intermediate in the synthesis of chloride-based herbicides, such as 2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy) propionic acid. It is also found near chlorocarbon factories. 2,4-DCP is white solid at room temperature but melts at low temperatures. It is soluble in ethyl alcohol, carbon tetrachloride, ethyl ether, benzene, and chloroform.

2,4-DCP is likely to partition to the air because of its high volatility (ATSDR, 1999). Once in the air, sunlight helps destroy it and rain washes it out of the air. It sticks to soils and to sediments at the bottom of lakes, rivers, or streams. Moreover, it causes a number of adverse health effects. Not only the inhalation of dust containing 2,4-DCP can irritate the respiratory tract but also the detrimental effects on kidneys, liver and blood-forming organs are known.

2.1.3 1,4-Dioxane

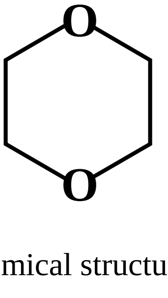


Figure 2.3 Chemical structure of 1,4-D

1,4-Dioxane is clear liquid that dissolves in water at all concentrations. It presents in the industrial stream as a solvent in the manufacture of chemicals such as detergents, lacquers, and varnishes (US.EPA, 1995). It has also been used as a laboratory reagent, a chemical intermediate, a part of a polymerization catalyst and an extraction medium of animal and vegetable oils. In addition, trace levels are also found in cosmetics and shampoos (ATSDR, 2004).

1,4-D is classified as toxic chemical and hazardous pollutant by US.EPA. It is suspected carcinogen. Moreover, it is essentially nonbiodegradable by microorganisms under conditions typically occurring in conventional industrial biotreatment processes. It has a very high water solubility, low partition coefficient and vapor pressure (US.EPA, 1995). In water, it is stable and is not easily degradable. In soil, 1,4-D does not stick to soil particles, so it can move from soil into groundwater. In air, it is presented as a vapor. It does not react directly with sunlight. However, in the atmosphere, sunlight can promote the formation of reactive compounds that can react with 1,4-D resulting in different compounds.

2.1.4 1,2,3-Trichloropropane

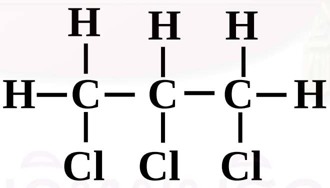


Figure 2.4 Chemical structure TCP

1,2,3-Trichloropropane is a synthetic chemical that has been used as an industrial solvent and extractive agent. Common uses have included a paint remover, a varnish remover, a cleaning and degreasing agent and a cleaning and maintenance reagent. In addition, it is used as a chemical intermediate, in the production of polysulfone liquid polymers and dichloropropene, synthesis of hexafluoropropylene, and as a crosslinking agent in the synthesis of polysulfides.

TCP is clear, colorless, strong odor and heavy liquid. It evaporates almost as fast as water does at normal temperatures. It is soluble in ethanol, ether, and chloroform, and slightly soluble in water. It can dissolve several substances, such as oils, fats and waxes, and reacts with active metals, strong caustics and oxidizers (WHO, 2003; ATSDR, 1992). TCP in the air will break down by sunlight. Most of the TCP that is released to the air will disappear in a month. Half of TCP in water will evaporate into the air within hours or several days. Very little of it will stick to the soil at the bottom of rivers, lakes, or ponds, and very little of it will be expected to concentrate in fish or other seafood. The prominent toxic effect is irritation of mucosa of eyes and nose and liver and kidney damage. Moreover, it is an irritant to mucous membranes.

Table 1 summarizes the physical and chemical properties of the above four compounds.

Table 2.1 Physical and chemical properties of the studied compounds

Property	TCE	2,4-DCP	1,4-D	1,2,3-TCP
Molecular formula	C_2HCl_3 [a]	$C_6H_4OCl_2$ [b]	$C_4H_8O_2$ [c]	$C_3H_5Cl_3$ [d]
Molecular weight	131.40 [a]	163.00 [b]	88.11 [c]	147.43 [d]
Melting point	-87.1°C [a]	45°C [b]	11.8 °C [c]	-14.7 °C [d]
Boiling point	86.7°C [a]	210°C [b]	101.1 °C [c]	156 °C [d]
Density	**1.465 g/ml [a]	* 1.383 g/ml [b]	** 1.033 g/ml [c]	** 1.38 g/ml [d]
Water Solubility	** 1.366 g/l [a]	* 4.5 g/l	Miscible [c]	** 1.75 g/l [d]
Partition coefficients:				
- Log K_{ow}	2.42 [a]	3.2 [b]	-0.27 [c]	1.98 [d]
- Log K_{oc}	2.03-2.66 [a]	2.42-3.98 [b]	1.23 [c]	1.99 [d]
Vapor pressure	* 74 mmHg [a]	* 0.14 mmHg [b]	* 38.1 mmHg [c]	* 3.11 mmHg [d]
Henry's law constant	* 0.011 atm-m^3/mol [a]	* 4.30x10^{-6} atm-m^3/mol [b]	* 4.80x10^{-6} atm-m^3/mol [c]	* 3.17x10^{-6} atm-m^3/mol [d]

*At 25°C,** At 20°C, As cited in ATSDR ([a]1997, [b]1999 , [c]2004 and [d]1992)

2.2 Applications of AOPs other than Fenton reagents for the degradation of the emerging compounds studied

Adams *et al.* (1994) investigated the use of O_3 and H_2O_2 for the degradation of 1,4-D. The experiments were conducted at near neutral pH with different combinations of O_3 and H_2O_2. When used alone, neither O_3 nor H_2O_2 readily oxidized 1,4-D. However, when used together, O_3 and H_2O_2 effectively degraded 1,4-D with associated increase in the biochemical oxygen demand.

Stefan and Bolton (1998) reported that the degradation kinetics of 1,4-D exposed to UV/H_2O_2 treatment followed first-order kinetics, and 90% reduction in 1,4-D was achieved in 5 min. They also observed a concomitant production of a variety of intermediates including aldehydes, organic acids, and the mono- and diformate esters of ethylene glycol. The pH of the solution also decreased from 5 to 3 during treatment, due to the formation of organic acids.

Viocu *et al.* (2001) found that the oxidation products of TCP were $CH_2ClC(O)CH_2Cl$, and small amounts of $HC(O)Cl$ and $CH_2ClC(O)Cl$ using Fourier transform infrared-smog chamber systems.

2.3 Fenton reagent and modified Fenton reagent

2.3.1 Principle

Fenton oxidation was first observed by Fenton in 1894. Its process is known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds (CO_2, water and inorganic salts). Moreover, it can reduce the COD and total organic carbon (TOC) contents in wastewater (Lipczynska-Kochany *et al.*, 1995; Safarzadeh *et al.*, 1996; Kang *et al.*, 2000).

Fenton's reagent is the combination of H_2O_2 and Fe^{+2} ion. As shown in equation (2.1), the reaction between H_2O_2 and Fe^{+2} ion generates the hydroxyl radicals ($OH^{\bullet}$), which has a powerful oxidizing ability to non-selectively degrade toxic contaminants.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{2.1}$$

$$OH^{\bullet} + \text{organic} \longrightarrow \text{products} \tag{2.2}$$

Moreover, the newly formed ferric ion (Fe^{3+}) may catalyst H_2O_2, causing it to be decomposed into water and oxygen. Ferrous ion and radical are also formed in the reactions. The reactions are as shown in equation (2.3) to (2.6). The reaction of H_2O_2 with Fe^{+3} is referred to as a Fenton-like reaction.

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{+2} + H^{+} \tag{2.3}$$

$$Fe\text{-}OOH^{+2} \longrightarrow OH_2^{\bullet} + Fe^{+2} \tag{2.4}$$

$$Fe^{+2} + OH_2^{\bullet} \longrightarrow Fe^{+3} + OH_2^{-} \tag{2.5}$$

$$Fe^{+3} + OH_2^{\bullet} \longrightarrow Fe^{+2} + O_2 + H^{+} \tag{2.6}$$

Hydrogen peroxide and Fe^{+2} concentrations are the key parameter in Fenton's oxidation. The decomposition of organic contaminants increased with the increasing of H_2O_2 and Fe^{+2} (Lu *et al.*, 1999). In contrast, excess amount of H_2O_2 and Fe^{+2} act as a $OH^{\bullet}$ scavenger (Casero *et al.*, 1997) as shown in the following equations:

$$OH^{\bullet} + H_2O_2 \longrightarrow H_2O + OH_2^{\bullet} \tag{2.7}$$

$$OH^{\bullet} + Fe^{+2} \longrightarrow OH^{-} + Fe^{+3} \tag{2.8}$$

$$2Fe^{+2} + H_2O_2 + 2H^{+} \longrightarrow 2Fe^{+3} + 2H_2O \tag{2.9}$$

Equation (2.9) suggests that the presence of H^{+} is required in the decomposition of H_2O_2. The hydroxyl radical generation is enhanced at low pH. Previous Fenton studies have shown that acidic pH level between 2 to 4 is usually optimum for Fenton's oxidation (Sedlak *et al.*, 1991; Tang *et al.*, 1996; Kwon *et al.*, 1999 and Lu *et al.*, 1999). At the solution pH values above 4, the degradation of the target organic compound may decrease due to the precipitation of Fe^{+2} (Faust and Hoigne, 1990).

Moreover, hydroxyl radicals are scavenged by inorganic ions, such as $CO_3^{\,2-}$, HCO_3^{-}, $PO_4^{\,3-}$, and Cl^{-}, as indicated in equations (2.10) to (2.13). Hydroxyl radical scavengers presented in many effluents can drastically reduce the efficiency of pollutant oxidation in direct proportion to their concentrations.

$$OH^{\bullet} + HCO_3^{-} \longrightarrow OH^{-} + HCO_3^{\bullet} \qquad (2.10)$$

$$OH^{\bullet} + CO_3^{2-} \longrightarrow OH^{-} + HCO_3^{-\bullet} \qquad (2.11)$$

$$OH^{\bullet} + PO_4^{3-} \longrightarrow OH^{-} + HPO_4^{2-\bullet} \qquad (2.12)$$

$$OH^{\bullet} + Cl^{-} \longrightarrow OH^{-} + Cl^{\bullet} \qquad (2.13)$$

Zero-valent iron (Fe^0) can be used as a source of Fe^{+2} catalyst in Fenton's oxidation process [equation (2.14)]. As Fe^0 corrodes, ferrous ions are released, coupled with the production of two electrons. The electrons promotion will be captured by other species present in the solution [equation (2.15)]. This reaction provides the basis for reductive dehalogenation. Since the solution present with Fe^{+2}, the reaction system will be shifted to Fenton's oxidation, once the H_2O_2 is dosed into the system.

$$Fe^{0} \longrightarrow Fe^{+2} + 2e^{-} \qquad (2.14)$$

$$RX + 2e^{-} + H^{+} \longrightarrow RH + X^{-} \qquad (2.15)$$

2.3.2 Applications of Fenton reagent and modified Fenton reagents for the degradation of organic contaminants other than the compounds studied

Pignatello (1992) focused on the mineralization of the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5- trichlorophenoxyacetic acid (2,4,5-T) by using Fe^{3+}/H_2O_2. pH of the solution was an important factor of herbicide transformation by Fe^{3+}/H_2O_2 with the optimum pH of 2.7-2.8. The methanol or chloride due to scavenging of the active oxidant and the sulfate due to complexation of Fe^{+3}, were the inhibiting substances for this reaction. The corresponding polychlorophenol was an intermediate. Dechlorination of 0.1 mM herbicide was rapid and quantitative, and conversed to CO_2 in the range of about 40-70%. The irradiation of visible light containing a small UV component was an effective accelerating factor for the mineralization of herbicides.

Sun and Pignatello (1993) studied the photoenhancement of Fenton-type ($Fe^{3+} + H_2O_2$) oxidation of 2,4-dichlorophenoxyacetic acid in the near-UV. To treat waste, $Fe^{3+}/H_2O_2/UV$ systems were investigated. Hydroxyl radical reactions mainly resulted in dechlorination and conversion of the first 40% of ring and carboxy carbon of 2,4-D to CO_2. After Photolysis/decarboxylation of Fe (III) complexes of degradation, the remaining 60% of carbon mineralization was intermediates. One of these intermediates was oxalic. The results indicated that the overall reaction used dioxygen which accelerates carbon mineralization.

Watts *et al.* (1993) investigated the using of the standard Fenton's reagent procedure, sequential addition of Fe^{+2} and H_2O_2, and a goethite (α-FeOOH)-H_2O_2 system to treat silica sand contaminated with pentachlorophenol (PCP). The results showed that the standard Fenton's procedure could not effectively degraded 10 mg/kg or 250 mg/kg particulate and sorbed PCP in silica sand, but was effective in degrading 10 mg/L soluble PCP. Particulate and sorbed PCP in silica sand was degraded by sequential addition of Fe^{+2}, but high concentration of H_2O_2. In this study, the best system for PCP degradation was found at the H_2O_2-goethite system. And the most efficient mechanism for the catalyzed hydrogen peroxide treatment of contaminated soils may be the iron oxyhydroxide fractions of the soil matrix catalyze Fenton-like reactions, and that these mineral-catalyzed reactions.

Khan *et al.* (1996) studied the Fenton-like reactions by using the iron oxyhydroxide goethite (α-FeOOH) as the sole source of the iron catalyst to treat perchloroethylene (PCE). The results showed that, within 96 hours, perchloroethylene was effectively degraded with the most efficient treatment stoichiometric amount of 0.15 mM of H_2O_2 at pH of 3. The degree of degradation using heterogeneous catalysis was also determined with an equivalent concentration of soluble iron. Up to 94% of the PCE was degraded within the first 24 hr. This modified Fenton's process with the concentration of 2 mM of H_2O_2 at pH of 3 could degraded 5 mg/l of PCE to 0.20 mg/l of PCE in natural subsurface materials after 96 hours.

Tang and Chen (1996) studied the degradation mechanism of H_2O_2/Fe^0 on Reactive Red 120, Direct Blue 160, and Acid Blue 40 removal. Fe^0 was added a few minutes before adding H_2O_2. They reported the H_2O_2/ Fe^0 system being effective and outperforming the conventional Fenton’s reagent system. The decreasing order of decolorization was Acid Blue 40 > Reactive Red 120 > Direct Blue when the initial dye concentration was not greater than 75 mg/l. The initial oxidation rates based on pseudo first order kinetics were reported.

Beltran *et al.* (1997) investigated the effects of concentrations of Fe^{+2} and H_2O_2 and pH on the degradation of polynuclear aromatic hydrocarbons subjected to Fenton degradation. The results showed that the oxidation rate of Fenton reagent is higher than those from other AOPs involving O_3, UV radiation and H_2O_2. They also reported that the optimal concentrations of H_2O_2 and Fe^{+2} were 10^{-3} M and $7x10^{-5}$ M, respectively.

Watts *et al*. (1997) investigated the oxidation of 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene sorbed on hematite (α-Fe2O3), the iron catalyst. Partitioning of the chlorobenzenes onto the hematite was reported and the sorbed state of the chlorobenzenes was determined. After desorption measurements, A function of chlorine substitution resulted in the rate of chlorobenzene desorption decreased. The desorption of 1,3,5- trichlorobenzene, 1,2.3,4-tetrachlorobenzene, and pentachlorobenzene had the first-order rate constants of 0.091,0.051, and 0.029 hr^{-1}, respectively. H_2O_2 concentrations ranging from 0.1 to 5% were used to treat Hematite-chlorobenzene slurries. Using H_2O_2 concentrations not more than 1% resulted in the degradation of 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene proceeded at rates less than their corresponding rates of desorption. These results suggested that the desorption controlled the rates of oxidation. The degradation rates of the three lower chlorobenzenes using H_2O_2 concentrations not more than 2% exceeded the rates of desorption. It can be suggested that the oxidation was occurred, at least in part, in the sorbed state. While the concentration of H_2O_2 less than 5% was used, hexachlorobenzene was not degraded. In all of the hematite-catalyzed systems, hydroxyl radical generation rates were not significantly changed according to the surface catalysis mechanisms were saturated with respect to H_2O_2, even at the lowest concentration of H_2O_2. The experimental results also showed that the rates of mineral-catalyzed H_2O_2 oxidations were significantly affected by sorption, and not more than 2% of H_2O_2 concentration.

Kitis *et al.* (1998) examined the feasibility and degradation efficiency of Fenton reagent on nonylphenol ethoxylates (NPEs), polypropylene glycol (PPG) and ethylene oxide/propylene oxide (EO/PO) block copolymers removal. The effects of Fe^{+2}/H_2O_2 molar ratio, pH and contact time were monitored. Fenton degradation proceeded rapidly and enhanced the biodegradability of NPEs, PPG and EO/PO block copolymers. Increasing oxidant dosage led to increase both rate and extent of biodegradation for each compound

Lu *et al.* (1999) investigated the Fenton reagent to oxidize dichlorvos. The dichlorvos decomposition in Fenton system was divided into two stages. The first stage was the reaction before 30 seconds in which the decomposition rate of dichlorvos was high; this stage was referred as Fe^{2+}/H_2O_2 reaction. The second stage was the reaction that took place after 30 seconds. The decomposition rate of dichlorvos in this stage was slower; this was Fe^{3+}/H_2O_2 reaction. The optimal pH was around 3 to 4. Increasing amount of hydrogen peroxide or ferrous ions increased the decomposition rate of dichlorvos.

Sheng *et al.* (1999) studied the kinetic of surfactant treatment by Fenton process. Anionic alkylbenzene sulfonate (ABS) and linear alkylbenzene sulfonate (LAS) were the surfactants studied. The optimal operating conditions of Fenton’s oxidation process were achieved at 90 mg/l $FeSO_4$, 60 mg/l H_2O_2, 50 minutes contact time and initial pH around 3. Under these conditions, the removal of those surfactants reached 95%. The results were fitted with the first order kinetics and the rate coefficient were reported.

Yeh *et al.* (2003), the Fenton-like oxidation of trichloroethylene (TCE) existing as DNAPL in natural silica sand (Fe =0.04 g/Kg) and the sand from an aquifer (Fe =2.01 g/Kg) was investigated in this study. To evaluate reactions between oxidant and TCE DNAPL, the batch experiments were organized with constant pH. And to assess dynamics of TCE and H_2O_2 during the oxidation, the column experiments were tested. In batch experiments, the results showed that mineral-catalyzed Fenton-like reaction directly oxidized TCE in non-aqueous liquid. In the column experiment, after passing 7 pore volumes (PVs) of 1.5 and 3% H_2O_2 solution, the remaining TCE in aquifer sand column was 12.0 and 2.6% of the initial added, respectively. While remaining TCE in silica sand column was 28.4% after passing 7 pore volumes 3% H_2O_2 solution. The amount of TCE in column and effluent showed the direct oxidation of TCE DNAPL occurring and solubilization of TCE DNAPL increased as the results from size reduction of DNAPL droplets.

Bergendahl and Thies (2004) investigated Fenton oxidation of MTBE using zero-valent iron as the source of catalytic Fe^{+2}. MTBE was degraded over 99% within 10 minutes. The second order rate constants for MTBE degradation were $1.9x10^8$ $M^{-1}s^{-1}$ at pH 7 and $4.4x10^8$ $M^{-1}s^{-1}$ at pH 4.

Burbano *et al.* (2005) reported the degradation of MTBE by Fenton oxidation. They found that the majority of MTBE degradation and generation of intermediates occurred during the initial phase which Fenton reaction occurred. The oxidation reaction followed pseudo-first order kinetics. The subsequent phase was controlled by Fenton-like process and had a negligible contribution to the overall degradation. The best result of MTBE degradation was observed at acidic experiment, and there was no significant difference in results at pH 3 and 5.

Hsueh *et al.* (2005) studied Fenton and Fenton-like degradation of azo dyes, namely Red MX-5B, Reactive Black 5 and Orange G. Both systems removed the color of these azo dyes completely. The optimum pH of both systems was about 2.5-3. For the Fenton-like system, increasing ferric sulfate dose enhanced the degradation of Red MX-5B. The optimum H_2O_2 concentration was about 200 mg/l for 0.1 mM Red MX-5B.

Khan *et al.* (2005) investigated the mineralization and biodegradability enhancement of low level *p*-nitrophenol in water using Fenton reagent. The results showed that Fe^{+2}:H_2O_2:DOC of *p*-nitrophenol ratio of 10:10:1 (mass basis) and pH 4 are the best conditions for maximizing a combination of DOC elimination and biodegradability increase. Under the optimal condition, the biodegradability was enhanced from 8% to 80%. More than 95% of DOC removal and BDOC formation was observed in the first 10 minutes of the reaction time.

2.3.3 Applications of Fenton reagent and modified Fenton reagents for the degradation of the compounds studied

Klecka and Gonsior (1986) used the combination of H_2O_2 and Fe^{+2}, Fenton's reagent, to degrade 1,4-D. They observed that 1,4-D was reduced by 97% after 10 hours of reaction at a 12:1 ratio of H_2O_2 to 1,4-D. 1,4-D concentration? Write a bit more on this study.

Tang and Huang (1996) developed the kinetic model of trichloroethylene (TCE) oxidation by Fenton's reagent based upon transition state theory. It was assumed that hydroxylated active complexes were the transition state after hydroxyl radicals have reacted with the organic compound. Because of the extremely high reactivity of both hydroxyl radicals and the active complexes, their steady-state concentration was assumed constant in developing the kinetic model. The developed model revealed that Fenton oxidation was the first order with respect to the organic concentration. The degree of oxidation relied on the dosage of H_2O_2 and Fe^{2+}. Neither H_2O_2 nor Fe^{2+} of them should be overdosed if the maximal reaction rate was reached because both of substances can also react with hydroxyl radicals. Three different chloroethylenes and chloroethane were used in the experiments to obtain the rate constants. The results indicated that the model could be used only for unsaturated aliphatic compounds such as TCE.

Tang and Huang (1997) studied the stoichiometry of Fenton's reagent in the oxidation of dichloroethylene (DCE), trichloroethylene (TCE), tetrachloroethylene (tetra-CE), and dichloroethane (DCEA). The stoichiometric ratio between H_2O_2 and Fe^{2+} was 11, while optimal ratio reported in the experiments was 5-11 at an optimal pH of 3.5. The quantity of H_2O_2 required to remove the organic compounds and the accumulation of Cl^- ion released depend on the initial organic concentration. The amount of H_2O_2 required for a certain percent removal ranks in the order of TCE < tetra-CE < DCE However, the amount of Cl^- ion detected at a constant concentration of H_2O_2 ranks in the order DCE < TCE < tetra-CE.

Raquel and José (2000) investigated the photo-Fenton process using potassium ferrioxalate in the degradation of organochloride compounds. The dichloroacetic acid (DCA) was used as a compound sample to study the influence of parameters such as hydrogen peroxide and ferrioxalate concentrations and initial pH under black-light lamp irradiation. An upflow annular photoreactor, operating in recirculating mode was utilized during photodegradation experiments with artificial light. To evaluate the photodegradation reaction, the amount of the release of chloride ions was measured at the optimum pH in the range of 2.5-2.8. The concentration of DCA decreased with increasing concentrations of H_2O_2 and potassium ferrioxalate, reaching a steady state after the addition of 6 and 1.5 mM/l of those reagents, respectively.

Weeks *et al.* (2000) applied Fenton's reaction for the degradation of TCE. This study was conducted in aqueous and soil slurry systems. In aqueous systems, higher concentrations of H_2O_2 and Fe^{+2} led to faster TCE degradation. The optimal ratio of H_2O_2:Fe^{+2}:TCE while minimizing H_2O_2 and cost was 19:1:1 molar ratio. In soil slurries with a high fraction of organic carbon (f_{oc}), a portion of the soluble iron tended to sorb to soil organics and/or soil particles. A f_{oc} of soil slurries up to approximately 1% and soil:water ratio of 1:5 (weight ratio) required about 10 times of the amount of H_2O_2 required in the aqueous solutions.

Chen *et al.* (2001) examined the Fenton's oxidation of TCE in groundwater and soil slurries via batch and column experiments. The results showed that under batch experiment conditions and pH of 3, Fenton's reagent was able to oxidize 93-100% and 98-100% (by weight) of dissolved TCE in groundwater and TCE in soil slurries, respectively. Moreover, Fenton's reagent was able to completely dechlorinate the aqueous-phase TCE with and without the presence of soil and no volatile organic compounds intermediates and by-products were found in the oxidation process. Fenton's reagent completely oxidized the dissolved phase TCE in the soil column experiment.

Teel *et al.* (2001) used two mineral-catalyzed modified Fenton's reaction, a standard Fenton's reaction and a modified soluble iron Fenton's reaction, to degrade TCE. The standard Fenton's system provided 78% degradation of TCE while the modified soluble iron system achieved 91% TCE degradation under the same. Over 99% TCE degradation was found in the pH of 3 goethite system.

Chamarro *et al.* (2001) used Fenton's reagent to enhance biodegradability of organic compounds, such as formic acid, 4-chlorophenol, 2,4-DCP, phenol and nitrobenzene. The ratio of BOD_5/COD was used as a parameter of biodegradability. Increasing H_2O_2 dose caused TOC reduction and biodegradability increase. The factors affecting the rate of Fenton's reaction were peroxide dose and iron concentration

Pera-Titus *et al.* (2003) summarized the main aspects dealing with the degradation and mineralization of chlorophenols (CPs) by means of AOPs. They found that the most effective method for the treatment of aqueous solution containing CPs was ozonation. However, AOPs based on H_2O_2 (Fenton, photo-Fenton, and

H_2O_2-UV) were reported to achieve the CPs degradation in shorter time. For tetrachlorophenol degradation, ozonation, the combination O_3/UV and photo-Fenton techniques were reported to achieve high reaction kinetic rates. On the other hand, the photo-Fenton process was suitable for treatment of DCP.

Momani *et al.* (2004) investigated the degradation of 2,4-DCP by using different AOPs (UV, UV/H_2O_2, Fenton and photo-Fenton). The results showed that the combination of Fenton with UV process was the most efficient for 2,4-DCP elimination. In 60 min of the reaction, 100 mg/l of 2,4-DCP were completely removed at 75 mg/l of H_2O_2 and 10 mg/l of Fe^{2+}. At these conditions, the first-order kinetic constant was 0.057 min^{-1}. On the other hand, Fenton reaction required 100 mg/l of H_2O_2 and 10 mg/l of Fe^{2+} to achieve total 2,4-DCP removal in 60 min. UV radiation alone and the combinations of UV with H_2O_2 slightly degraded 2,4-DCP. The degradation rate was influenced by many factors, such as initial H_2O_2 concentration, initial iron concentration, pH and temperature.

Chu *et al.* (2005) studied the degradation of 2,4-DCP by the photo Fenton-like. They found that the reaction kinetics of 2,4-DCP in photo Fenton-like system depended on the initial Fe^{+3} concentration. A pseudo first-order kinetic was observed at a low concentration of Fe^{+3} while at a higher concentration of Fe^{+3}, non-conventional kinetic applied. The intermediates that were identified were chlorohydroquinone (CHQ), 4-chlorocatechol, 2-chloro-1,4-benzoquinone, 3,5-dichlorocatechol, 2,4-dichlororesorcinol, 4,6-dichlororesorcinol and 3,5-dichloro-2-hydroxy-1,4-benzoquinone.

CHAPTER III

METHODOLOGY

3.1 Contaminant solution preparation

Analytical grade solutions of TCE, 2,4-DCP, 1,4-D and 1,2,3-TCP (Sigma Aldrich) were diluted with deionized (DI) water to prepare the contaminant solutions. The contaminant concentrations of the diluted solutions were 20 mg/l. All the diluted solutions were used in the Fenton's and modified Fenton's oxidation experiments immediately after their preparations.

3.2 Experimental procedure

The experiments were divided into 3 groups according to the types of Fenton's reagent:

1. Ferrous ion (Fe^{+2})
2. Ferric ion (Fe^{+3})
3. Zero valent iron (Fe^0)

The experiments were started with the concentration of TCE, 2,4-DCP, 1,4-D and TCE of 20 mg/l. Three different Fe:H_2O_2:DOC of 5:10:1, 10:10:1 (Khan *et al.*, 2005), and 10:20:1 (mass basis) were applied to examine the effect of the initial concentration of H_2O_2 and iron on the mineralization and biodegradability. The pH values were varied as 2, 3 and 4. The selection of these pH values was based on the optimum pH range of 2-4 reported in previous studies for Fenton's degradation of various organic contaminants (Pignatello, 1992; Tang and Huang, 1996; Kwon *et al.*, 1999; and Lu *et al.*, 1999). The effect of reaction time on mineralization and biodegradability increase was also determined by taking samples at reaction time of 5, 15, 30, 60, 120, 180 and 240 minutes.

Experimental procedure – All the solutions with the same amount of contaminants were prepared in the bottle and then the initial pH were adjusted to the desire level by using either sulfuric acid (Merck, analytical grade) or sodium hydroxide (Merck, analytical grade). First, contaminant solution samples were collected for later DOC measurement. The amounts of ferrous sulfate (Sigma Aldrich, analytical grade) were added into the 250 milliliters glass vials. For the modified Fenton's reagents, ferric chloride (Sigma Aldrich, analytical grade) or iron powder (< 10 µm, Merck) was added instead of ferrous sulfate. Next step was the distribution of those solutions into the vials, which were then sealed immediately with aluminum crimp caps with Teflon faced septum. In the case of iron powder, after adding the contaminant solution, the contaminant solution was shaken for about 10 minutes before dosing H_2O_2. Hydrogen peroxide (35% Merck, analytical grade) was then added into the solution using a syringe via the septum. The mixing was provided by a shaker (Ratex, Model DLS) at 180 rpm. All experiments were conducted at room temperature approximately 25°C.

After 5, 30, 60, 120, 180 and 240 minutes, the oxidation was terminated by using 1 ml of sodium thiosulfate solution (Merck, analytical grade) to quench the residual H_2O_2 concentration in the vial. The solution of sodium thiosulfate was prepared by dissolving 23.7 grams of sodium thiosulfate in 100 milliliters DI water to make a concentration of 1.5 M. The DOC, BDOC, and degradation by-products were monitored with reaction time by sacrificing one vial at the final time. Ten milliliters of the mixture from the vial were used for DOC measurement while the remaining was used for measuring BDOC and by-products analysis.

The experimental procedure is shown in the Figure 3.1.

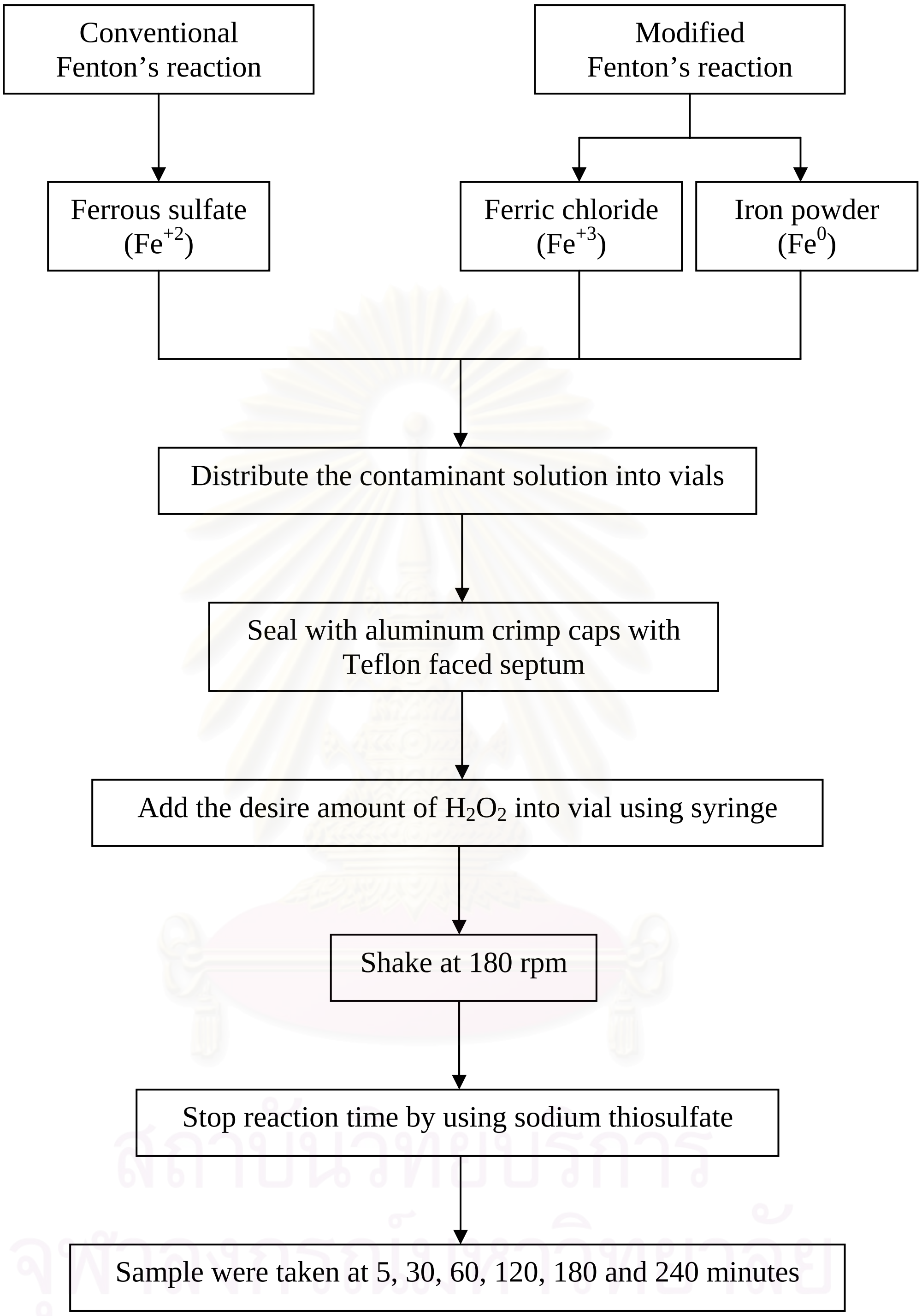


Figure 3.1 The scheme of experiment

3.3 Analytical methods

The mineralization and biodegradability were indicated by DOC and BDOC/DOC ratio, respectively. The DOC was analyzed using a TOC analyzer (Shimadzu, Model 5000A) after the samples were filtered through 0.7µm GF/F.

BDOC was determined following the procedure of Khan *et al.* (1998) as shown in the Figure 4.2. The sample was adjusted to pH of 6.5-7.5 with concentrated sodium hydroxide. Then, the sample was filtered through 0.7µm glass fiber filter (GF/F, Whatman), and measured for DOC. Next, the sample was placed in a 100 milliliters vial. One milliliter of mixed liquor suspended solids was added to the vial. The mixture was incubated at 20°C for 5 days. After the incubation, DOC was measured again. A blank control was included by using DI water as a sample. The difference of DOC reduction of the sample and the blank during the incubation was BDOC.

The degradation by-products were analyzed using a gas chromatograph/mass spectrometer (Thermo Finnigan) with the ZB-5 column (Company). The following experimental conditions during GC/MS analysis:

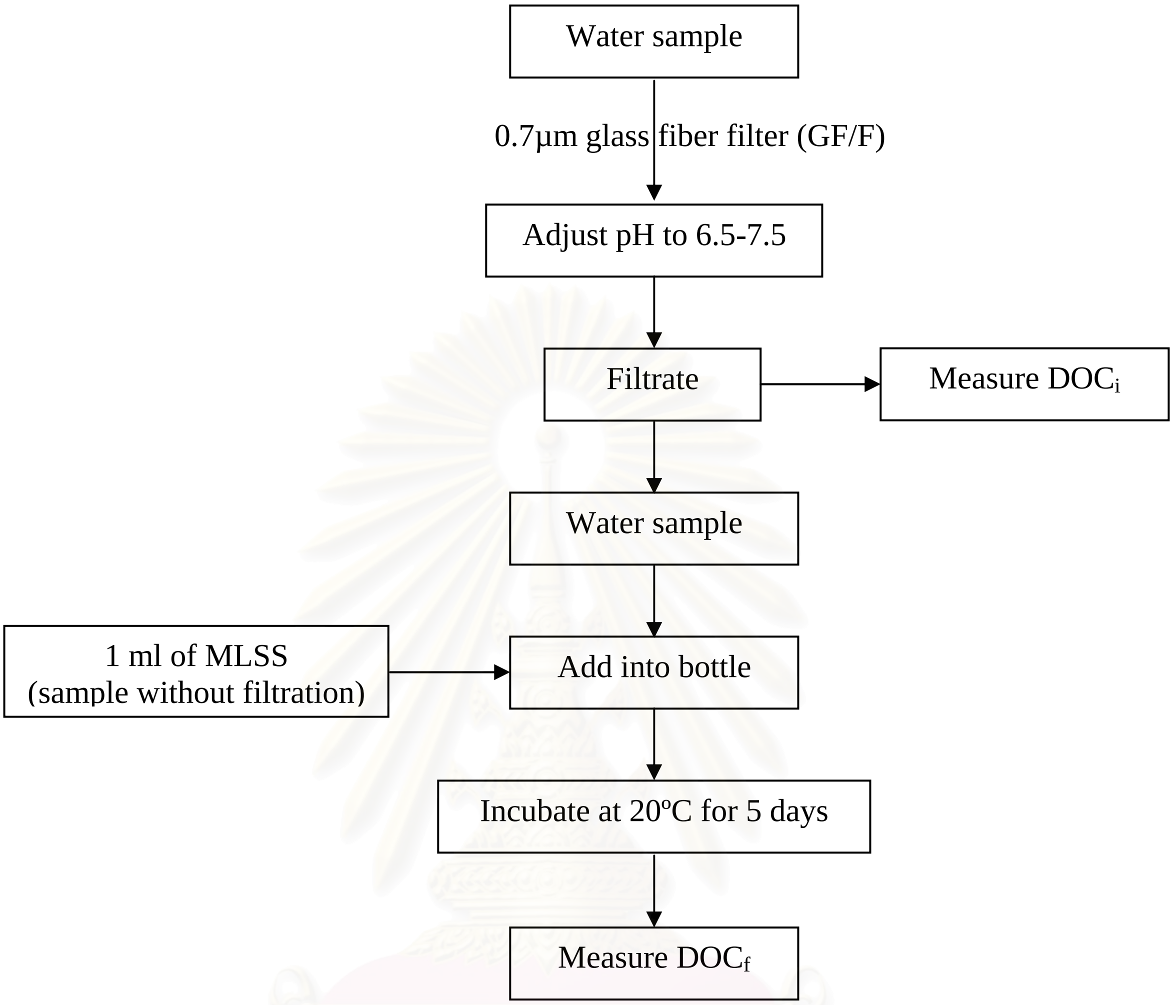
TCE – the injection port and detector temperature were maintained at 250ºC and 300ºC. The initial oven temperature was set at 60ºC programmed at the rate of 10ºC/min to a temperature of 80ºC, then programmed at the rate of 50ºC/min to a final temperature of 200ºC and kept for 4 min.

2,4-DCP – the oven temperature was programmed to increase from 100ºC to 200ºC with the rate of 25ºC/min and held for 5 min. the injection port and detector temperature were maintained at 270ºC and 300ºC.

1,4-D – the initial oven temperature of 60ºC and held for 2 min follows by a temperature ramp of 15ºC/min for 4 min and holding at 120ºC for 1 min. The injection port and detector temperature were maintained at 250ºC and 300ºC.

TCP – the initial temperature of 40ºC and held for 4 min, then programmed at the rate of 10ºC/min to 250ºC and kept for 5 min at 250ºC. The injection port and detector temperature were maintained at 270ºC and 300ºC, respectively.

The pH was measured using a pH meter (Hach, Model EC-30).



BDOC (mg/l) = $DOC_i - DOC_f$

Figure 3.2 The procedure of BDOC

Table 3.1 The matrix of the experiments

Conditions		$Fe^{+2}:H_2O_2:DOC$			$Fe^{+3}:H_2O_2:DOC$			$Fe^{0}:H_2O_2:DOC$		
		5:10:1	10:10:1	10:20:1	5:10:1	10:10:1	10:20:1	5:10:1	10:10:1	10:20:1
TCE	pH=2	*	*	*	*	*	*	*	*	*
	pH=3	*	*	*	*	*	*	*	*	*
	pH=4	*	*	*	*	*	*	*	*	*
2,4-DCP	pH=2	*	*	*	*	*	*	*	*	*
	pH=3	*	*	*	*	*	*	*	*	*
	pH=4	*	*	*	*	*	*	*	*	*
1,4-D	pH=2	*	*	*	*	*	*	*	*	*
	pH=3	*	*	*	*	*	*	*	*	*
	pH=4	*	*	*	*	*	*	*	*	*
TCP	pH=2	*	*	*	*	*	*	*	*	*
	pH=3	*	*	*	*	*	*	*	*	*
	pH=4	*	*	*	*	*	*	*	*	*

Where * = taken sample time 5, 30, 60,120.180 and 240 minutes

CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 Trichloroethene or -ethylene

The initial DOC (DOC_0), BDOC ($BDOC_0$) and biodegradability ($BDOC_0/DOC_0$) of the TCE solutions are shown in Appendix A. The initial DOC ranged from 2.90 mg/l to 3.21 mg/l while the initial BDOC were between 0.04 mg/l and 0.19 mg/l. The initial biodegradability of the sample was low (<0.1). This agrees with the fact that TCE is the biorefractory.

4.1.1 Effects of Fe^{+2}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

The mineralization presented herein is indicated by the normalized DOC. The normalized DOC is DOC at reaction time *t* divided by initial DOC (DOC_t/DOC_0), while the biodegradability increase is defined as ($BDOC_t$-$BDOC_0$)/DOC_0 where $BDOC_t$ is BDOC at reaction time *t*.

Figure 4.1 illustrates the normalized DOC and biodegradability increase of TCE versus reaction time for (a) and (b) Fe^{+2}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+2}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

As shown in Figure 4.1 (a, c and e), the initial pH had a minimal effect on the DOC reduction, as indicated by 48-56%, 43-53% and 39-44% DOC reduction at pH of 3, 4 and 2, respectively. Moreover, increasing of Fe^{+2} concentration was slightly increase of DOC reduction, as shown by increasing of double amount of Fe^{+2}, the DOC reduction was 2% increase. The higher H_2O_2 provided higher DOC elimination due to the production of the large amount of $OH^{\bullet}$. The remaining DOC can be divided into two groups, which are refractory DOC (RDOC) and BDOC. From Figure 4.1 (b, d and f), it could be seen that during 30 minutes, the biodegradability was exponentially increased. A small increase of biodegradability was observed between

30-240 minutes. This is probably because Fenton’s reaction preferentially reacted with simpler DOC that can be easily oxidized to CO_2 during 30 minutes. Slightly effect of pH on biodegradability increase was observed. The biodegradability enhancement at pH of 4 was slightly more than those reactions at pH of 2 and 3. Mineralization of total DOC was 90% observed after 120 minutes, while 90% of total biodegradability increase occurred within 30 minutes of the reaction time.

4.1.2 Effects of Fe^{+3}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.2 shows the normalized DOC and biodegradability increase of TCE versus reaction time for (a) and (b) Fe^{+3}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+3}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4.

According to the reaction between Fe^{+3} and H_2O_2, the Fe^{+2} are formed and then combined with H_2O_2 in the solution. During the reaction, the $OH^{\bullet}$ was produced and rapidly oxidized the contaminant. As presented in Figure 4.2 (a, c and e), a slightly difference of DOC reduction was observed at three initial experimental pHs, as presented by 35-38%, 36-43% and 40-43% at pH of 2, 3 and 4, respectively. The higher Fe^{+3} and H_2O_2 did not influence the increasing of DOC removal. This result is agreed with Casero *et al.*, (1997), they found that the excess amount of H_2O_2 and Fe^{+2} act as $OH^{\bullet}$ scavenger because the $OH^{\bullet}$ reacts with Fe^{+2} and H_2O_2 resulting in the inhibition of oxidation reaction. Then, the increase of Fe^{+3} and H_2O_2 were not necessarily increase DOC elimination. The DOC reduction for all ratios was found between 40% and 45%. Most of DOC reduction took place in 2 hours. The highest decrease of DOC was obtained at pH of 4. From Figure 4.2 (b, d and f), it could be seen that the increase of biodegradability was not dependent on the initial pH and concentration of Fe^{+2} and H_2O_2. Almost 25% biodegradability increase was occurred in all conditions. Approximately 90% of the total biodegradability increase was observed after the reaction time of 60 minutes.

4.1.3 Effects of Fe^0:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.3 presents the normalized DOC and biodegradability increase versus reaction time of TCE for (a) and (b) Fe^0:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^0:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^0:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4.

Due to the fact that the Fe^0 corrodes, Fe^{+2} are released and coupled with the production of two electrons. Fe^{+2} are combined with H_2O_2 to form the Fenton’s reaction. During the Fenton process, the reactive $OH^\bullet$ is generated which is the key of oxidation mechanism. The electrons promotion will be captured by other species present in the solution. As illustrated in Figure 4.3 (a, c and e), the initial pHs of 2, 3 and 4 were slightly effect on the DOC elimination. The increasing of Fe^{+2} and H_2O_2 ratios were not necessarily raised DOC removal. The excess amount of H_2O_2 acts as $OH^\bullet$ scavenger leading to the decreasing of organic compound oxidation. The optimal pH and ratio of Fe^0:H_2O_2:DOC were observed at 3 and 10:10:1, respectively. Figure 4.3 (b, d and f) shows the biodegradability increase, it could be seen that not only the studied pHs but also the concentration of Fe^{+2} and H_2O_2 were insignificantly for enhancement of biodegradability. About 25% biodegradability increase was occurred at all conditions. The biodegradability increased significantly for the first 5 minutes and approximately 95% of the total increase was observed after a reaction time of 30 minutes.

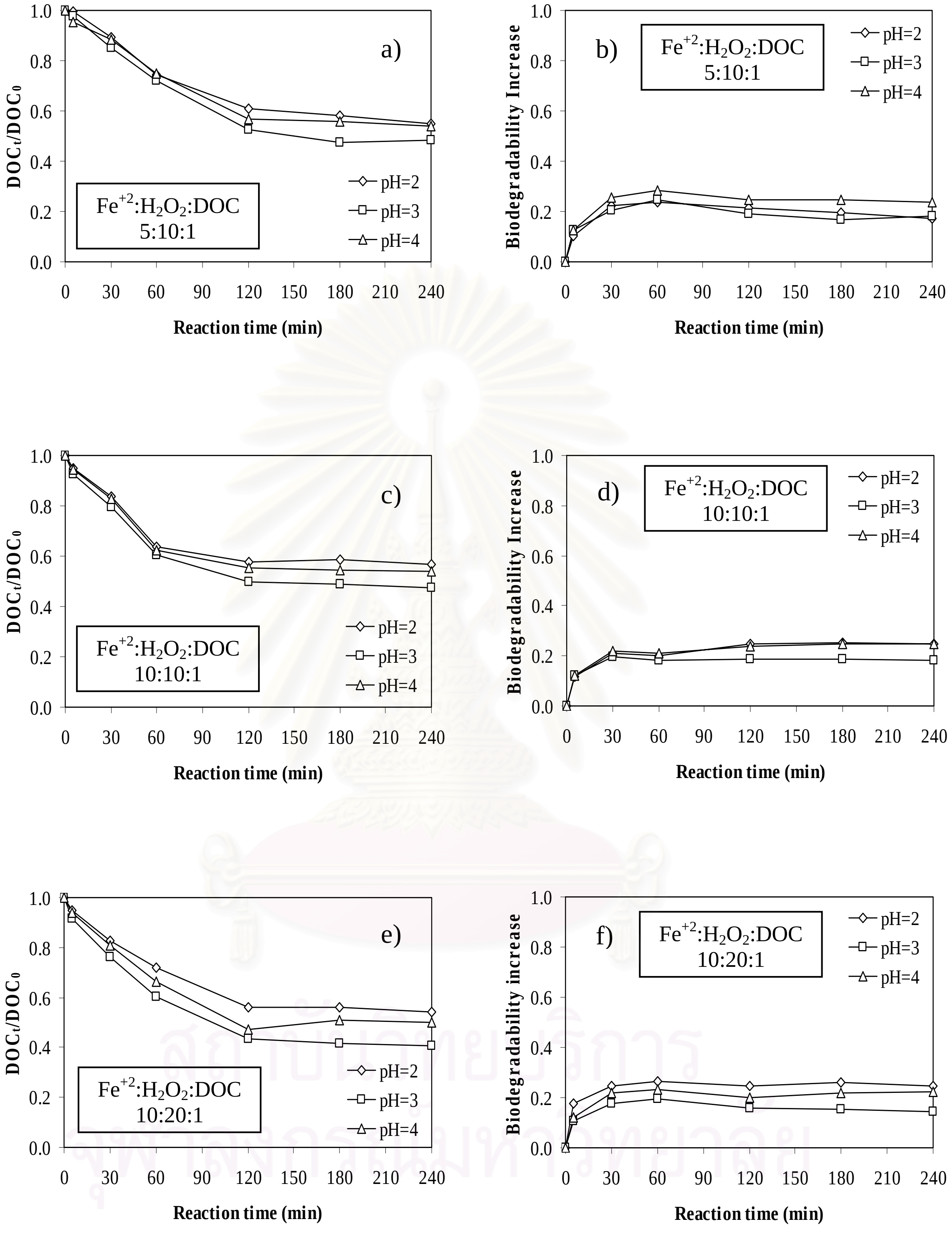


Figure 4.1 Dissolved organic carbon and biodegradability increase of TCE versus reaction time for (a) and (b) Fe^{+2}:H$_2$O$_2$:DOC of 5:10:1; (c) and (d) Fe^{+2}:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

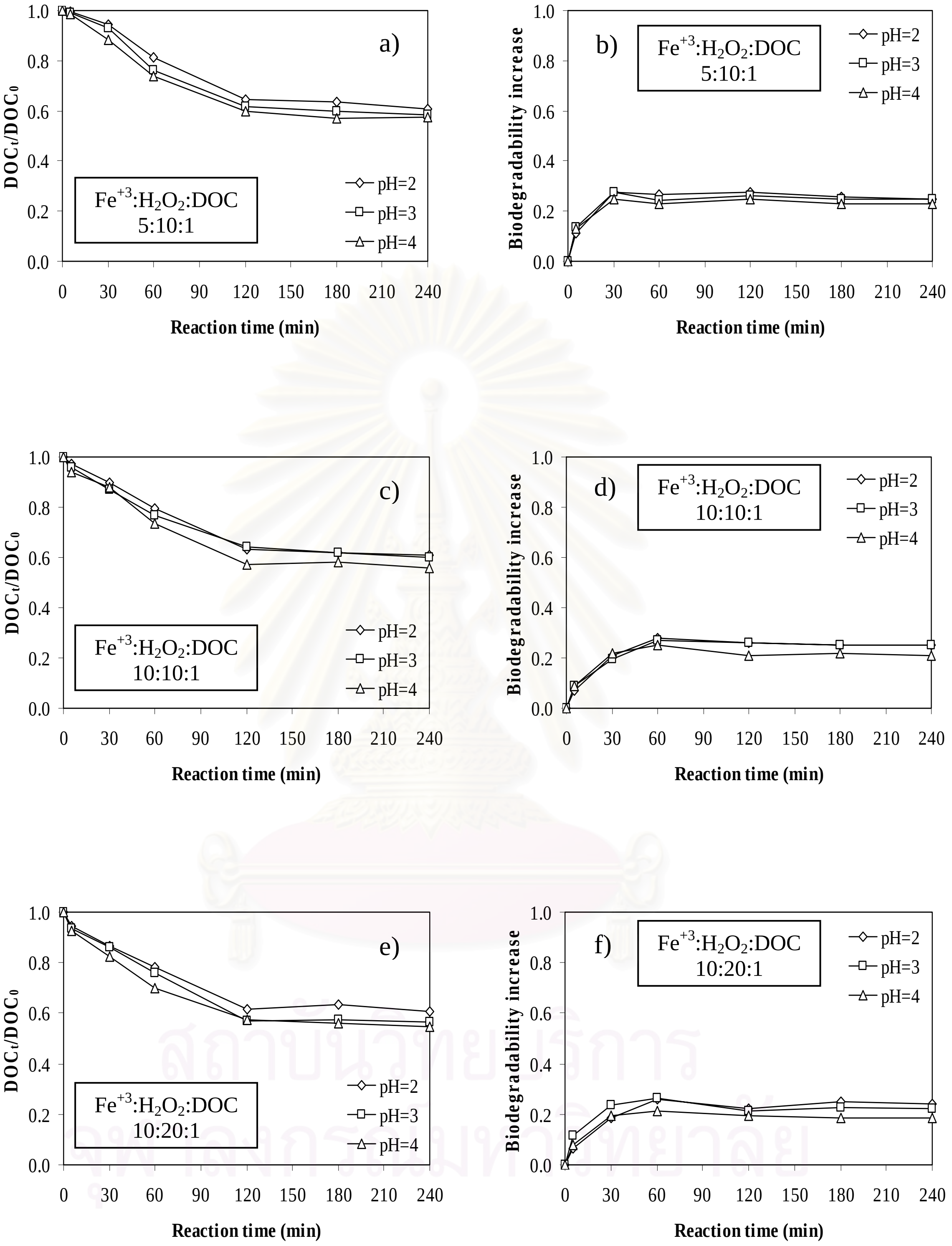


Figure 4.2 Dissolved organic carbon and biodegradability increase of TCE versus reaction time for (a) and (b) Fe^{+3}:H$_2$O$_2$:DOC of 5:10:1; (C) and (d) Fe^{+3}:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

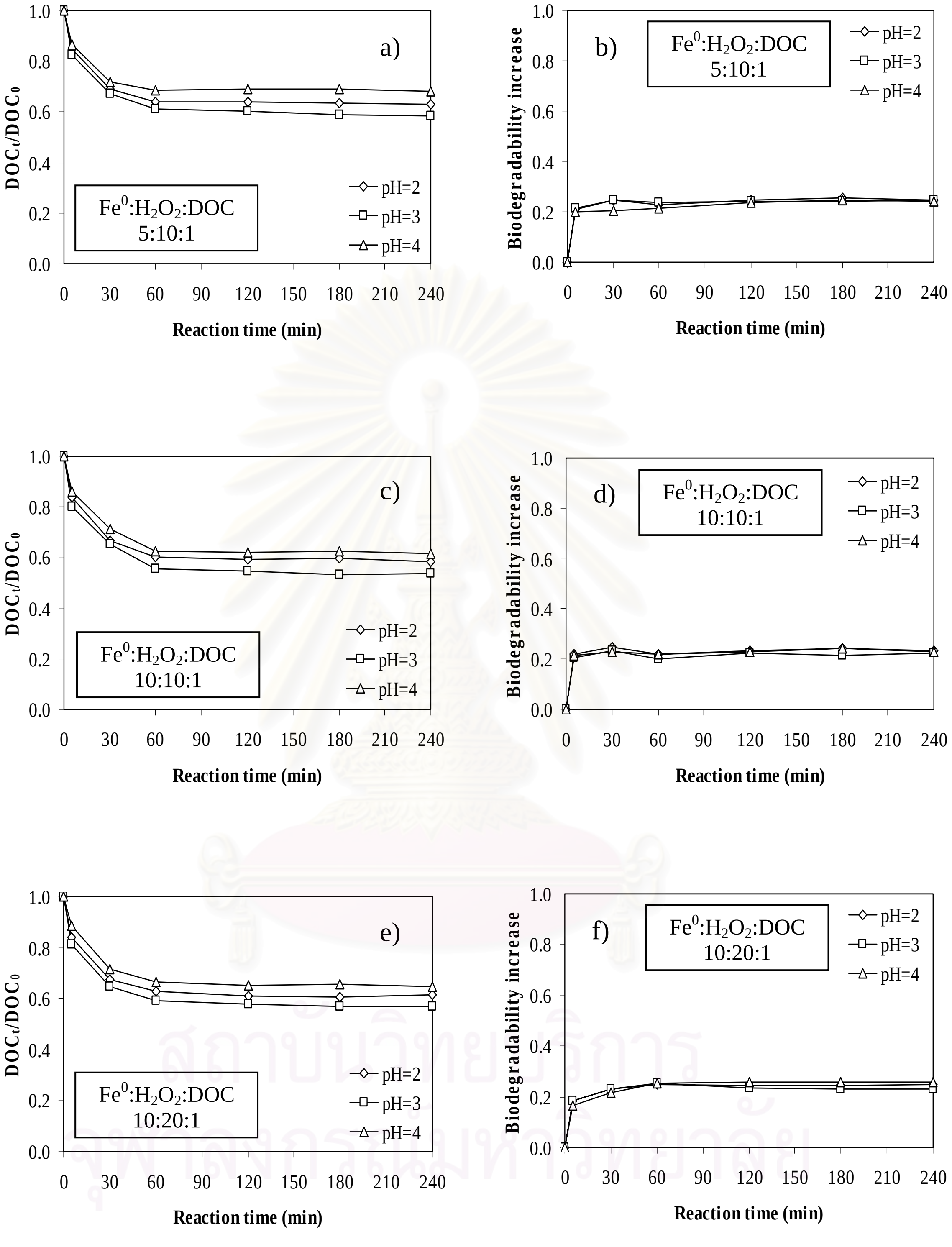


Figure 4.3 Dissolved organic carbon and biodegradability increase of TCE versus reaction time for (a) and (b) Fe^0:H$_2$O$_2$:DOC of 5:10:1; (C) and (d) Fe^0:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^0:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

4.1.4 Effects of type of iron on mineralization and biodegradability increase performances and their kinetics

The results of DOC elimination, biodegradability increase and refractory fractions at the optimal reaction time and initial biodegradability of the TCE solution are shown in Figure 4.4. The refractory fraction was calculated from the following mass balance:

DOC elimination fraction + biodegradability increase fraction + initial biodegradability + refractory fraction = 1.

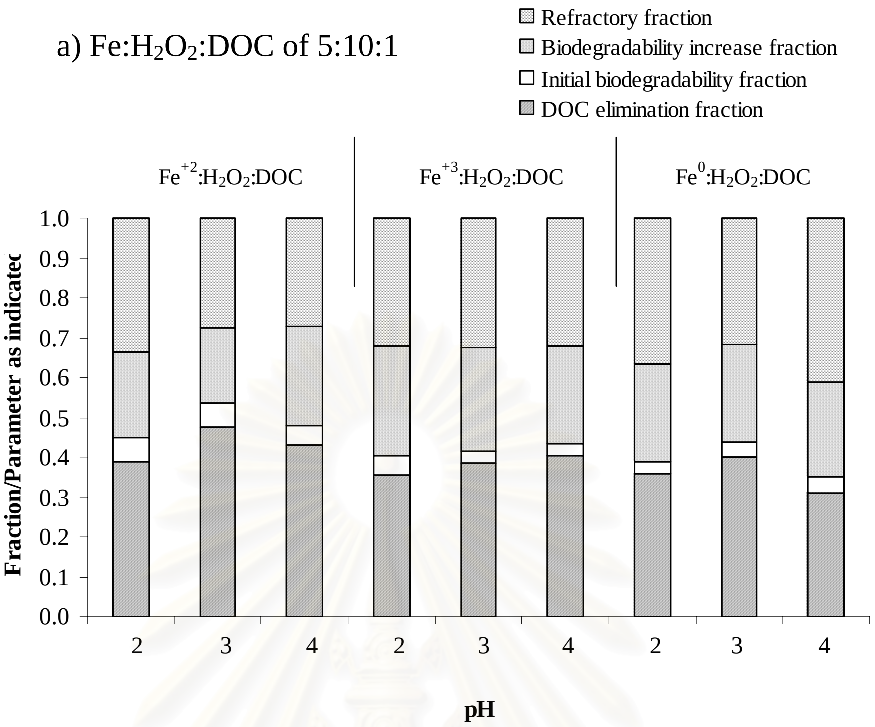
The mass balance equation indicates that in the Fenton's oxidation process, a part of DOC in the solution can be completely oxidized to CO_2 while there is some remaining part. Such remaining DOC could be separated into 2 groups, which are BDOC and refractory DOC (RDOC).

Therefore, DOC elimination fraction = DOC_t/DOC_0

Biodegradability increase fraction = $(BDOC_t-BDOC_0)/DOC_0$

Initial biodegradability = $BDOC_0/DOC$

Figure 4.4 indicates the values of initial biodegradability fraction ranged from 0.01 to 0.06. Fe^{+2} provided the highest mineralization compared with Fe^{+3} and Fe^0 with the same pH and ratio. The maximum DOC elimination was found at the ratio of 10:20:1 and pH of 3. For the biodegradability, the most effective conditions of the TCE solution was at the ratio of Fe^{+3}:H_2O_2:DOC of 5:10:1 and pH of 2. The biodegradability increase was 5.6 times of initial biodegradability. Furthermore, the refractory DOC remained at all conditions of Fenton reagents applied for degrading TCE solution. The combination of mineralization and biodegradability increase was not significantly different under the same conditions of pH and ratio. The values of refractory fraction were ranged from 0.22 to 0.41. To achieve the least amount of the remaining refractory fraction, pH of 4 or Fe^{+2}:H_2O_2:DOC of 10:20:1 should be applied.



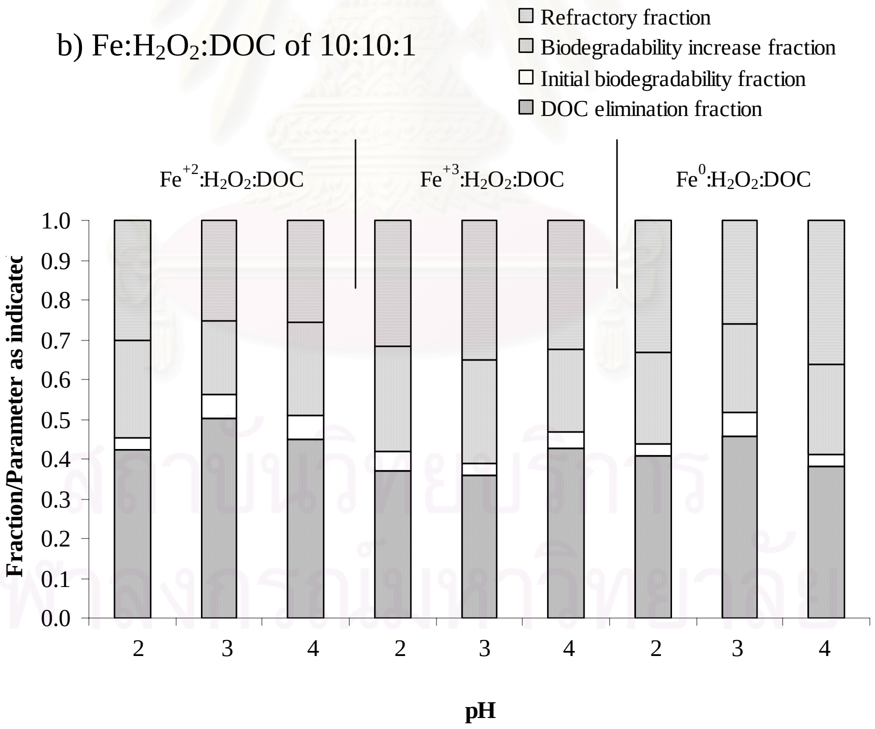


Figure 4.3 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the TCE solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

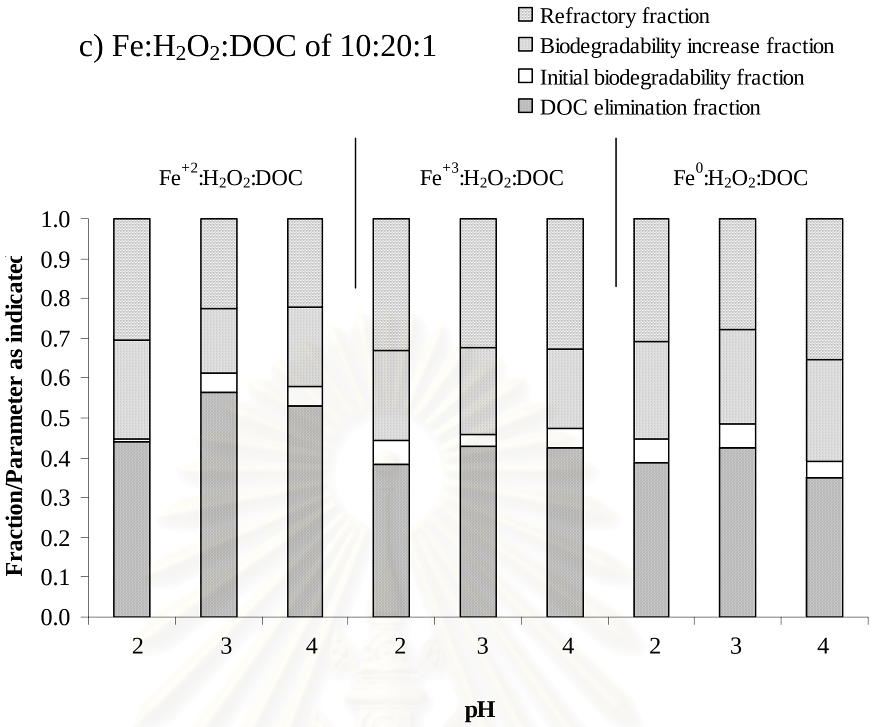


Figure 4.3 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the TCE solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

4.1.5 Effects of pH, Fe:H_2O_2:DOC ratio, type of iron on mineralization and biodegradability increase kinetics

The kinetic mineralization of TCE was also considered as presented in Table 4.1. In this study, the mineralization of the TCE solution was occurred during 120 minutes. Beyond this period, the reaction was slow down as the concentration of H_2O_2 and iron might not be sufficient. Therefore, the mineralization rate of TCE was discussed only the initial stage at 60 minutes. To determine the kinetic of mineralization, the experimental data was fitted to pseudo-first order reaction for Fe^{+2} and Fe^{+3}. However, Fe^0 was found to follow the second order reaction. Increasing the amount of Fe^{+2} and Fe^0 were found to influence more mineralization rate of the TCE solution. This result agreed with Lu *et al.*, (1999), they found that the decomposition rate of organic contaminants increased with the increasing the amount of Fe^{+2}. Again, it could be stated that the mineralization rate constant was dependent on the quantity of Fe^{+2} or Fe^0. For H_2O_2 was not obvious effect on the rate constant of mineralization. The effect of initial pH was slightly on their initial rate constant of mineralization. Comparing the types of iron on mineralization, the maximum rate constant was obtained by the Fe^{+2} for all three pHs and ratios.

From the results of kinetic biodegradability of TCE shown in Table 4.2, the kinetic biodegradability was best fitted to the zero order reaction. The initial rate of biodegradability was considered for the first 30 minutes of reaction time. It was noted that the effect of quantity of Fe and H_2O_2 as well as pH on the rate constant of biodegradability were not evidently resulted. In the other words, the biodegradability rate constant was independent with the initial pH, Fe and H_2O_2.

Table 4.1 The mineralization kinetic of TCE

Type of iron	**Fe:H_2O_2:DOC**	**pH**	**Rate constant (k)**	**R^2**
Fe^{+2}	5:10:1	2	0.0050 1/min	0.9838
		3	0.0055 1/min	0.9999
		4	0.0046 1/min	0.9818
	10:10:1	2	0.0073 1/min	0.9845
		3	0.0081 1/min	0.9904
		4	0.0076 1/min	0.9824
	10:20:1	2	0.0054 1/min	0.9915
		3	0.0081 1/min	0.9923
		4	0.0066 1/min	0.9958
Fe^{+3}	5:10:1	2	0.0034 1/min	0.9517
		3	0.0045 1/min	0.9429
		4	0.0050 1/min	0.9917
	10:10:1	2	0.0038 1/min	0.9966
		3	0.0042 1/min	0.9945
		4	0.0047 1/min	0.9700
	10:20:1	2	0.0039 1/min	0.9783
		3	0.0042 1/min	0.9729
		4	0.0056 1/min	0.9837
Fe^0	5:10:1	2	0.0028 L/min-mg	0.8918
		3	0.0029 L/min-mg	0.8867
		4	0.0023 L/min-mg	0.8508
	10:10:1	2	0.0031 L/min-mg	0.9176
		3	0.0038 L/min-mg	0.9268
		4	0.0029 L/min-mg	0.9499
	10:20:1	2	0.0028 L/min-mg	0.8831
		3	0.0032 L/min-mg	0.8853
		4	0.0064 L/min-mg	0.8809

Table 4.2 The biodegradability kinetic of TCE

Type of iron	**Fe:H_2O_2:DOC**	**pH**	**Rate constant (k)**	**R^2**
Fe^{+2}	5:10:1	2	0.0201 mg/L-min	0.9031
		3	0.0166 mg/L-min	0.7848
		4	0.0239 mg/L-min	0.8803
	10:10:1	2	0.0194 mg/L-min	0.8350
		3	0.0165 mg/L-min	0.7690
		4	0.0195 mg/L-min	0.8166
	10:20:1	2	0.0192 mg/L-min	0.6738
		3	0.0153 mg/L-min	0.7848
		4	0.0199 mg/L-min	0.8361
Fe^{+3}	5:10:1	2	0.0267 mg/L-min	0.9389
		3	0.2550 mg/L-min	0.8840
		4	0.0210 mg/L-min	0.8547
	10:10:1	2	0.0208 mg/L-min	0.9649
		3	0.0169 mg/L-min	0.9029
		4	0.0197 mg/L-min	0.9376
	10:20:1	2	0.0169 mg/L-min	0.9560
		3	0.0215 mg/L-min	0.8710
		4	0.0180 mg/L-min	0.9431
Fe^0	5:10:1	2	0.0193 mg/L-min	0.5233
		3	0.0202 mg/L-min	0.5167
		4	0.0146 mg/L-min	0.4085
	10:10:1	2	0.0199 mg/L-min	0.4933
		3	0.0179 mg/L-min	0.5061
		4	0.0170 mg/L-min	0.4433
	10:20:1	2	0.0191 mg/L-min	0.5814
		3	0.0191 mg/L-min	0.5814
		4	0.0183 mg/L-min	0.6068

4.1.6 Degradation by-products

Fenton oxidation using Fe^{+2} and Fe^{+3} can degrade TCE. No remaining TCE concentration was found after the reaction time of 240 minutes. Phosgene and dichloroacetyle chloride (DCAC) were significant detected as the major by-products. Several previous studies suggested that phosgene and DCAC are the by-products this which are generated when the solvents such as TCE are oxidized in photocatalysis. The same by products generated in Fenton's reaction using Fe^{+2} and Fe^{+3} is due to the similar oxidation mechanism of TCE by the attack of $OH^{\bullet}$. While ethene, ethane and vinyl chloride (VC) were found as the by-products of TCE degradation, using Fe^0 in Fenton reaction. The explanation of the reaction using Fe0 is as follows. Firstly, the corrosion of Fe^0 releases the Fe^{+2} and electrons into the solution. Secondly, the electrons transfer to the compound (TCE) leading to the replacement of a chloride ion with hydrogen atom and liberation of chloride ion. Thirdly, Fenton's oxidation is formed while the released Fe^{+2} react with H_2O_2. The amount of $OH^{\bullet}$ is generated to oxidize the TCE. The modified Fenton's reaction using Fe^0 as the source of Fe^{+2} performs not only reduction but also oxidation.

4.2 2,4-Dichlorophenol

The DOC_0, $BDOC_0$ and $BDOC_0/DOC_0$ of the 2,4-DCP solutions are shown in Appendix A. The initial DOC ranged from 8.25 mg/l to 8.97 mg/l while the initial BDOC were between 0.28 mg/l and 0.52 mg/l. The initial biodegradability of the sample was low (<0.1). This agrees with the fact that 2,4-DCP is the biorefractory.

4.2.1 Effects of Fe^{+2}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.5 illustrates the normalized DOC and biodegradability increase of 2,4-DCP versus reaction time for (a) and (b) Fe^{+2}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+2}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

As shown in Figure 4.5 (a, c and e), the initial pH had a minimal effect on the DOC reduction. A pH of 4 provided slightly higher DOC reduction than those at pH of 3 and 2, respectively. Increasing of Fe^{+2} did not influenced to an increase of DOC reduction. The higher H_2O_2 quantity provided slightly higher DOC elimination. The DOC removal at any conditions was in the range of 34% and 44%. From Figure 4.5 (b, d and f), the biodegradability was significantly increase at the first 5 minutes of reaction time. The biodegradability increase during the period of 30-240 minutes were likely constant. Moreover, such increases were not dependent on the initial pH. Slightly effect on the enhancement of biodegradability was found while increasing the concentration of Fe^{+2} and H_2O_2. The biodegradability increase was in the range between 19% and 28%. The optimal time for DOC elimination was 120 minutes, while the biodegradability increase occurred within 30 minutes.

4.2.2 Effects of Fe^{+3}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

As presented in Figure 4.6 the normalized DOC and biodegradability increase versus reaction time of 2,4-DCP for (a) and (b) Fe^{+3}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+3}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

The results of normalized DOC are illustrated in Figure 4.6 (a, c and e), a very small difference of mineralization was noted for each studied pH. The DOC removal was between 30% and 42% for all conditions. However, the optimal pH was found at pH of 4. Furthermore, the DOC reduction tended to rise with increasing the concentration of Fe^{+3} and H_2O_2. Figure 4.6 (b, d and f) shows the enhancement of biodegradability. It can be seen that the initial pH was not significant for increasing biodegradability of the 2,4-DCP solution. Biodegradability increase from 20% to 23% when the amount of Fe^{+3} was doubled. For the increasing of H_2O_2, the biodegradability was still the same. At all conditions, DOC was continually reduced up to 180 minutes, then, the reduction rate was constant. While the biodegradability was rapidly increased within 5 minutes and then slightly increase until 60 minutes. The optimal reaction times were investigated at 180 minutes and 60 minutes for DOC elimination and biodegradability increase, respectively. The enhancements of mineralization and biodegradability were occurred almost 95%.

4.2.3 Effects of Fe^0:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.7 presents the normalized DOC reduction and biodegradability increase versus reaction time of 2,4-DCP for (a) and (b) Fe^0:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^0:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^0:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4.

As illustrated in Figure 4.7 (a, c and e), the increase of DOC was slightly influenced by the initial pHs. However, pH of 2 provided higher DOC reduction than those at pH of 3 and 4, respectively. pH of 2 could be considered as the optimal.

Increasing of both Fe^0 and H_2O_2 enhanced the increase of DOC elimination. The DOC removal was in the range of 31% to 47%. Figure 4.7 (b, d and f) reveals that the biodegradability increase was in the range of 27% to 32% for all conditions. A minimal difference of biodegradability increase was observed on the initial pH of 2, 3 and 4. Moreover, the concentration of Fe^{+2} and H_2O_2 were insignificantly for enhancement of biodegradability. The reaction time of 120 minutes was considered as the optimal for DOC elimination, while the reaction time of 60 minutes was considered for biodegradability increase.

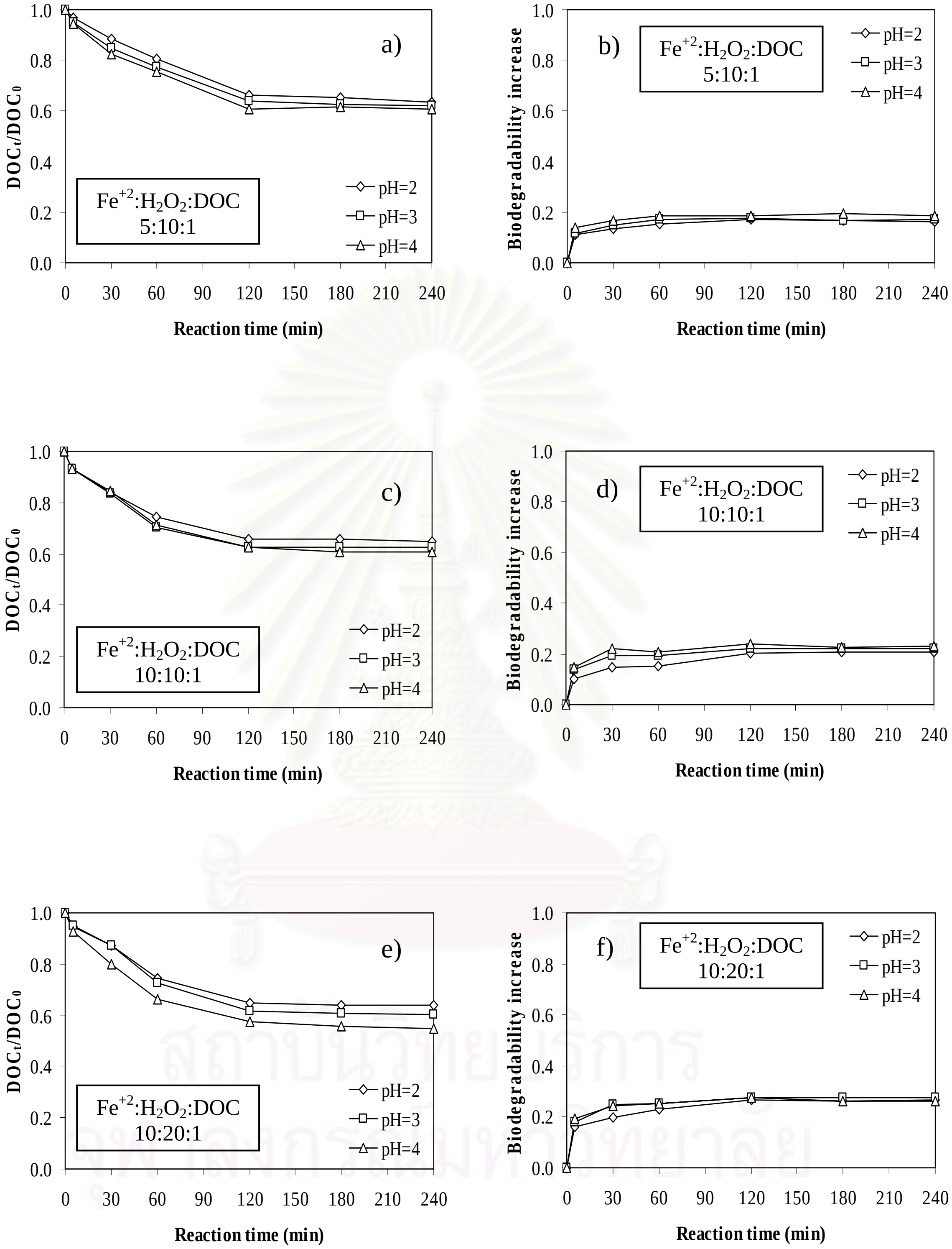


Figure 4.5 Dissolved organic carbon and biodegradability increase of 2,4-DCP versus reaction time for (a) and (b) Fe^{+2}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+2}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H_2O_2:DOC of 10:20:1 at pH of 2, 3, and 4

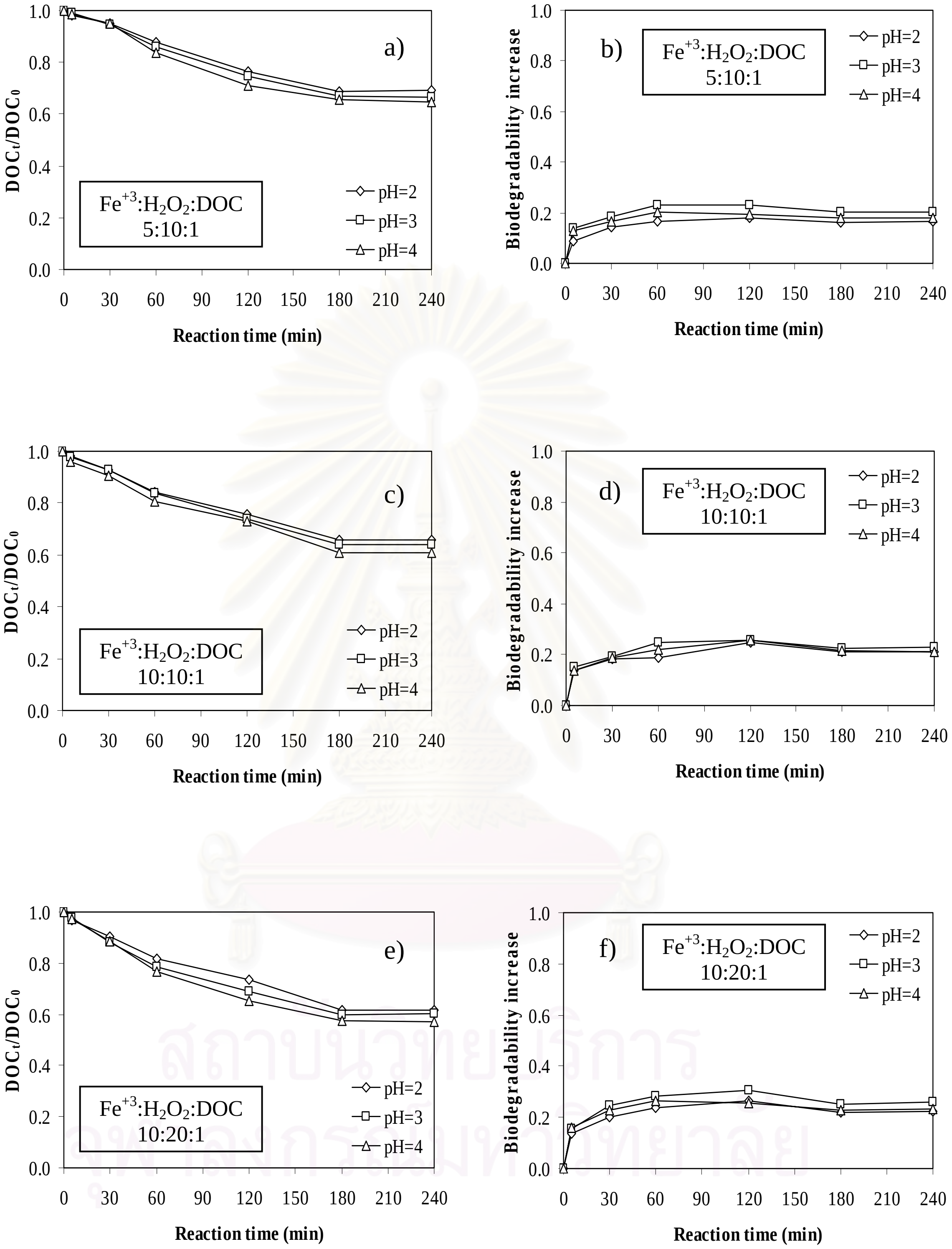


Figure 4.6 Dissolved organic carbon and biodegradability increase versus reaction time of 2,4-DCP for (a) and (b) Fe^{+3}:H$_2$O$_2$:DOC of 5:10:1; (C) and (d) Fe^{+3}:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

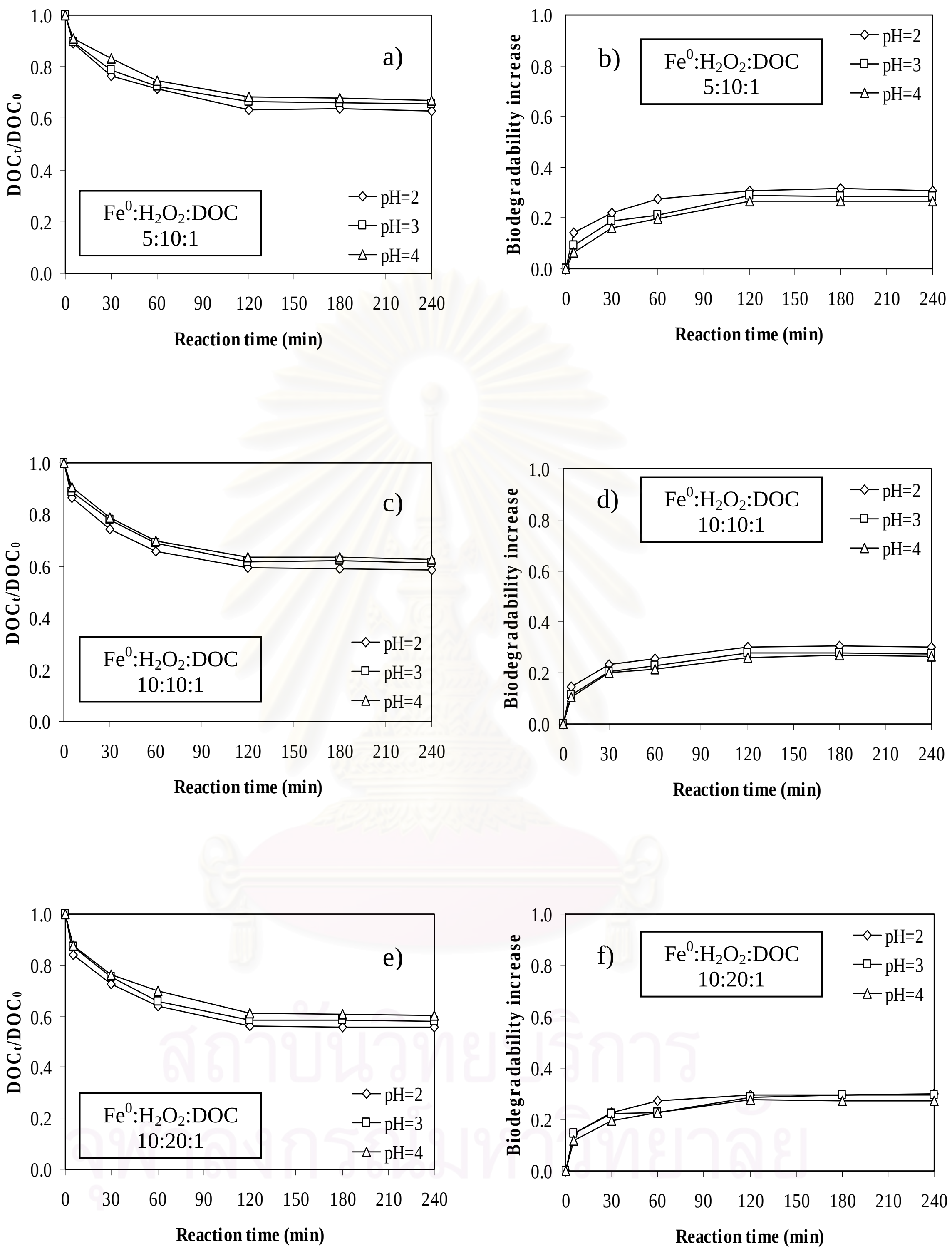
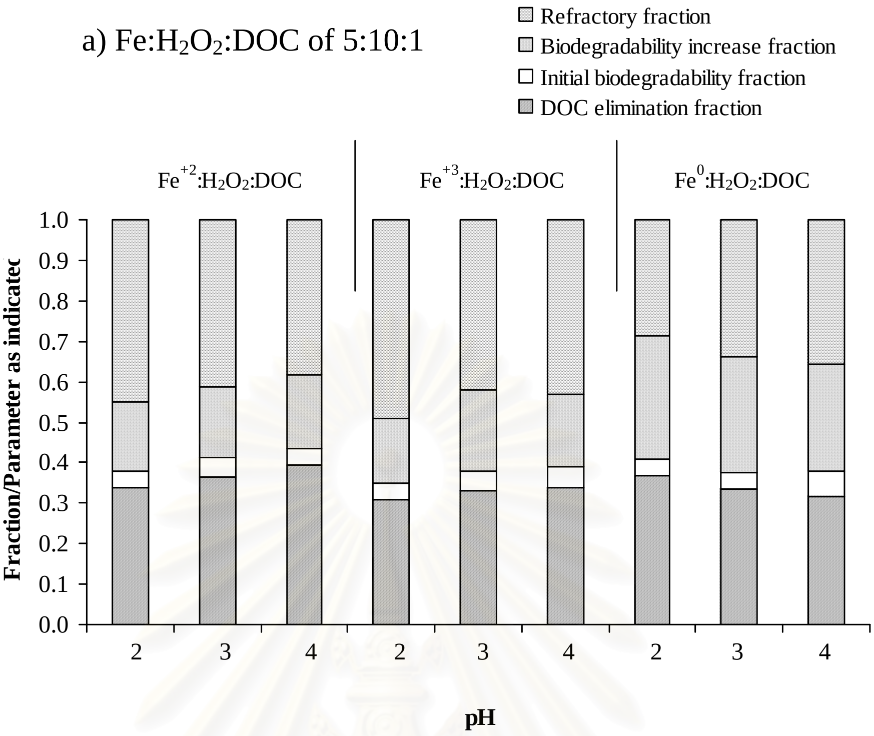


Figure 4.7 Dissolved organic carbon and biodegradability increase versus reaction time of 2,4-DCP for (a) and (b) Fe^0:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^0:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^0:H_2O_2:DOC of 10:20:1 at pH of 2, 3, and 4

4.2.4 Effects of type of iron on mineralization and biodegradability increase performances and their kinetics

Figure 4.8 presents the DOC elimination, biodegradability increase and refractory fractions at the optimal reaction time and initial biodegradability of the 2,4-DCP solution. The initial biodegradability fractions were low in the range of 0.03 to 0.05. The most effective condition for DOC elimination was the ratio of Fe^0:H_2O_2:DOC of 10:20:1 and pH of 2. The biodegradability increase fractions were found in the range between 0.16 and 0.31. Moreover, the increases of biodegradability were in the range of 4 to 7.75 times of the initial biodegradability. The best condition for a combination of DOC elimination and biodegradability increase was the ratio of Fe^0:H_2O_2:DOC of 10:20:1 and pH of 2 and the remaining refractory fraction was about 0.21. Although the ratio of 10:20:1 of Fe^0:H_2O_2:DOC provided the least refractory fraction at pH of 2, it should not be implemented because it resulted a slightly lower refractory than Fe^{+2}:H_2O_2:DOC of 10:20:1 and pH of 4. In addition, the pH of 4 was preferred because less acid required to lower the pH of the 2,4-DCP solution.



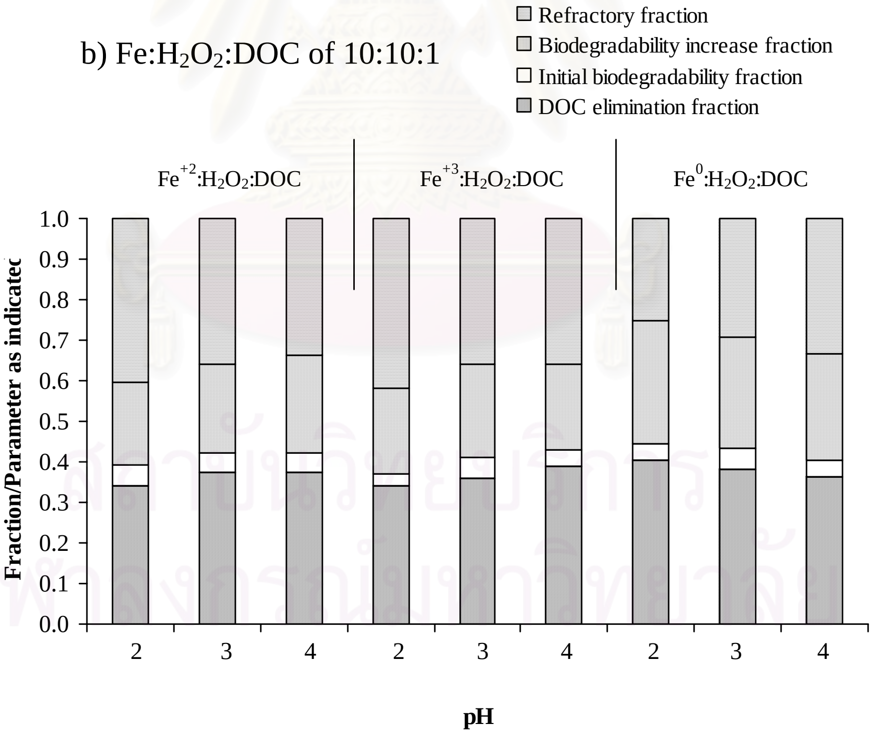


Figure 4.8 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the 2,4-DCP solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

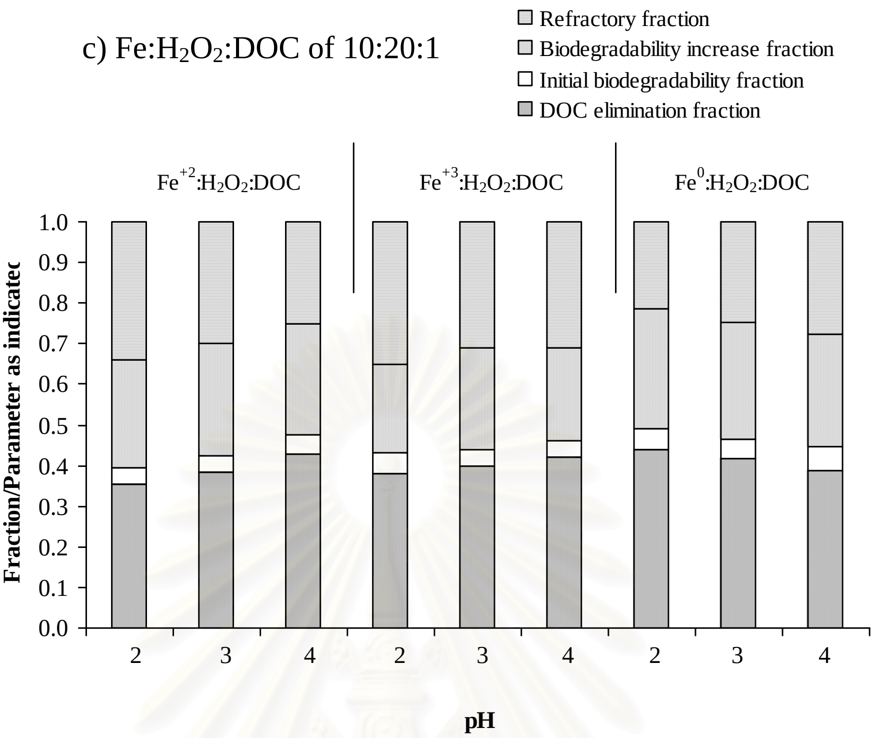


Figure 4.8 Dissolved organic carbon elimination, biodegradability increase and refractory fractions at the optimal reaction time and initial biodegradability of 2,4-DCP for each type of iron in Fenton's reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1 at pH of 2, 3, and 4

4.2.5 Effects of pH, Fe:H_2O_2:DOC ratio, type of iron on mineralization and biodegradability increase kinetics

The kinetic for mineralization of 2,4-DCP is presented in Table 4.3. The mineralization kinetics were fitted to the pseudo-first order for Fe^{+2} and Fe^{+3} and the second order for Fe^0, respectively. The rate constant of mineralization was strongly dependent on the amount of Fe. At the higher amount of Fe, the more mineralization rate of 2,4-DCP was performed. For H_2O_2 effect, increasing the amount of H_2O_2 resulted to the higher rate constant for Fe^{+3} and Fe^0. However, increasing the initial pH indicated a slightly increasing of the rate constant of mineralization. Again, Fe^{+2} provided the highest rate of mineralization of the 2,4-DCP solution in all conditions.

The results of kinetic biodegradability of 2,4-DCP is shown Table 4.4, the rate constant of biodegradability was fitted to the zero order reaction rate. The highest rate constant was found for the Fe^0 of which this type of iron presented the best R^2.

Table 4.3 The mineralization kinetic of 2,4-DCP

Type of iron	Fe:H_2O_2:DOC	pH	Rate constant (k)	R^2
Fe^{+2}	5:10:1	2	0.0035 1/min	0.9904
		3	0.0042 1/min	0.9743
		4	0.0046 1/min	0.9599
	10:10:1	2	0.0046 1/min	0.9734
		3	0.0056 1/min	0.9878
		4	0.0053 1/min	0.9833
	10:20:1	2	0.0046 1/min	0.9862
		3	0.0051 1/min	0.9807
		4	0.0066 1/min	0.9912
Fe^{+3}	5:10:1	2	0.0021 1/min	0.9732
		3	0.0025 1/min	0.9786
		4	0.0028 1/min	0.9523
	10:10:1	2	0.0028 1/min	0.9909
		3	0.0029 1/min	0.9882
		4	0.0034 1/min	0.9832
	10:20:1	2	0.0033 1/min	0.9953
		3	0.0040 1/min	0.9990
		4	0.0043 1/min	0.9976
Fe^0	5:10:1	2	0.0007 L/min-mg	0.9036
		3	0.0007 L/min-mg	0.9252
		4	0.0006 L/min-mg	0.9569
	10:10:1	2	0.0009 L/min-mg	0.9406
		3	0.0008 L/min-mg	0.9564
		4	0.0008 L/min-mg	0.9667
	10:20:1	2	0.0010 L/min-mg	0.9232
		3	0.0009 L/min-mg	0.9539
		4	0.0007 L/min-mg	0.9147

Table 4.4 The biodegradability kinetic of 2,4-DCP

Type of iron	Fe:H_2O_2:DOC	pH	Rate constant (k)	R^2
Fe^{+2}	5:10:1	2	0.0292 mg/L-min	0.5823
		3	0.0332 mg/L-min	0.5981
		4	0.0354 mg/L-min	0.5366
	10:10:1	2	0.0336 mg/L-min	0.7041
		3	0.0444 mg/L-min	0.6701
		4	0.0507 mg/L-min	0.7147
	10:20:1	2	0.0416 mg/L-min	0.5635
		3	0.0555 mg/L-min	0.6643
		4	0.0513 mg/L-min	0.5911
Fe^{+3}	5:10:1	2	0.0328 mg/L-min	0.7721
		3	0.0400 mg/L-min	0.6221
		4	0.0362 mg/L-min	0.5941
	10:10:1	2	0.0400 mg/L-min	0.6369
		3	0.0422 mg/L-min	0.5939
		4	0.0412 mg/L-min	0.6580
	10:20:1	2	0.0464 mg/L-min	0.7027
		3	0.0589 mg/L-min	0.7582
		4	0.0503 mg/L-min	0.6864
Fe^0	5:10:1	2	0.0510 mg/L-min	0.7500
		3	0.0455 mg/L-min	0.8807
		4	0.0405 mg/L-min	0.9317
	10:10:1	2	0.0542 mg/L-min	0.7482
		3	0.0493 mg/L-min	0.8356
		4	0.0497 mg/L-min	0.8618
	10:20:1	2	0.0544 mg/L-min	0.7531
		3	0.0511 mg/L-min	0.7306
		4	0.0481 mg/L-min	0.7761

4.2.6 Degradation by-products

The by-products of 2,4-DCP degradation generated by Fenton's reaction using different 3 types of iron were studied. None of 2,4-DCP concentration was found after the reaction occurred. For the oxidation of Fe^{+2} and Fe^{+3} catalysts, chlorohydroquinone, 2-chloro-1,4-benzoquinone and 4,6-dichlororesorcinol were determined as the major by-products. Similar to the previous AOPs study, Chu *et al.*, 2005, identified the reaction pathway of the photo degradation of 2,4-DCP in photo Fenton-like oxidation. They found chlorohydroquinone, 4-chlorocatechol, 2,chloro-1,4-benzoquinone, 3,5-dichlororesorcinol and 4,6-dichlororesorcinol as the intermediates. According to the same by-products of 2,4-DCP degradation by Fenton reaction using Fe^{+2} and Fe^{+3} generated, it is because of the mechanism of both methods are similar. Both Fe^{+2} and Fe^{+3} combine with H_2O_2 can produce $OH^\bullet$ which is the key of oxidation reaction. The major by-products of Fe^0 catalyst were hydroquinone and catechol. As above explanation, the electrons released from the corrosion of Fe^0 provide the basis for reductive dechlorination of 2,4-DCP. At the same time, Fe^{+2} can be released from such corrosion. The released Fe^{+2} in the solution is combined with H_2O_2, the reaction shifts to Fenton's oxidation. The $OH^\bullet$ is generated to oxidize the organic compounds in the solution. The mechanisms played in Fe^0 catalyst in Fenton's reaction are both reduction and oxidation.

4.3 1,4-Dioxane

The DOC_0, $BDOC_0$ and $BDOC_0/DOC_0$ of the 1,4-D solutions are shown in Appendix A. The initial DOC ranged from 12.29 mg/l to 13.68 mg/l while the initial BDOC were between 0.37 mg/l and 0.60 mg/l. The initial biodegradability of the sample was low about 0.03 and 0.04.

4.3.1 Effects of Fe^{+2}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.9 illustrates the normalized DOC and biodegradability increase of 1,4-D versus reaction time for (a) and (b) Fe^{+2}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+2}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

As presented in Figure 4.9 (a, c and e), a little difference on the DOC reduction was indicated between pH of 2, 3 and 4. The optimal pH on elimination of DOC was found at pH of 3. The results presented that less than 10% of the elimination of DOC was observed. Increasing of Fe^{+2} and H_2O_2 were not obviously shown the effect on increasing of the DOC reduction. Most of DOC reduction occurred in the reaction time of 120 minutes, which was considered as optimal. The biodegradability increase is shown in Figure 4.9 (b, d and f), the enhancement of biodegradability was implied as the pH dependent. pH of 3 provided the higher biodegradability increase than pH of 4 and 2, respectively. The higher biodegradability increase was obtained while increasing the concentration of Fe^{+2} as well as H_2O_2. Moreover, 90% of total biodegradability increase was occurred within 60 minutes.

4.3.2 Effects of Fe^{+3}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

As presented in Figure 4.10 the normalized DOC and biodegradability increase of 1,4-D versus reaction time for (a) and (b) Fe^{+3}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+3}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

The results of normalized DOC are illustrated in Figure 4.10 (a, c and e), the results shown that approximately 5% of DOC reduction was occurred. The initial pH had a slightly effect on the DOC reduction. Also, increasing of the amount of Fe^{+3} and H_2O_2 did not significantly enhance the elimination of DOC. As shown in Figure 4.10 (b, d and f), the biodegradability was observed increase depending on the ratio of Fe^{+3}:H_2O_2:DOC. While increase the amount of $Fe^{+}3$ the biodegradability provided increase. Increasing the amount of H_2O_2 did not evidently show an effect to increase the enhancement of biodegradability. The largest biodegradability was found at the pH of 2. The optimal reaction times were investigated at 120 minutes and 60 minutes for DOC elimination and biodegradability increase, respectively.

4.3.3 Effects of Fe^0:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.11 illustrates the normalized DOC reduction and biodegradability increase of 1,4-D versus reaction time for (a) and (b) Fe^0:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^0:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^0:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4.

As shown in Figure 4.11 (a, c and e), mostly, the DOC reduction were obtained approximately 5%. The initial pH of 2, 3 and 4 was slightly effect on DOC removal. Also, The increasing of Fe^{+2} and H_2O_2 ratios were not necessarily enhanced DOC removal. From Figure 4.11 (b, d and f), it could be seen that the biodegradability was increased in the range of 37% to 52% for three pHs and ratios. The effect of the initial pH was indicated to raise the biodegradability of the 1,4-D solution. At pH of 3 provided higher the biodegradability than that pH of 4 and 2, respectively. In addition, increasing of the Fe^0 quantity affected to the larger biodegradability performance while increasing the amount of H_2O_2 was not significantly to provide the higher biodegradability. The reaction time of 120 minutes was considered as the optimal of DOC elimination while the reaction time of 60 minutes was indicated the optimal time of biodegradability increase.

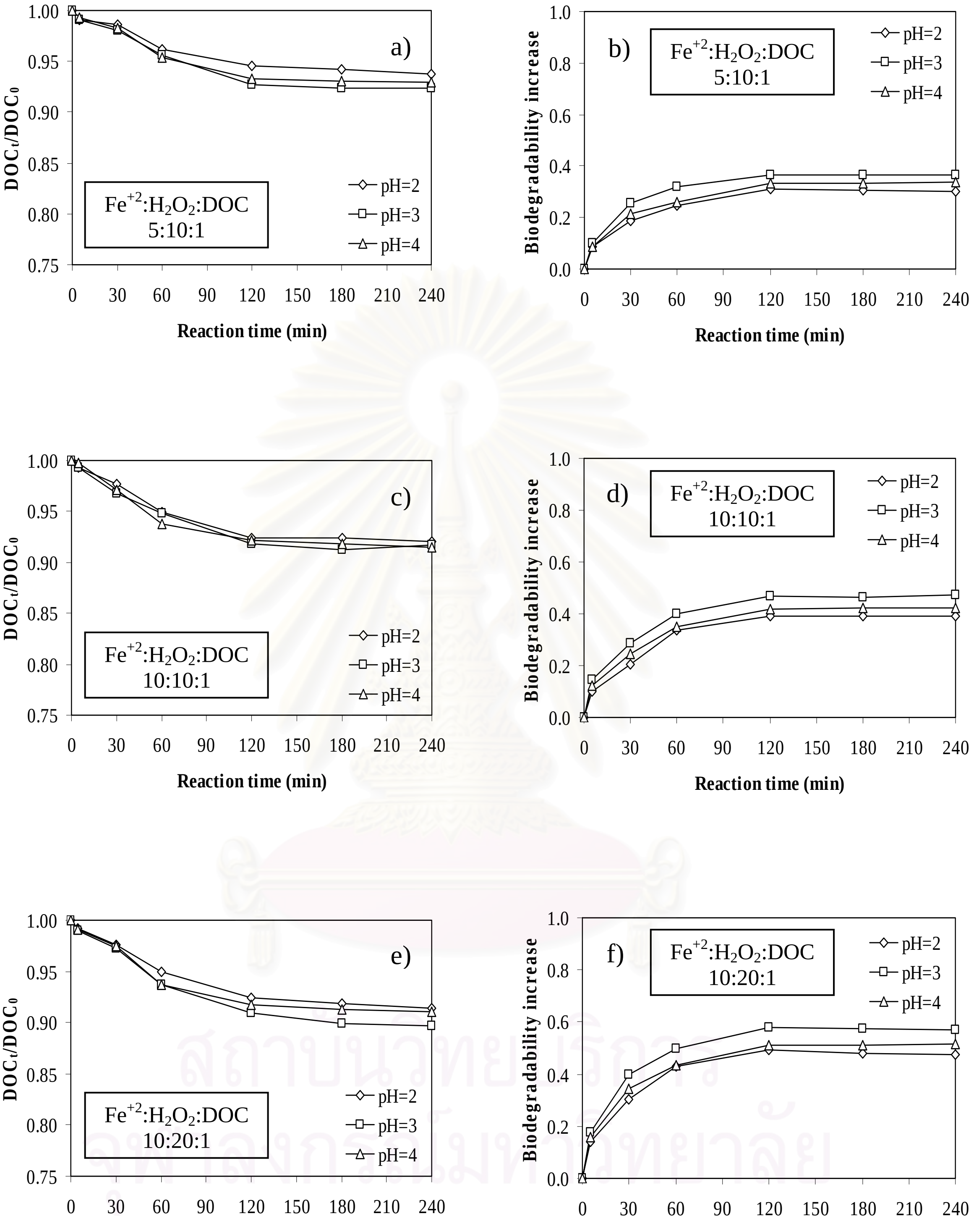


Figure 4.9 Dissolved organic carbon and biodegradability increase of 1,4-D versus reaction time for (a) and (b) Fe^{+2}:H$_2$O$_2$:DOC of 5:10:1; (C) and (d) Fe^{+2}:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

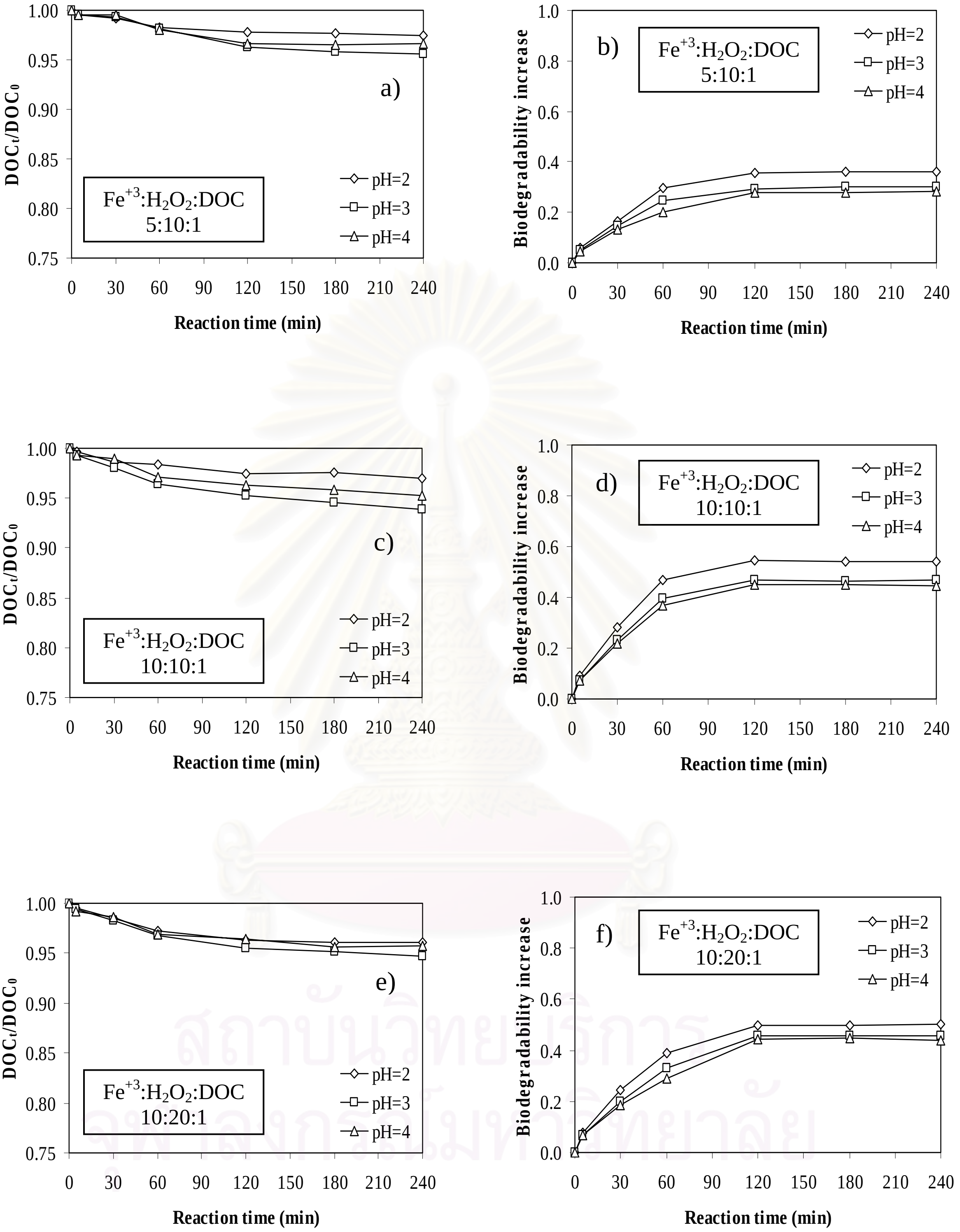


Figure 4.10 Dissolved organic carbon and biodegradability increase of 1,4-D versus reaction time for (a) and (b) Fe^{+3}:H$_2$O$_2$:DOC of 5:10:1; (C) and (d) Fe^{+3}:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

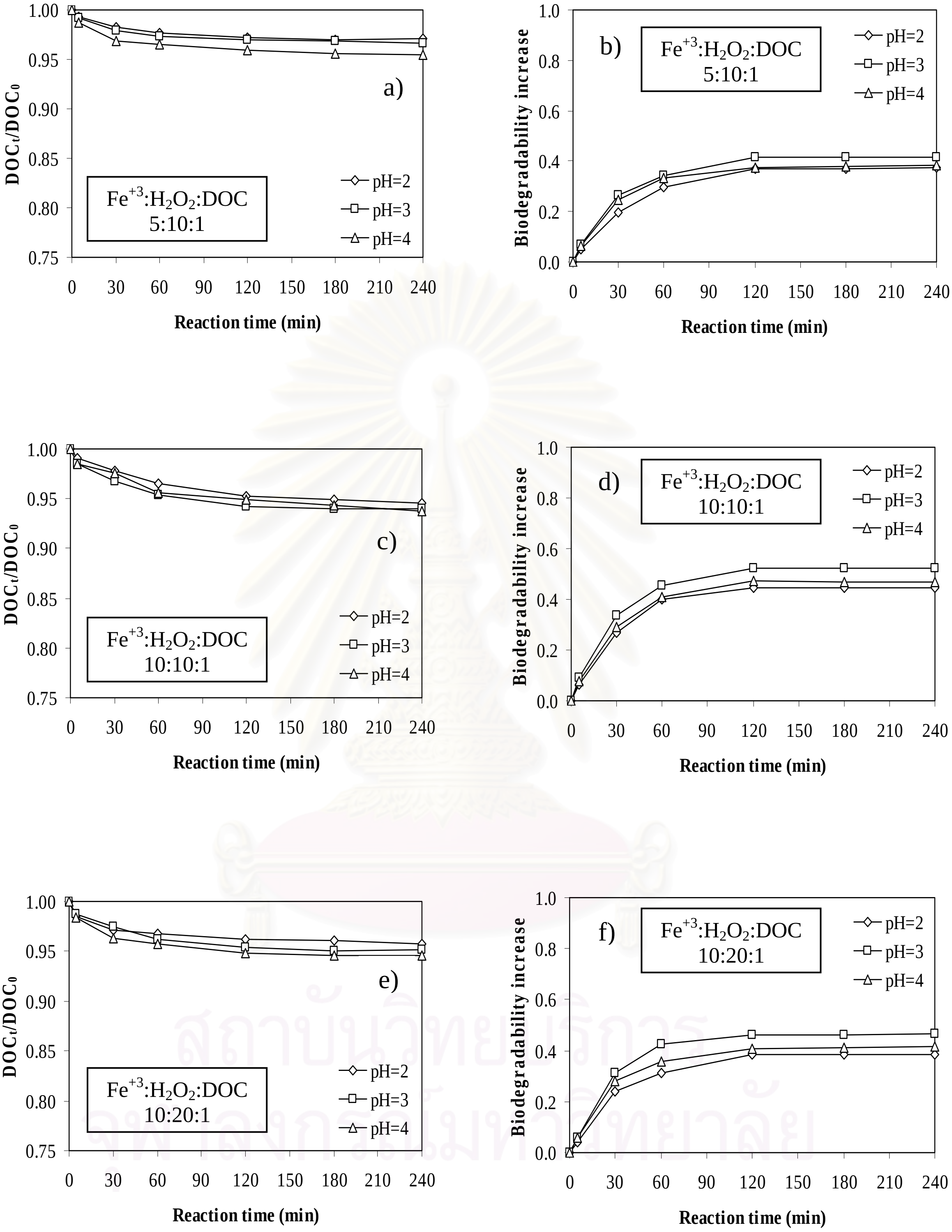
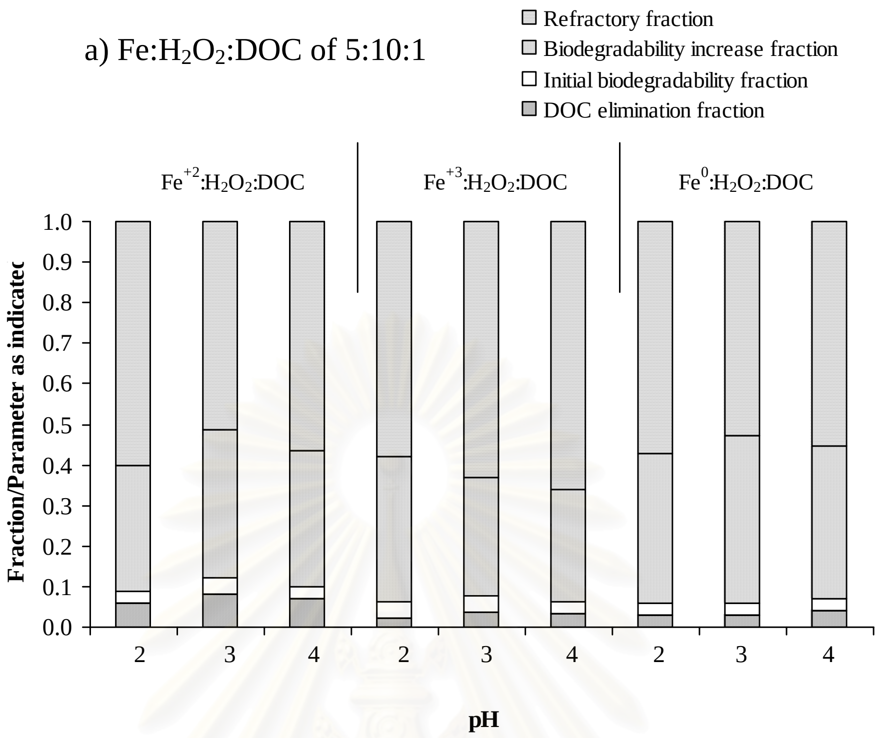


Figure 4.11 Dissolved organic carbon and biodegradability increase versus reaction time of 1,4-D for (a) and (b) Fe^0:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^0:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^0:H_2O_2:DOC of 10:20:1 at pH of 2, 3, and 4

4.3.4 Effects of type of iron on mineralization and biodegradability increase performances and their kinetics

Figure 4.12 presents the DOC elimination, biodegradability increase and refractory fractions at the optimal reaction time and initial biodegradability of the 1,4-D solution. The initial biodegradability fractions were observed in the range 0.03 to 0.04. Mostly, the fractions of DOC elimination were observed about 0.08. The range of biodegradability increase fraction was from 0.28 to 0.58. At the ratio of Fe^{+2}:H_2O_2:DOC of 10:20:1 and pH of 3 were provided as the best condition for biodegradability increase of the 1,4-D solution. The biodegradability increase was approximately 14.5 times of initial biodegradability. Again, the best condition for combination of DOC elimination and biodegradability increase was at the ratio Fe^{+2}:H_2O_2:DOC of 10:20:1 and pH of 3. Refractory DOC remained at all studied conditions for the 1,4-D solution. Thus, such condition should be applied to provide the least amount of remaining refractory fraction.



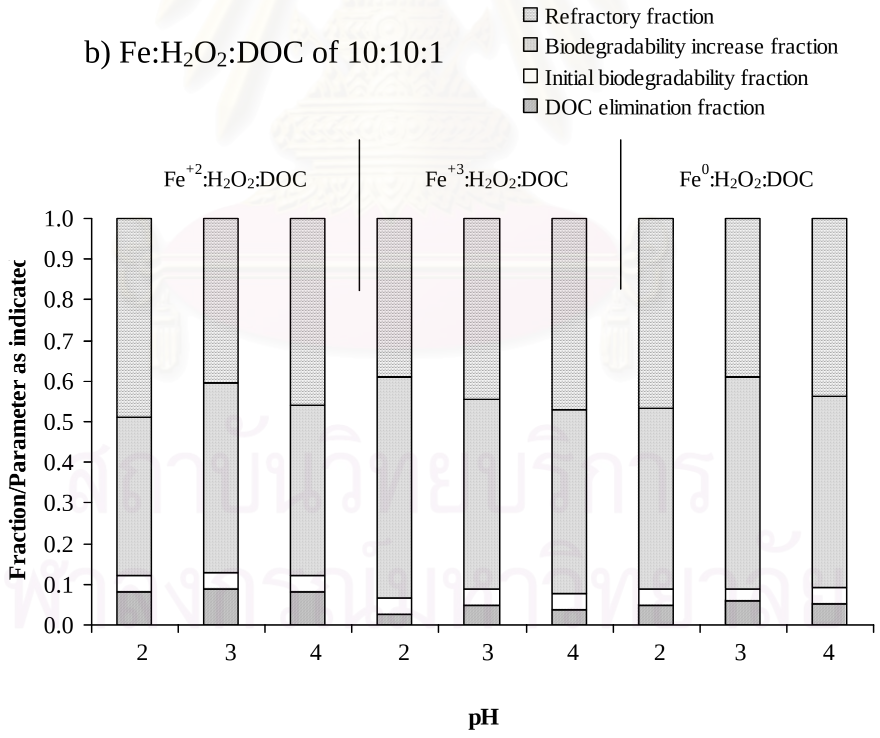


Figure 4.12 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the 1,4-D solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

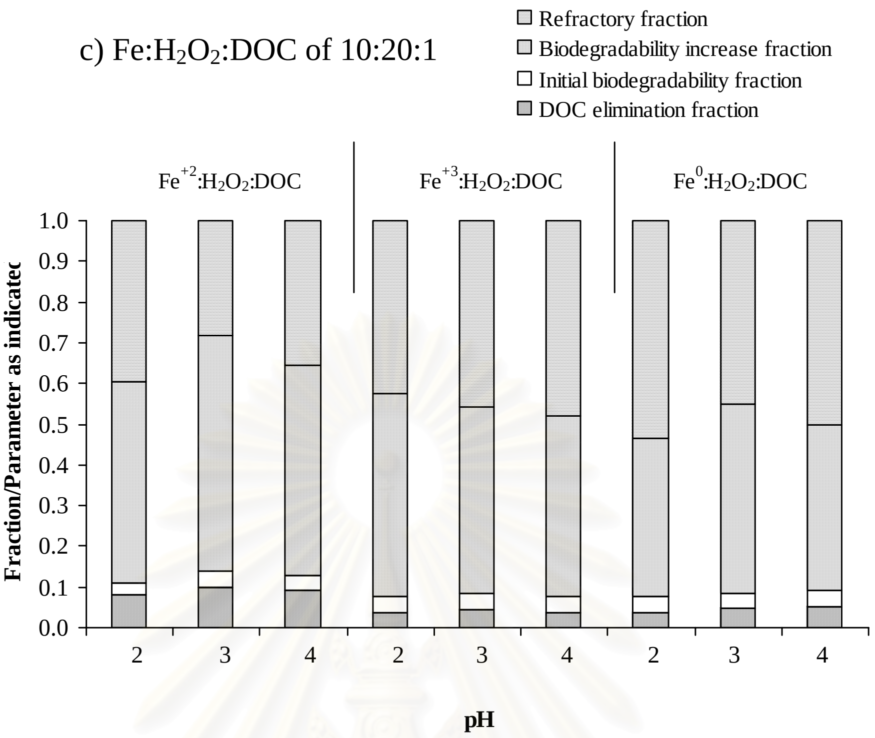


Figure 4.12 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the 1,4-D solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

4.3.5 Effects of pH, Fe:H_2O_2:DOC ratio, type of iron on mineralization and biodegradability increase kinetics

As shown in Table 4.5, the mineralization kinetics of 1,4-D were best fitted to the pseudo-first order reaction for any type of studied Fe. The rate constant mineralization was slightly changed while increasing the Fe and H_2O_2 quantity. The values of rate constant were in the range of 0.0003 to 0.0011 min^{-1}. In addition, the initial pH of 2, 3 and 4 were not significantly effect to the reaction constant rate.

The biodegradability kinetic of 1,4-D was revealed in Table 4.6, The results shown that the rate constants of biodegradability for Fe^{+2} and Fe^0 at the pH of 3 indicated slightly higher than pH of 4 and 2, respectively. For Fe^{+3}, the highest rate constant was obtained at pH of 2 as presented by 0.0683-0.1191 mg/l-min. Increasing the amount of Fe^{+3} and/or Fe^0 affected to increase the rate constant. Furthermore, the rate constant was the same when the amount of Fe^{+3} was doubled. In addition, the more dosing the H_2O_2 influenced the rate constant of Fe^{+2}. For Fe^{+3}, increasing the dose of H_2O_2, decrease rate constant was occurred. The iron type of Fe^0 provided maximum rate constant for biodegradability of 1,4-D comparing to Fe^{+2} and Fe^{+3} in each pH and ratio.

Table 4.5 The mineralization kinetic of 1,4-D

Type of iron	Fe:H_2O_2:DOC	pH	Rate constant (k)	R^2
Fe^{+2}	5:10:1	2	0.0006 1/min	0.9285
		3	0.0007 1/min	0.9685
		4	0.0008 1/min	0.9625
	10:10:1	2	0.0008 1/min	0.9897
		3	0.0009 1/min	0.9847
		4	0.0011 1/min	0.9969
	10:20:1	2	0.0008 1/min	0.9918
		3	0.0010 1/min	0.9844
		4	0.0010 1/min	0.9784
Fe^{+3}	5:10:1	2	0.0003 1/min	0.9621
		3	0.0003 1/min	0.9331
		4	0.0003 1/min	0.8596
	10:10:1	2	0.0003 1/min	0.8752
		3	0.0006 1/min	0.9859
		4	0.0004 1/min	0.9413
	10:20:1	2	0.0004 1/min	0.9943
		3	0.0005 1/min	0.9906
		4	0.0005 1/min	0.9538
Fe^0	5:10:1	2	0.0004 1/min	0.8973
		3	0.0004 1/min	0.8890
		4	0.0005 1/min	0.8176
	10:10:1	2	0.0005 1/min	0.9578
		3	0.0007 1/min	0.9163
		4	0.0007 1/min	0.9304
	10:20:1	2	0.0005 1/min	0.7712
		3	0.0006 1/min	0.9291
		4	0.0007 1/min	0.8296

Table 4.6 The biodegradability kinetic of 1,4-D

Type of iron	**Fe:H_2O_2:DOC**	**pH**	**Rate constant (k)**	**R^2**
Fe^{+2}	5:10:1	2	0.0756 mg/L-min	0.9064
		3	0.1052 mg/L-min	0.9373
		4	0.0810 mg/L-min	0.9338
	10:10:1	2	0.0734 mg/L-min	0.8770
		3	0.1080 mg/L-min	0.8657
		4	0.0889 mg/L-min	0.8672
	10:20:1	2	0.1180 mg/L-min	0.9012
		3	0.1506 mg/L-min	0.9119
		4	0.1325 mg/L-min	0.9019
Fe^{+3}	5:10:1	2	0.0683 mg/L-min	0.9555
		3	0.0593 mg/L-min	0.9640
		4	0.0505 mg/L-min	0.9689
	10:10:1	2	0.1191 mg/L-min	0.9709
		3	0.0990 mg/L-min	0.9786
		4	0.0843 mg/L-min	0.9703
	10:20:1	2	0.1035 mg/L-min	0.9762
		3	0.0823 mg/L-min	0.9649
		4	0.0692 mg/L-min	0.9501
Fe^0	5:10:1	2	0.0833 mg/L-min	0.9909
		3	0.1167 mg/L-min	0.9908
		4	0.1063 mg/L-min	0.9889
	10:10:1	2	0.1097 mg/L-min	0.9940
		3	0.1447 mg/L-min	0.9875
		4	0.1155 mg/L-min	0.9881
	10:20:1	2	0.1076 mg/L-min	0.9999
		3	0.1357 mg/L-min	0.9991
		4	0.1189 mg/L-min	0.9978

4.3.5 Degradation by-products

The degradation of 1,4-D by different types of iron in Fenton’s oxidation does not completely mineralization to CO_2. It could be confirmed by the remaining DOC in the solution. Anyway, the decreasing of DOC and increasing BDOC were indicated the partial oxidation of 1,4-D and transformation of this compound into more biodegradable intermediates. The degradation by-product of 1,4-D in each type of Fenton’s reagents was studied. The results showed that 1,2-ethanediol monoformate, 1,2-ethanediol diformate, formic acid and methoxyacetic acid were found to be the major by-products. It is confirmed in many previous studies, the degradation of 1,4-D using several AOPs such as TiO_2 photocatalysis, UV/H_2O_2 and O_3/H_2O_2 (Maurino *et al.*, 1997; Stefan and Bolton, 1998; and Suh and Mohseni, 2004) were examined, in each case the intermediates found was 1,2-ethanediol diformate ester. According to 1,4-D does not have the halogens group presented in the molecular structure. The by-products of 3 types of iron in Fenton reaction were detected the same. The use of Fe^{+2} and Fe^{+3} in Fenton’s reaction performed 1,4-D oxidation by using strong oxidizing agent, $OH^{\bullet}$. For the corrosion of Fe^{0}, Fe^{+2} and two electrons are released into the solution. Fenton’s oxidation is formed while the Fe^{+2} react with H_2O_2. The amount of $OH^{\bullet}$ is produced to oxidize 1,4-D. None of the effect was presented on the reductive halogens by the electrons transfer.

4.4 1,2,3-Trichloropropane

The DOC_0, $BDOC_0$ and $BDOC_0/DOC_0$ of the TCP solutions are shown in Appendix A. The initial DOC ranged from 4.26 mg/l to 4.56 mg/l while the initial BDOC were between 0.13 mg/l and 0.24 mg/l. The initial biodegradability of the sample was low (<0.05). This supports the fact that TCP is difficult to degrade by traditional biological treatment.

4.4.1 Effects of Fe^{+2}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.13 illustrates the normalized DOC and biodegradability increase of TCP versus reaction time for (a) and (b) Fe^{+2}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+2}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+2}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

From the Figure 4.13 (a, c and e), the initial pH had slightly effect on the DOC reduction. A pH of 3 provided little higher DOC removal than pH of 4 and 2, respectively. The higher quantity of Fe^{+2} provided the higher DOC elimination. Moreover, H_2O_2 did not Influenced to the reduction of DOC. The DOC removal was obtained in the range of 25% to 35%. As presented in Figure 4.13 (b, d and f), the biodegradability enhanced significantly during the reaction time of 60 minutes. Their increases were slightly dependent on the initial pH. Small effect on the enhancement of biodegradability was found while increasing the amount of Fe^{+2} and H_2O_2. The biodegradability increase was ranged from 20% to 30%. Ninety percent of the total mineralization of elimination was observed after 180 minutes while 90% of total biodegradability increase occurred within 60 minutes. Thus, the reaction time of 180 minutes and 60 minutes were considered as the optimal reaction time of mineralization and biodegradability enhancement, respectively.

4.4.2 Effects of Fe^{+3}:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

The Figure 4.14 presents the normalized DOC and biodegradability increase of TCP versus reaction time for (a) and (b) Fe^{+3}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+3}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4**.**

The results of normalized DOC are illustrated in Figure 4.14 (a, c and e), slightly difference of DOC reduction was found in each initial pH. At pH of 3 was considered as optimal pH because it provided slightly more DOC reduction than that pH of 4 and 2. The DOC removal was observed in the range of 30% and 35%. The trend of DOC reduction was slightly increased with increasing the concentration of Fe^{+3} and H_2O_2. From the Figure 4.14 (b, d and f) shows the biodegradability increase, it could be seen that the initial pH was not significantly to increase the biodegradability of the TCP solution. The range of biodegradability increase was provided from 20% to 40%. Increasing both of Fe^{+3} and H_2O_2 quantity provided more biodegradability enhancement. The optimal reaction times were investigated at 180 minutes and 60 minutes for DOC elimination and biodegradability increase, respectively according to their enhancements were occurred almost 90%.

4.4.3 Effects of Fe^0:H_2O_2:DOC and pH on mineralization and biodegradability increase performances

Figure 4.15 presents the normalized DOC reduction and biodegradability increase of TCP versus reaction time for (a) and (b) Fe^0:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^0:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^0:H_2O_2:DOC of 10:20:1 at pH of 2, 3 and 4.

As illustrated in Figure 4.15 (a, c and e), the increase of DOC was slightly depended on the initial pHs of 2, 3 and 4. A pH of 2 provided highest the DOC reduction and considered the optimal. Increasing double amount of Fe^0 led to slightly more DOC elimination. The effect of H_2O_2 was not of obvious clear for increasing the DOC removal. The DOC removal was ranging from 30% to 40%. From Figure 4.15

(b, d and f), it can be seen that the biodegradability was increased while increasing the amount of Fe^0. In other words, increasing the amount of H_2O_2 was not enhanced the removal of DOC. The initial pH of 3 obtained the least biodegradability increase while the other pHs of 3 and 4 provided the same value of biodegradability increase.

Besides, the optimal reaction times of DOC and biodegradability enhancement were found at 120 minutes and 60 minutes, respectively.

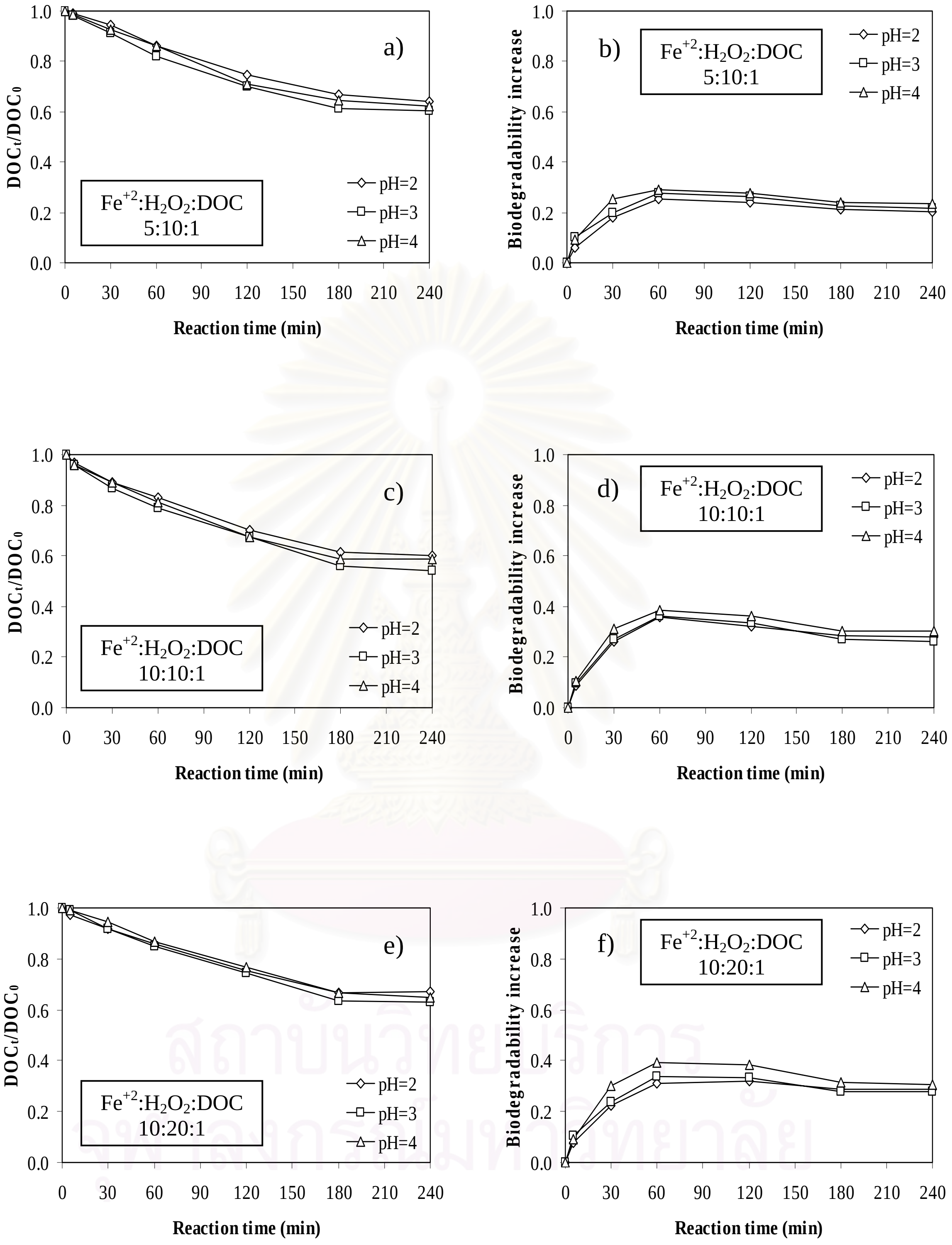


Figure 4.13 Dissolved organic carbon and biodegradability increase of TCP versus reaction time for (a) and (b) $Fe^{+2}:H_2O_2:DOC$ of 5:10:1; (C) and (d) $Fe^{+2}:H_2O_2:DOC$ of 10:10:1; and (e) and (f) $Fe^{+2}:H_2O_2:DOC$ of 10:20:1 at pH of 2, 3, and 4

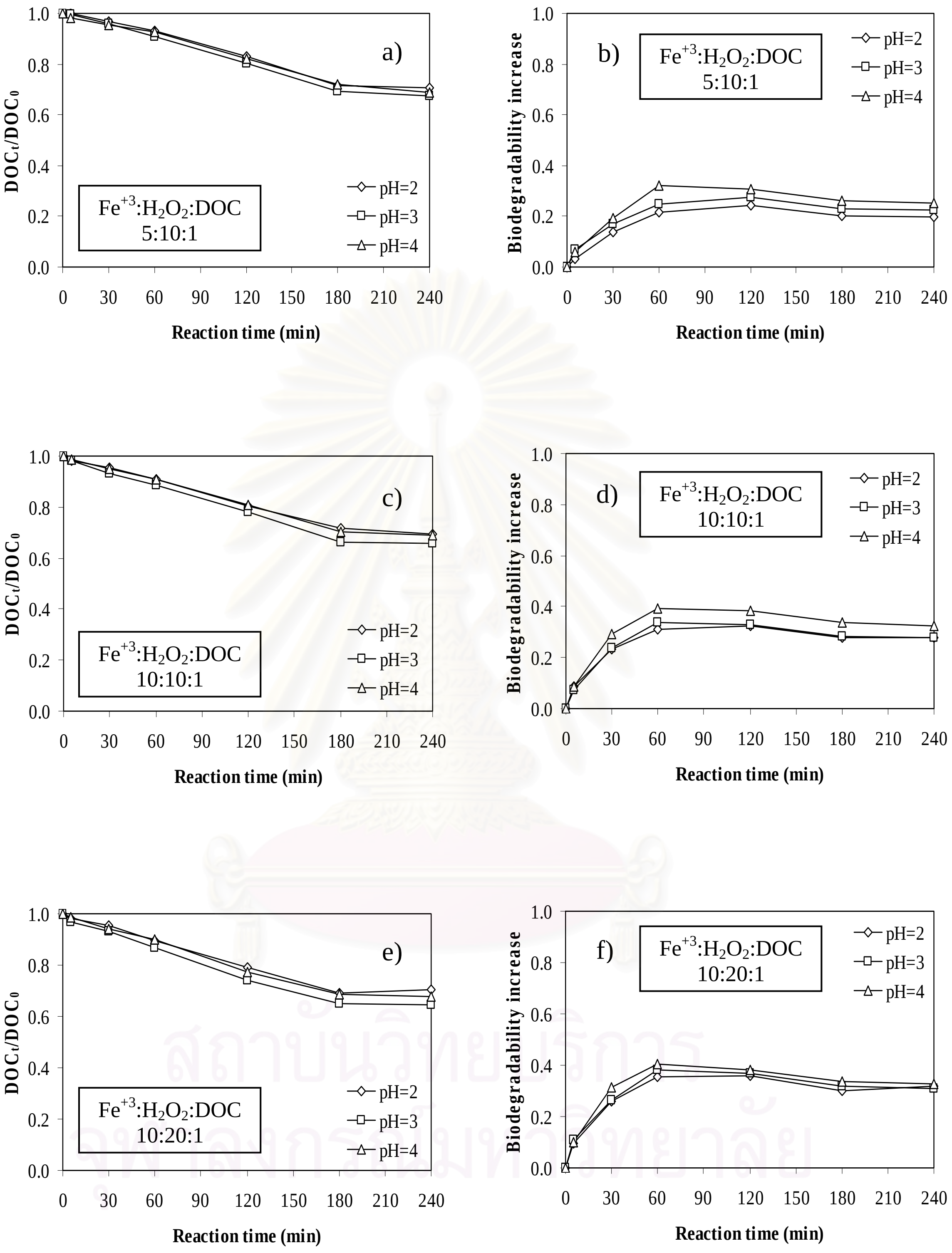


Figure 4.14 Dissolved organic carbon and biodegradability increase of TCP versus reaction time for (a) and (b) Fe^{+3}:H_2O_2:DOC of 5:10:1; (C) and (d) Fe^{+3}:H_2O_2:DOC of 10:10:1; and (e) and (f) Fe^{+3}:H_2O_2:DOC of 10:20:1 at pH of 2, 3, and 4

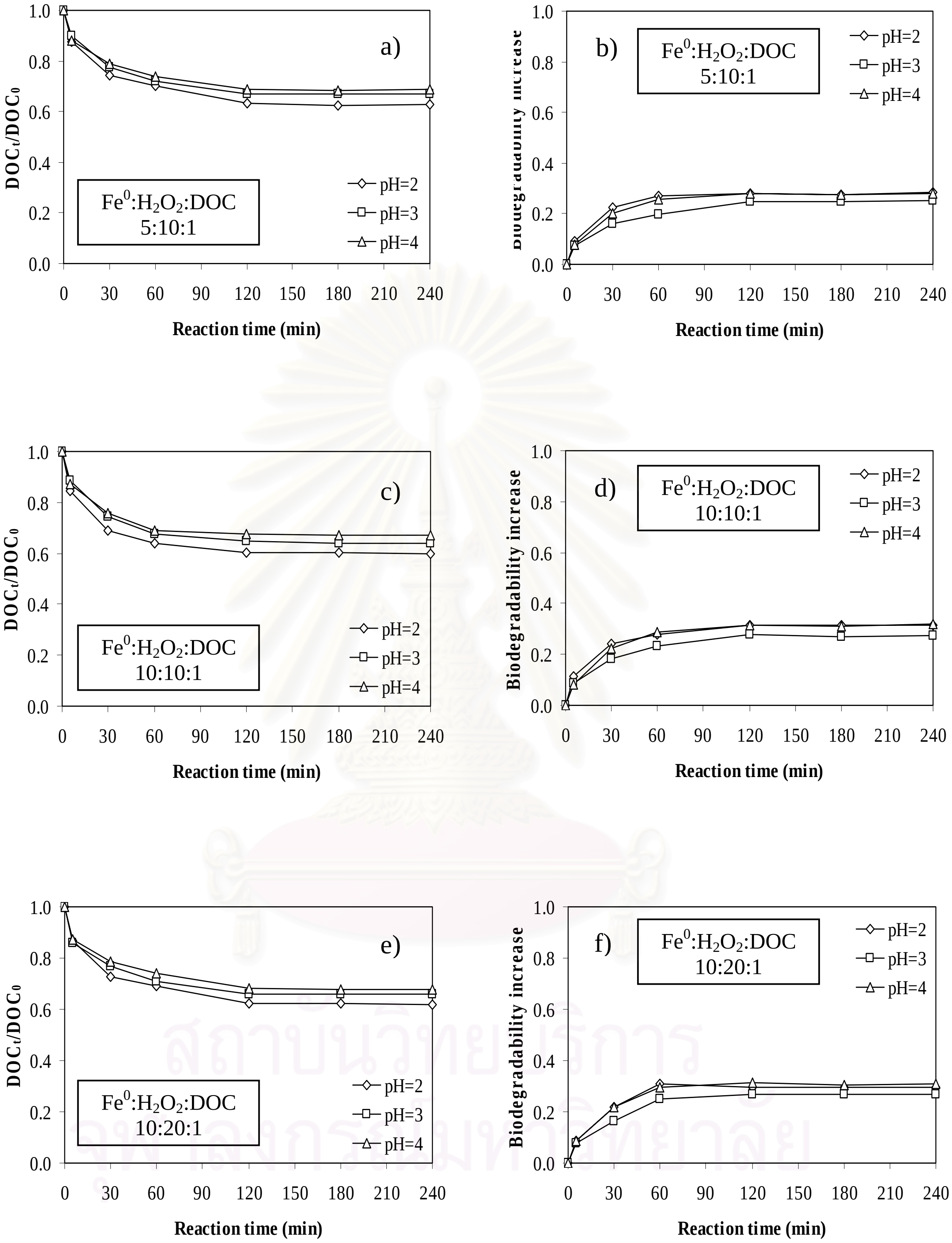
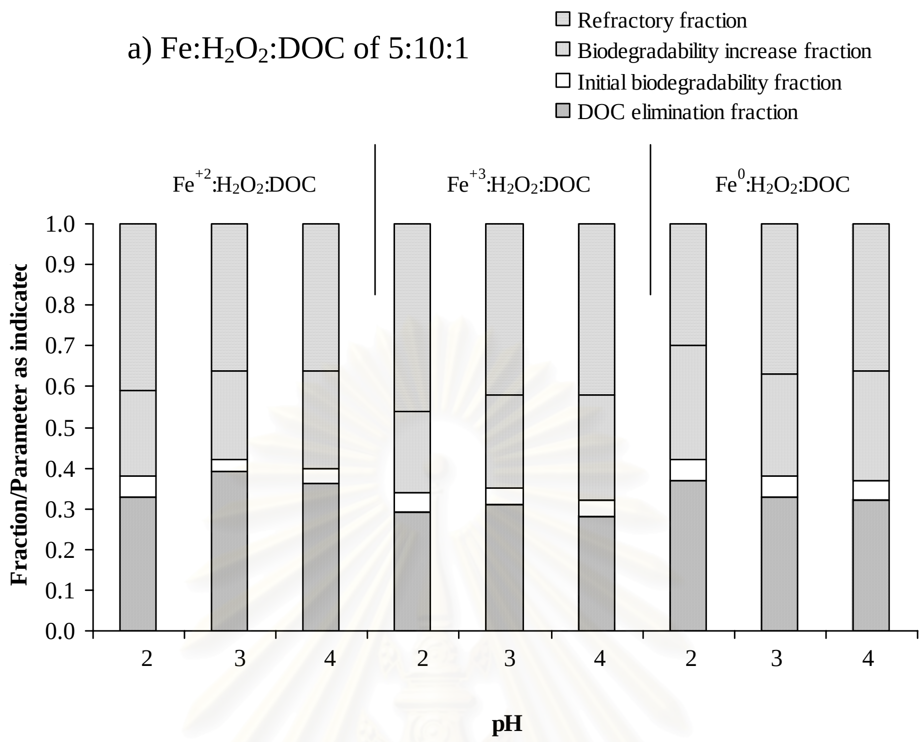


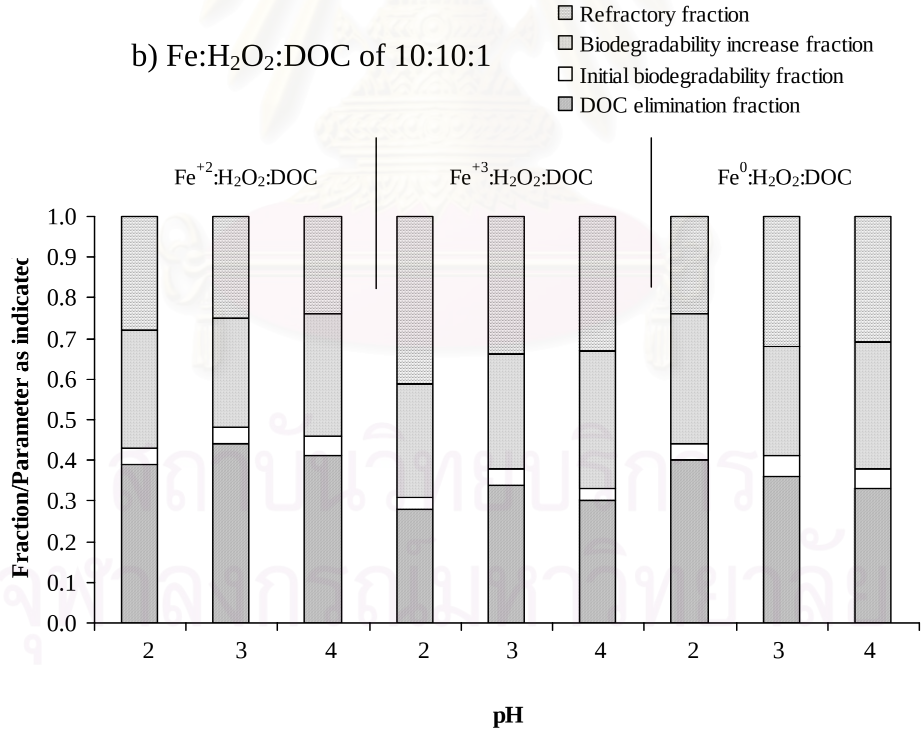
Figure 4.15 Dissolved organic carbon and biodegradability increase of TCP versus reaction time for (a) and (b) Fe^0:H$_2$O$_2$:DOC of 5:10:1; (C) and (d) Fe^0:H$_2$O$_2$:DOC of 10:10:1; and (e) and (f) Fe^0:H$_2$O$_2$:DOC of 10:20:1 at pH of 2, 3, and 4

4.4.4 Effects of type of iron on mineralization and biodegradability increase performances and their kinetics

Figure 4.15 presents the DOC elimination, biodegradability increase and refractory fractions at the optimal reaction time and initial biodegradability of the TCP solution. The initial biodegradability fractions were observed in the range of 0.03 to 0.05. The best condition for DOC reduction was at the ratio of Fe^{+2}:H_2O_2:DOC of 10:10:1 and pH of 3. The largest biodegradability increase was observed at the ratio of Fe^{+3}: H_2O_2:DOC of 10:10:1 and 10:20:1 and pH of 4. The optimal condition for biodegradability increase of the TCP solution was 10:10:1 and pH of 4 because less amount of H_2O_2 was added. In addition, the best conditions for a combination of DOC elimination and biodegradability increase were found as the ratio of iron (Fe^{+2} and Fe^0) H_2O_2:DOC of 10:10:1 and pH of 4 and 2, respectively. The maximum increase of biodegradability was 11.33 times of the initial biodegradability. To achieve the least quantity of refractory fraction, the ratio of Fe^{+2}: H_2O_2:DOC of 10:10:1 and pH of 4 should be adopted because less acid was needed to lower the pH of the TCP solution.



a) Fe:H_2O_2:DOC of 5:10:1



b) Fe:H_2O_2:DOC of 10:10:1

Figure 4.16 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the TCP solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

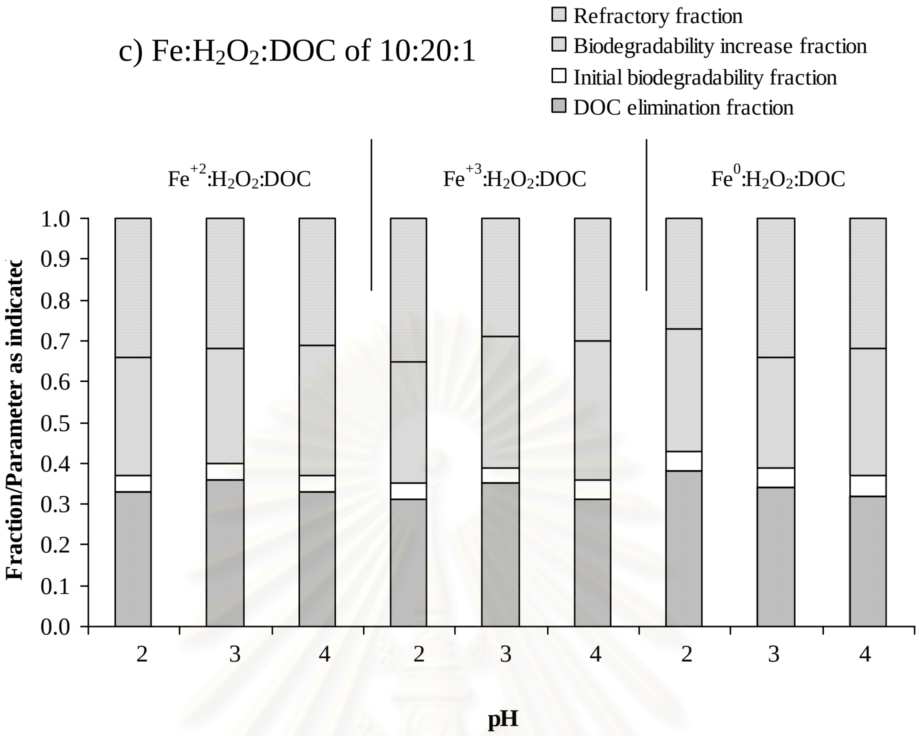


Figure 4.16 Dissolved organic carbon elimination, biodegradability increase, and refractory fractions at the optimal reaction time and initial biodegradability of the TCP solution for each type of iron in Fenton reaction (a) 5:10:1; (b) 10:10:1; and (c) 10:20:1.

4.3.5 Effects of pH, Fe:H_2O_2:DOC ratio, type of iron on mineralization and biodegradability increase kinetics

The mineralization kinetic of TCP was presented in the Table 4.7. From this Table, it could be seen that the pseudo-first order reaction was fitted to Fe^{+2} as well as Fe^{+3} while the second order reaction was best fitted to Fe^0. For the pseudo-first order, in order to increasing the rate constant, more the amount of Fe should be added. While double dosing of H_2O_2 affected to increase the rate constant of Fe^{+2} and Fe^0. In contrast, higher amount of H_2O_2 provided to decrease rate constant of Fe^{+3}. This could be explained that the higher amount of H_2O_2 could inhibit the reaction by hydroxyl scavenger. Moreover, pH was not evidently effect to rate constant.

Table 4.9 shows the rate constant of biodegradability of TCP, it could be said that the rate constant increased while increasing the amount of Fe. The more quantity of H_2O_2 was not significantly increase the rate constant of biodegradability. pH of 4 provided the highest rate constant, except Fe^0 and the pH of 2. The rate constant was not significant difference in each condition of Fenton processes.

Table 4.7 The mineralization kinetic of TCP

Type of iron	**Fe:H_2O_2:DOC**	**pH**	**Rate constant (k)**	**R^2**
Fe^{+2}	5:10:1	2	0.0024 1/min	0.9841
		3	0.0032 1/min	0.9987
		4	0.0025 1/min	0.9992
	10:10:1	2	0.0030 1/min	0.9821
		3	0.0038 1/min	0.9848
		4	0.0033 1/min	0.9860
	10:20:1	2	0.0024 1/min	0.9906
		3	0.0028 1/min	0.9993
		4	0.0023 1/min	0.9876
Fe^{+3}	5:10:1	2	0.0013 1/min	0.9945
		3	0.0016 1/min	0.9986
		4	0.0012 1/min	0.9734
	10:10:1	2	0.0015 1/min	0.9887
		3	0.0019 1/min	0.9884
		4	0.0016 1/min	0.9957
	10:20:1	2	0.0017 1/min	0.9778
		3	0.0022 1/min	0.9821
		4	0.0017 1/min	0.9915
Fe^0	5:10:1	2	0.0015 L/min-mg	0.8784
		3	0.0014 L/min-mg	0.9160
		4	0.0012 L/min-mg	0.8740
	10:10:1	2	0.0019 L/min-mg	0.8798
		3	0.0017 L/min-mg	0.9381
		4	0.0016 L/min-mg	0.9192
	10:20:1	2	0.0016 L/min-mg	0.8607
		3	0.0014 L/min-mg	0.8780
		4	0.0012 L/min-mg	0.8419

Table 4.8 The biodegradability kinetic of TCP

Type of iron	**Fe:H_2O_2:DOC**	**pH**	**Rate constant (k)**	**R^2**
Fe^{+2}	5:10:1	2	0.0247 mg/L-min	0.9705
		3	0.0265 mg/L-min	0.8752
		4	0.0345 mg/L-min	0.9549
	10:10:1	2	0.0367 mg/L-min	0.9667
		3	0.0365 mg/L-min	0.9595
		4	0.0438 mg/L-min	0.9661
	10:20:1	2	0.0310 mg/L-min	0.9621
		3	0.0321 mg/L-min	0.9108
		4	0.0423 mg/L-min	0.9785
Fe^{+3}	5:10:1	2	0.0195 mg/L-min	0.9953
		3	0.0223 mg/L-min	0.9267
		4	0.0262 mg/L-min	0.9800
	10:10:1	2	0.0309 mg/L-min	0.9500
		3	0.0331 mg/L-min	0.9789
		4	0.0412 mg/L-min	0.9827
	10:20:1	2	0.0341 mg/L-min	0.9533
		3	0.0350 mg/L-min	0.9298
		4	0.0436 mg/L-min	0.9750
Fe^0	5:10:1	2	0.0297 mg/L-min	0.9387
		3	0.0213 mg/L-min	0.9014
		4	0.0278 mg/L-min	0.9458
	10:10:1	2	0.0322 mg/L-min	0.8847
		3	0.0241 mg/L-min	0.8892
		4	0.0304 mg/L-min	0.9512
	10:20:1	2	0.0284 mg/L-min	0.9445
		3	0.0206 mg/L-min	0.8923
		4	0.0289 mg/L-min	0.9433

4.4.6 Degradation by-products

From the study, 100% of the initial concentration of TCP was depleted, while 4 main products namely 1,3-dichloro-2-propanone, 2,3-dichloro-1-propene, isopropanol and propionic aldehyde were generated depending on the types of Fe. For the Fe^{+2} and Fe^{+3} in Fenton’s reaction of TCP found 1,3-dichloro-2-propanone and 2,3-dichloro-1-propene as the major by-products. These by-products undergo further oxidative degradation initiated by $OH^{\bullet}$ which is generated from the reaction between Fe^{+2}/Fe^{+3} and H_2O_2 as explanation above. Hydroxyl radical can oxidize organic substrates by different types of reactions (Legrini, 1993; Hoigne, 1998) such as electron transfer, hydrogen abstraction and electrophilic addition. For Fe^0, isopropanol and propionic aldehydes were identified as the major by-products. It can be explained by as follows. Firstly, Fe^0 corrodes, Fe^{+2} is released into aqueous phase, couple with the production of two electrons. Then, the presence of Fe^{+2}, the reaction system is shifted to Fenton’s oxidation and the electrons provide the reductive dechlorination of TCP.

4.5 Comparisons of results of compounds studied

Mostly, the optimal time for mineralization of compounds studied was found at 120 minutes for all conditions except 2,4-DCP with Fe^{+3} and TCP with both Fe^{+2} and Fe^{+3} ratios. For the biodegradability, the optimal time provided for the most effective was observed at 60 minutes. The kinetic of mineralization and biodegradability were also considered in order to understand the enhancement of both mineralization and biodegradability. Regarding the mineralization, the reaction rate of pseudo-first order and second order were obtained. The amount of iron presented the effect on mineralization by increasing the rate constant. While the biodegradability reaction, the zero order was found for all studied compounds and conditions. Increasing the amount of H_2O_2 and iron did not evidently show an effect to increase the rate of biodegradability.

Table 4.9 illustrates the optimal conditions for Fenton degradation of TCE, 2,4-DCP, 1,4-D and TCP at the optimal reaction time for each compound. For the elimination of DOC, pH 3 was the most effective for TCE, 1,4-D and TCP while pH 2 provided the maximum DOC reduction of 2,4-DCP. Fe^{+2} was considered the best type of iron for DOC elimination of TCE, 1,4-D and TCP. Moreover, the higher amount of H_2O_2 provided the more DOC removal, except for TCP. In addition, the optimal condition for DOC elimination and biodegradability increase were not necessarily to be the same. For the combination of DOC elimination and biodegradability increase, the optimal conditions were 10:20:1 as Fe^{+2} and pH 4 and 3 for TCE, 2,4-DCP and 1,4-D, respectively. For TCP, the optimal conditions for DOC elimination combined with biodegradability increase were Fe^{+2}:H_2O_2:DOC of 10:10:1 and pH 4.

Table 4.9 Optimal conditions for TCE, 2,4-DCP, 1,4-D and TCP solution in DOC elimination, biodegradability increase and a combination of DOC elimination and biodegradability increase

	TCE	**2,4-DCP**	**1,4-D**	**TCP**
DOC elimination	^{a} 10:20:1 pH = 3	^{c} 10:20:1 pH = 2	^{a} 10:20:1 pH = 3	^{a} 10:10:1 pH = 3
Biodegradability increase	^{b} 5:10:1 pH = 2	^{c} 5:10:1 pH = 2	^{a} 10:20:1 pH = 3	^{b} 10:10:1 pH = 4
DOC elimination + biodegradability increase	^{a} 10:20:1 pH = 4	^{a}10:20:1 pH = 4	^{a} 10:20:1 pH = 3	^{a} 10:10:1 pH = 4

^{a} Fe^{+2}: H_2O_2:DOC, ^{b} Fe^{+3}:H_2O_2:DOC and ^{c} Fe^0:H_2O_2:DOC

CHAPTER V
CONCLUSIONS AND RECOMMENTDATIONS

5.1 Conclusions

This research attempted to compare the mineralization and biodegradability increase and their combination of two traditional and two emerging organic contaminants by Fenton reagents with three different types of iron, Fe^{2+}, Fe^{3+}, and Fe^0. The traditional contaminants investigated were TCE and 2,4-DCP while 1,4-D and TCP were studied for the emerging contaminants. Three ratios of Fe:H_2O_2:DOC and pH of 2, 3 and 4 were tested at reaction time of 5, 15, 30, 60, 120, 180 and 240 minutes. The mineralization and biodegradability were represented by DOC reduction and BDOC/DOC, respectively.

For all four contaminants, Fenton reagent using Fe^{+2} was more effective in the DOC reduction than the modified Fenton's reagents using Fe^{+3} and Fe^0. The optimum Fe:H_2O_2:DOC for DOC elimination were Fe^{+2}: H_2O_2:DOC of 10:20:1 for TCE, 1,4-D and TCP and Fe^{+2}:H_2O_2:DOC of 10:10:1 for 2,4-DCP. Increasing of H_2O_2 dose provided increase in the DOC reduction. Refractory DOC remained at all conditions for all four contaminants. The types of Fe that provided maximum biodegradability increase were not the same for the four compounds. The optimum Fe: H_2O_2:DOC for biodegradability increase were Fe^{+3}:H_2O_2:DOC of 5:10:1, Fe^0:H_2O_2:DOC of 5:10:1, Fe^{+2}:H_2O_2:DOC of 10:20:1 and Fe^{+3}: H_2O_2:DOC of 10:10:1 for TCE, 2,4-DCP, 1,4-D and TCP, respectively.

The initial pH of the experiments between 2 and 4 did not obviously influence on the DOC reduction and biodegradability increase. An optimum pH of 3 was observed for DOC reduction of TCE, 1,4-D and TCP solutions while the optimum pH for 2,4-DCP solution was 2. The initial pH of 2 was the optimum pH of TCE and 2,4-DCP, for biodegradability increase except for the 1,4-D and TCP solution were found the optimum pH of 3 and 4, respectively.

It was found that the optimum conditions (pH and ratio of Fe:H_2O_2:DOC) for DOC elimination and biodegradability increase were not necessarily to be the same.

The most effective Fe: H_2O_2:DOC and pH of TCE, 2,4-DCP, 1,4-D and TCP for the combination of DOC elimination and biodegradability increase were Fe^{+2}: H_2O_2:DOC of 10:20:1 and pH 4, Fe^0:H_2O_2:DOC of 10:20:1 and 2, Fe^{+2}:H_2O_2:DOC of 10:20:1 and pH 3 and Fe^{+2}:H_2O_2:DOC of 10:10:1 and pH 4, respectively.

The DOC reduction occurred mostly within 120 minutes except for Fe^{+3} in Fenton reagent for 2,4-DCP and TCP and Fe^{+2} in Fenton reagent for TCP were 180 minutes. The biodegradability enhancement for all reactions was completed within 60 minutes. The oxidation at such reaction times could accomplish 90% of the DOC reduction and biodegradability increase.

The mineralization kinetics of TCE, 2,4-DCP, and TCP were fitted to the pseudo-first order reaction for Fe^{+2} and Fe^{+3}, while the second order reaction was considered for Fe^0. In case of 1,4-dioxane performed the pseudo-first order reaction for all three iron, Fe^{+2}, Fe^{+3} and Fe^0. For the kinetic of biodegradability, the zero order reaction was obtained for all compounds and conditions.

Due to the remaining of DOC throughout each experiment indicated the organic contaminants were incomplete oxidized to CO_2. The contaminants were transformed into intermediates by Fenton and modified Fenton oxidation. Phosgene, DCAC ethene, ethane and VC were formed as the by-products of TCE while chlorohydroquinone, 4-chlorocatechol, 2,chloro-1,4-benzoquinone, 3,5-dichlororesorcinol, 4,6-dichlororesorcinol hydroquinone and catechol were detected as the by-products of 2,4-DCP.For 1,4-D, 1,2-ethanediol monoformate, 1,2-ethanediol diformate, formic acid and methoxyacetic acid were produced and some or all of them remained in the reaction mixture. 1,3-dichloro-2-propanone, 2,3-dichloro-1-propene, isopropanol and propionic aldehyde were generated as the by-products of TCP.

5.2 Recommendations

Recommendations for future studies are as follows.

1) This research studied the oxidation by-products of Fenton and modified Fenton's processes. Analysis the by-products after BDOC incubation to see which by-product(s) contribute to BDOC and which are recalcitrant should be investigated. Also, monitoring the parent compound through the entire experiment (including after BDOC incubation) of contaminants should be studied in the future.

2) Using Fe^{+2}, Fe^{+3} and Fe^0 as the major sources of iron in Fenton process was tested. A study on the other source of iron in Fenton's oxidation should be investigated.

3) In this research only 4 synthetic wastewater sample were examined, therefore the different types of wastewater sample such as real wastewater and other complex synthetic organic compounds should be applied. Adjustments of H_2O_2:DOC ratio and pH ranges tested also may be required.

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APPENDICES

APPENDIX A

Table A-1 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the TCE solution used in the Fe^{+2}:H_2O_2:DOC

Condition Fe^{+2}:H_2O_2:DOC	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	3.05	0.18	0.06
	3	2.90	0.17	0.06
	4	3.18	0.15	0.05
10:10:1	2	3.21	0.10	0.03
	3	3.05	0.19	0.06
	4	3.17	0.18	0.06
10:20:1	2	2.94	0.04	0.01
	3	3.14	0.17	0.05
	4	3.17	0.17	0.05

Table A-2 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the TCE solution used in the Fe^{+3}:H_2O_2:DOC

Condition Fe^{+3}:H_2O_2:DOC	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	3.17	0.17	0.05
	3	3.13	0.09	0.03
	4	2.93	0.08	0.03
10:10:1	2	3.20	0.16	0.05
	3	2.89	0.10	0.03
	4	2.95	0.11	0.04
10:20:1	2	2.99	0.19	0.06
	3	3.16	0.10	0.03
	4	3.01	0.15	0.05

Table A-3 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the TCE solution used in the $Fe^0:H_2O_2:DOC$

Condition $Fe^0:H_2O_2:DOC$	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	3.22	0.11	0.03
	3	3.36	0.14	0.04
	4	3.15	0.13	0.04
10:10:1	2	3.35	0.11	0.03
	3	3.18	0.19	0.06
	4	3.21	0.11	0.03
10:20:1	2	3.27	0.19	0.06
	3	3.33	0.21	0.06
	4	3.35	0.15	0.04

Table A-4 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the 2,4-DCP solution used in the $Fe^{+2}:H_2O_2:DOC$

Condition $Fe^{+2}:H_2O_2:DOC$	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	8.53	0.33	0.04
	3	8.84	0.43	0.05
	4	8.66	0.32	0.04
10:10:1	2	8.65	0.47	0.05
	3	8.73	0.41	0.05
	4	8.60	0.39	0.05
10:20:1	2	8.48	0.35	0.04
	3	8.62	0.37	0.04
	4	8.42	0.38	0.05

Table A-5 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the 2,4-DCP solution used in the Fe^{+3}:H_2O_2:DOC

Condition	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
Fe^{+3}:H_2O_2:DOC				
5:10:1	2	8.27	0.35	0.04
	3	8.48	0.45	0.05
	4	8.63	0.42	0.05
10:10:1	2	8.55	0.28	0.03
	3	8.73	0.42	0.05
	4	8.47	0.32	0.04
10:20:1	2	8.72	0.44	0.05
	3	8.66	0.36	0.04
	4	8.36	0.31	0.04

Table A-6 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the 2,4-DCP solution used in the Fe^0:H_2O_2:DOC

Condition	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
Fe^0:H_2O_2:DOC				
5:10:1	2	8.44	0.34	0.04
	3	8.25	0.37	0.04
	4	8.41	0.49	0.06
10:10:1	2	8.59	0.34	0.04
	3	8.33	0.39	0.05
	4	8.48	0.36	0.04
10:20:1	2	8.73	0.45	0.05
	3	8.56	0.40	0.05
	4	8.97	0.52	0.06

Table A-7 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the 1,4-D solution used in the Fe^{+2}:H_2O_2:DOC

Condition Fe^{+2}:H_2O_2:DOC	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	13.57	0.47	0.03
	3	13.58	0.53	0.04
	4	12.41	0.37	0.03
10:10:1	2	12.32	0.44	0.04
	3	13.01	0.50	0.04
	4	12.43	0.41	0.03
10:20:1	2	13.14	0.55	0.04
	3	12.73	0.50	0.04
	4	13.11	0.53	0.04

Table A-8 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the 1,4-D solution used in the Fe^{+3}:H_2O_2:DOC

Condition Fe^{+3}:H_2O_2:DOC	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	13.46	0.58	0.04
	3	13.24	0.50	0.04
	4	12.35	0.38	0.03
10:10:1	2	13.44	0.56	0.04
	3	13.47	0.58	0.04
	4	12.30	0.49	0.04
10:20:1	2	13.47	0.52	0.04
	3	13.29	0.52	0.04
	4	12.29	0.50	0.04

Table A-9 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the 1,4-D solution used in the Fe^0:H_2O_2:DOC

Condition Fe^0:H_2O_2:DOC	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	13.34	0.37	0.03
	3	13.63	0.40	0.03
	4	13.56	0.37	0.03
10:10:1	2	12.54	0.49	0.04
	3	13.55	0.42	0.03
	4	12.43	0.47	0.04
10:20:1	2	13.42	0.60	0.04
	3	13.29	0.57	0.04
	4	12.86	0.53	0.04

Table A-9 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the TCP solution used in the Fe^{+2}:H_2O_2:DOC

Condition Fe^{+2}:H_2O_2:DOC	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
5:10:1	2	4.39	0.20	0.05
	3	4.54	0.12	0.03
	4	4.39	0.19	0.04
10:10:1	2	4.51	0.18	0.04
	3	4.38	0.19	0.04
	4	4.49	0.23	0.05
10:20:1	2	4.48	0.18	0.04
	3	4.55	0.16	0.04
	4	4.42	0.19	0.04

Table A-11 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the TCP solution used in the $Fe^{+3}:H_2O_2:DOC$

Condition	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
$Fe^{+3}:H_2O_2:DOC$				
5:10:1	2	4.42	0.22	0.05
	3	4.40	0.16	0.04
	4	4.35	0.17	0.04
10:10:1	2	4.34	0.13	0.03
	3	4.42	0.17	0.04
	4	4.44	0.12	0.03
10:20:1	2	4.29	0.17	0.04
	3	4.38	0.18	0.04
	4	4.43	0.24	0.05

Table A-12 Initial DOC, BDOC, and biodegradability (BDOC/DOC) of the TCP solution used in the $Fe^0:H_2O_2:DOC$

Condition	pH	DOC_0 (mg/l)	$BDOC_0$ (mg/l)	$BDOC_0/DOC_0$
$Fe^0:H_2O_2:DOC$				
5:10:1	2	4.32	0.20	0.05
	3	4.47	0.23	0.05
	4	4.55	0.23	0.05
10:10:1	2	4.56	0.20	0.04
	3	4.48	0.22	0.05
	4	4.39	0.21	0.05
10:20:1	2	4.26	0.23	0.05
	3	4.30	0.23	0.05
	4	4.31	0.21	0.05

Table A-13 Dissolved organic carbon of TCE for the ratio of $Fe^{+2}:H_2O_2:DOC$ of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:10:1, pH=2**		**5:10:1, pH=3**		**5:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	3.05	2.87	2.90	2.73	3.18	3.03
5	3.03	2.54	2.83	2.30	3.03	2.48
30	2.73	1.87	2.47	1.70	2.81	1.84
60	2.27	1.36	2.09	1.27	2.38	1.33
120	1.86	1.03	1.52	0.80	1.81	0.87
180	1.77	1.00	1.37	0.72	1.77	0.84
240	1.68	0.97	1.40	0.71	1.72	0.82

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-14 Dissolved organic carbon of TCE for the ratio of $Fe^{+2}:H_2O_2:DOC$ of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	3.21	3.11	3.05	2.86	3.17	2.99
5	3.05	2.58	2.83	2.27	2.99	2.42
30	2.68	1.90	2.43	1.64	2.63	1.76
60	2.04	1.29	1.84	1.10	1.98	1.13
120	1.85	0.96	1.52	0.76	1.75	0.82
180	1.88	0.97	1.49	0.73	1.72	0.75
240	1.82	0.93	1.45	0.70	1.71	0.74

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-15 Dissolved organic carbon of TCE for the ratio of Fe^{+2}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	2.94	2.90	3.14	2.97	3.17	3.00
5	2.79	2.23	2.88	2.38	2.98	2.43
30	2.43	1.66	2.39	1.67	2.57	1.70
60	2.11	1.29	1.90	1.12	2.10	1.20
120	1.65	0.88	1.37	0.70	1.49	0.69
180	1.65	0.85	1.31	0.66	1.61	0.74
240	1.59	0.82	1.27	0.64	1.59	0.71

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-16 Dissolved organic carbon of TCE for the ratio of Fe^{+3}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:10:1, pH=2**		**5:10:1, pH=3**		**5:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	3.17	3.00	3.13	3.04	2.93	2.85
5	3.15	2.63	3.10	2.59	2.89	2.43
30	2.99	1.94	2.91	1.95	2.59	1.78
60	2.58	1.56	2.38	1.53	2.17	1.42
120	2.05	1.00	1.93	1.02	1.75	0.95
180	2.01	1.02	1.87	1.00	1.67	0.92
240	1.93	0.97	1.83	0.97	1.68	0.93

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-17 Dissolved organic carbon of TCE for the ratio of Fe^{+3}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	3.20	3.04	2.89	2.79	2.95	2.84
5	3.11	2.72	2.77	2.41	2.77	2.40
30	2.87	2.04	2.52	1.85	2.59	1.83
60	2.54	1.48	2.22	1.34	2.17	1.32
120	2.02	1.02	1.85	1.00	1.69	0.96
180	1.98	1.01	1.79	0.96	1.71	0.95
240	1.95	0.98	1.74	0.92	1.65	0.92

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-18 Dissolved organic carbon of TCE for the ratio of Fe^{+3}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	2.99	2.80	3.16	3.06	3.01	2.86
5	2.83	2.44	2.95	2.41	2.79	2.41
30	2.59	1.85	2.72	1.88	2.48	1.74
60	2.34	1.38	2.40	1.47	2.11	1.32
120	1.84	0.98	1.80	1.02	1.73	0.99
180	1.90	0.96	1.82	1.00	1.68	0.97
240	1.82	0.91	1.79	0.99	1.65	0.94

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-19 Dissolved organic carbon of TCE for the ratio of Fe^0:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:20:1, pH=2**		**5:20:1, pH=3**		**5:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	3.22	3.11	3.36	3.22	3.15	3.02
5	2.73	1.94	2.77	1.91	2.73	1.97
30	2.22	1.32	2.25	1.28	2.26	1.49
60	2.05	1.21	2.06	1.13	2.16	1.35
120	2.06	1.16	2.02	1.06	2.17	1.29
180	2.04	1.11	1.98	1.02	2.17	1.27
240	2.03	1.13	1.96	0.99	2.15	1.26

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-20 Dissolved organic carbon of TCE for the ratio of Fe^0:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	3.35	3.24	3.18	2.99	3.21	3.10
5	2.80	1.95	2.55	1.71	2.77	1.97
30	2.24	1.30	2.08	1.15	2.29	1.45
60	2.01	1.16	1.77	0.94	2.01	1.20
120	1.99	1.10	1.73	0.83	1.99	1.15
180	2.00	1.08	1.70	0.82	2.00	1.11
240	1.96	1.06	1.71	0.80	1.98	1.13

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-21 Dissolved organic carbon of TCE for the ratio of Fe^0:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC$_i$	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**
0	3.27	3.08	3.33	3.12	3.35	3.20
5	2.75	1.95	2.70	1.88	2.96	2.25
30	2.21	1.26	2.16	1.19	2.40	1.53
60	2.05	1.04	1.97	0.91	2.23	1.23
120	2.00	1.01	1.92	0.92	2.18	1.17
180	1.98	0.99	1.90	0.93	2.20	1.18
240	2.01	1.00	1.90	0.92	2.17	1.16

DOC$_i$ = DOC (mg/l) before the incubation; DOC$_f$ = DOC (mg/l) after the incubation

Table A-22 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^{+2}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:20:1, pH=2**		**5:20:1, pH=3**		**5:20:1, pH=4**	
	DOC$_i$	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**
0	8.53	8.20	8.84	8.41	8.66	8.34
5	8.24	6.98	8.40	6.94	8.17	6.63
30	7.53	6.04	7.49	5.75	7.14	5.38
60	6.88	5.26	6.82	4.88	6.53	4.59
120	5.64	3.85	5.63	3.65	5.25	3.33
180	5.57	3.80	5.52	3.61	5.35	3.35
240	5.42	3.71	5.47	3.54	5.24	3.32

DOC$_i$ = DOC (mg/l) before the incubation; DOC$_f$ = DOC (mg/l) after the incubation

Table A-23 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^{+2}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	8.65	8.18	8.73	8.32	8.60	8.21
5	8.05	6.72	8.15	6.53	8.02	6.36
30	7.27	5.54	7.29	5.19	7.28	5.00
60	6.43	4.63	6.13	4.03	6.11	3.92
120	5.70	3.47	5.48	3.15	5.39	2.93
180	5.68	3.40	5.46	3.11	5.24	2.89
240	5.61	3.35	5.46	3.10	5.21	2.84

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-24 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^{+2}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	8.48	8.13	8.62	8.25	8.42	8.04
5	8.03	6.31	8.18	6.28	7.82	5.83
30	7.38	5.36	7.53	5.04	6.73	4.32
60	6.32	4.04	6.24	3.71	5.57	3.07
120	5.48	2.87	5.32	2.56	4.83	2.15
180	5.42	2.84	5.24	2.50	4.68	2.11
240	5.42	2.83	5.19	2.44	4.62	2.02

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-25 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^{+3}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	5:10:1, pH=2		5:10:1, pH=3		5:10:1, pH=4	
	DOC_i	DOC_f	DOC_i	DOC_f	DOC_i	DOC_f
0	8.27	7.92	8.48	8.03	8.63	8.21
5	8.12	7.04	8.42	6.78	8.51	6.96
30	7.87	6.33	8.03	6.02	8.19	6.34
60	7.25	5.52	7.28	4.86	7.24	5.08
120	6.32	4.48	6.33	3.94	6.13	4.03
180	5.70	4.00	5.67	3.50	5.67	3.70
240	5.72	3.99	5.65	3.48	5.59	3.63

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-26 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^{+3}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	10:10:1, pH=2		10:10:1, pH=3		10:10:1, pH=4	
	DOC_i	DOC_f	DOC_i	DOC_f	DOC_i	DOC_f
0	8.55	8.27	8.73	8.31	8.47	8.15
5	8.38	6.94	8.54	6.80	8.14	6.67
30	7.93	6.10	8.10	6.01	7.68	5.78
60	7.22	5.32	7.30	4.73	6.82	4.62
120	6.48	4.09	6.43	3.76	6.19	3.70
180	5.64	3.55	5.59	3.20	5.16	3.03
240	5.62	3.53	5.60	3.17	5.15	3.05

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-27 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^{+3}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	8.72	8.28	8.66	8.30	8.36	8.05
5	8.46	6.83	8.47	6.76	8.12	6.48
30	7.89	5.71	7.63	5.12	7.39	5.18
60	7.12	4.62	6.82	3.99	6.43	3.92
120	6.41	3.66	5.98	2.98	5.46	3.01
180	5.38	3.01	5.18	2.65	4.81	2.59
240	5.36	2.98	5.20	2.59	4.79	2.54

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-28 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^0:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:20:1 pH=2**		**5:20:1 pH=3**		**5:20:1 pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	8.44	8.10	8.25	7.88	8.41	7.92
5	7.53	6.00	7.39	6.26	7.66	6.62
30	6.44	4.23	6.51	4.58	7.01	5.18
60	6.02	3.37	5.99	3.89	6.28	4.14
120	5.34	2.41	5.48	2.74	5.74	3.01
180	5.37	2.36	5.46	2.74	5.71	2.99
240	5.31	2.37	5.41	2.70	5.63	2.90

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-29 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^0:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1 pH=2**		**10:10:1 pH=3**		**10:10:1 pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	8.59	8.25	8.33	7.94	8.48	8.12
5	7.42	5.81	7.40	6.07	7.66	6.42
30	6.38	4.05	6.48	4.36	6.68	4.60
60	5.64	3.09	5.73	3.42	5.92	3.73
120	5.11	2.17	5.15	2.45	5.40	2.82
180	5.07	2.11	5.17	2.47	5.38	2.74
240	5.03	2.09	5.11	2.44	5.32	2.70

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-30 Dissolved organic carbon of 2,4-DCP for the ratio of Fe^0:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1 pH=2**		**10:20:1 pH=3**		**10:20:1 pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	8.73	8.28	8.56	8.16	8.97	8.45
5	7.34	5.63	7.46	5.82	7.87	6.29
30	6.32	3.88	6.43	4.14	6.83	4.57
60	5.58	2.76	5.62	3.28	6.26	3.70
120	4.89	1.86	5.00	2.13	5.49	2.49
180	4.86	1.83	5.00	2.06	5.44	2.46
240	4.85	1.79	4.98	2.05	5.41	2.45

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-31 Dissolved organic carbon of 1,4-D for the ratio of Fe^{+2}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:20:1, pH=2**		**5:20:1, pH=3**		**5:20:1, pH=4**	
	DOC$_i$	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**
0	13.57	13.10	13.58	13.05	12.41	12.04
5	13.44	11.82	13.45	11.53	12.32	10.86
30	13.38	10.36	13.32	9.32	12.20	9.15
60	13.05	9.25	12.98	8.13	11.83	8.21
120	12.83	8.16	12.59	7.08	11.57	7.06
180	12.79	8.19	12.54	7.04	11.55	7.02
240	12.72	8.16	12.55	7.04	11.54	7.00

DOC$_i$ = DOC (mg/l) before the incubation; DOC$_f$ = DOC (mg/l) after the incubation

Table A-32 Dissolved organic carbon of 1,4-D for the ratio of Fe^{+2}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC$_i$	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**
0	12.32	11.88	13.01	12.51	12.43	12.02
5	12.23	10.55	12.92	10.53	12.40	10.44
30	12.04	9.08	12.59	8.36	12.07	8.59
60	11.69	7.11	12.34	6.64	11.65	6.88
120	11.38	6.13	11.95	5.37	11.46	5.84
180	11.38	6.10	11.87	5.31	11.42	5.76
240	11.34	6.08	11.93	5.30	11.37	5.72

DOC$_i$ = DOC (mg/l) before the incubation; DOC$_f$ = DOC (mg/l) after the incubation

Table A-33 Dissolved organic carbon of 1,4-D for the ratio of Fe^{+2}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	13.14	12.59	12.73	12.23	13.11	12.58
5	13.04	10.66	12.60	9.86	12.99	10.41
30	12.83	8.29	12.38	6.82	12.78	7.77
60	12.47	6.27	11.93	5.10	12.29	6.05
120	12.15	5.11	11.57	3.70	12.03	4.77
180	12.07	5.24	11.45	3.64	11.97	4.74
240	12.01	5.19	11.41	3.63	11.94	4.67

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-34 Dissolved organic carbon of 1,4-D for the ratio of Fe^{+3}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:10:1, pH=2**		**5:10:1, pH=3**		**5:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	13.46	12.88	13.24	12.74	12.35	11.97
5	13.40	12.01	13.18	12.02	12.29	11.37
30	13.35	10.55	13.15	10.74	12.29	10.29
60	13.23	8.64	13.00	9.23	12.11	9.24
120	13.17	7.78	12.74	8.38	11.94	8.14
180	13.15	7.73	12.69	8.22	11.92	8.11
240	13.11	7.68	12.66	8.18	11.94	8.06

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-35 Dissolved organic carbon of 1,4-D for the ratio of Fe^{+3}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	13.44	12.88	13.47	12.89	12.30	11.81
5	13.39	11.58	13.37	11.83	12.22	10.84
30	13.25	8.88	13.21	9.49	12.17	8.98
60	13.22	6.36	12.99	7.10	11.95	6.92
120	13.10	5.23	12.83	5.95	11.84	5.80
180	13.11	5.27	12.74	5.90	11.79	5.76
240	13.04	5.20	12.65	5.79	11.72	5.77

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-36 Dissolved organic carbon of 1,4-D for the ratio of Fe^{+3}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	13.47	12.95	13.29	12.77	12.29	11.79
5	13.41	11.86	13.21	11.78	12.19	10.84
30	13.27	9.46	13.06	9.89	12.12	9.36
60	13.10	7.35	12.86	7.94	11.91	7.83
120	12.98	5.74	12.69	6.11	11.85	5.88
180	12.94	5.70	12.64	6.03	11.75	5.76
240	12.95	5.65	12.58	6.00	11.77	5.87

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-37 Dissolved organic carbon of 1,4-D for the ratio of Fe^0:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:20:1 pH=2**		**5:20:1 pH=3**		**5:20:1 pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	13.34	12.97	13.63	13.23	13.56	13.19
5	13.24	12.20	13.52	12.18	13.38	12.12
30	13.10	10.14	13.34	9.31	13.14	9.45
60	13.03	8.68	13.27	8.18	13.09	8.22
120	12.97	7.65	13.22	7.18	13.01	7.55
180	12.94	7.62	13.20	7.15	12.96	7.43
240	12.95	7.58	13.17	7.10	12.95	7.39

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-38 Dissolved organic carbon of 1,4-D for the ratio of Fe^0:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1 pH=2**		**10:10:1 pH=3**		**10:10:1 pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	12.54	12.05	13.55	13.13	12.43	11.96
5	12.42	11.11	13.34	11.68	12.24	10.79
30	12.27	8.39	13.11	8.16	12.13	8.05
60	12.11	6.62	12.93	6.33	11.88	6.32
120	11.94	5.85	12.76	5.26	11.79	5.46
180	11.90	5.81	12.73	5.20	11.73	5.42
240	11.86	5.77	12.74	5.21	11.66	5.37

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-39 Dissolved organic carbon of 1,4-D for the ratio of Fe^0:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	10:20:1 pH=2		10:20:1 pH=3		10:20:1 pH=4	
	DOC_i	DOC_f	DOC_i	DOC_f	DOC_i	DOC_f
0	13.42	12.82	13.29	12.72	12.86	12.33
5	13.22	12.05	13.12	11.74	12.65	11.35
30	13.03	9.19	12.95	8.26	12.38	8.22
60	12.99	8.18	12.78	6.53	12.31	7.19
120	12.91	7.13	12.68	5.96	12.20	6.44
180	12.89	7.11	12.63	5.92	12.17	6.32
240	12.85	7.07	12.64	5.90	12.16	6.29

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-40 Dissolved organic carbon of TCP for the ratio of Fe^{+2}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	5:20:1, pH=2		5:20:1, pH=3		5:20:1, pH=4	
	DOC_i	DOC_f	DOC_i	DOC_f	DOC_i	DOC_f
0	4.39	4.19	4.54	4.42	4.39	4.20
5	4.34	3.88	4.46	3.89	4.32	3.72
30	4.15	3.16	4.14	3.11	4.06	2.75
60	3.79	2.47	3.73	2.36	3.78	2.32
120	3.27	2.02	3.18	1.87	3.12	1.72
180	2.93	1.79	2.79	1.65	2.83	1.59
240	2.81	1.72	2.74	1.63	2.74	1.51

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-41 Dissolved organic carbon of TCP for the ratio of Fe^{+2}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1, pH=2**		**10:10:1, pH=3**		**10:10:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	4.51	4.33	4.38	4.19	4.49	4.26
5	4.36	3.78	4.20	3.59	4.31	3.60
30	4.02	2.66	3.80	2.43	3.99	2.35
60	3.74	1.94	3.46	1.68	3.65	1.69
120	3.16	1.53	2.96	1.30	3.03	1.17
180	2.77	1.30	2.46	1.08	2.64	1.05
240	2.71	1.27	2.38	1.04	2.63	1.05

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-42 Dissolved organic carbon of TCP for the ratio of Fe^{+2}:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	4.48	4.30	4.55	4.39	4.42	4.23
5	4.36	3.83	4.50	3.86	4.37	3.77
30	4.12	2.94	4.18	2.94	4.18	2.65
60	3.85	2.28	3.86	2.16	3.84	1.92
120	3.38	1.77	3.38	1.70	3.40	1.52
180	2.99	1.52	2.89	1.47	2.94	1.35
240	3.00	1.53	2.87	1.44	2.87	1.32

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-43 Dissolved organic carbon of TCP for the ratio of Fe^{+3}:H_2O_2:DOC of 5:10:1 at different pHs of 2, 3, and 4

Time, min	5:10:1, pH=2		5:10:1, pH=3		5:10:1, pH=4	
	DOC_i	DOC_f	DOC_i	DOC_f	DOC_i	DOC_f
0	4.42	4.20	4.40	4.24	4.35	4.18
5	4.42	4.06	4.37	3.90	4.27	3.85
30	4.27	3.45	4.21	3.31	4.16	3.16
60	4.11	2.93	4.00	2.74	4.03	2.48
120	3.67	2.37	3.54	2.17	3.57	2.07
180	3.16	2.05	3.05	1.89	3.13	1.83
240	3.13	2.04	2.97	1.82	3.00	1.74

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-44 Dissolved organic carbon of TCP for the ratio of Fe^{+3}:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	10:10:1, pH=2		10:10:1, pH=3		10:10:1, pH=4	
	DOC_i	DOC_f	DOC_i	DOC_f	DOC_i	DOC_f
0	4.34	4.34	4.42	4.25	4.44	4.32
5	4.27	4.27	4.33	3.84	4.38	3.88
30	4.15	4.15	4.12	2.90	4.21	2.79
60	3.94	3.94	3.92	2.25	4.03	2.17
120	3.48	3.48	3.46	1.84	3.59	1.76
180	3.11	3.11	2.93	1.51	3.12	1.49
240	3.02	3.02	2.90	1.50	3.07	1.51

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-45 Dissolved organic carbon of TCP for the ratio of $Fe^{+3}:H_2O_2:DOC$ of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1, pH=2**		**10:20:1, pH=3**		**10:20:1, pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	4.29	4.12	4.38	4.20	4.43	4.19
5	4.21	3.63	4.25	3.59	4.36	3.68
30	4.10	2.82	4.08	2.74	4.17	2.54
60	3.85	2.16	3.81	1.95	3.99	1.96
120	3.39	1.68	3.24	1.44	3.43	1.49
180	2.96	1.50	2.84	1.27	3.04	1.30
240	3.03	1.50	2.82	1.28	3.00	1.32

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-46 Dissolved organic carbon of TCP for the ratio of $Fe^0:H_2O_2:DOC$ of 5:10:1 at different pHs of 2, 3, and 4

Time, min	**5:20:1 pH=2**		**5:20:1 pH=3**		**5:20:1 pH=4**	
	DOC_i	**DOC_f**	**DOC_i**	**DOC_f**	**DOC_i**	**DOC_f**
0	4.32	4.12	4.47	4.24	4.55	4.32
5	3.78	3.19	4.02	3.46	4.00	3.42
30	3.22	2.04	3.46	2.51	3.59	2.45
60	3.03	1.66	3.22	2.10	3.36	1.96
120	2.73	1.33	2.99	1.65	3.14	1.63
180	2.70	1.31	3.00	1.67	3.11	1.63
240	2.71	1.29	2.99	1.64	3.13	1.62

DOC_i = DOC (mg/l) before the incubation; DOC_f = DOC (mg/l) after the incubation

Table A-47 Dissolved organic carbon of TCP for the ratio of Fe^0:H_2O_2:DOC of 10:10:1 at different pHs of 2, 3, and 4

Time, min	**10:10:1 pH=2**		**10:10:1 pH=3**		**10:10:1 pH=4**	
	DOC$_i$	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**
0	4.56	4.36	4.48	4.26	4.39	4.18
5	3.85	3.12	3.96	3.35	3.82	3.24
30	3.14	1.84	3.34	2.30	3.33	2.13
60	2.92	1.46	3.02	1.76	3.02	1.55
120	2.75	1.12	2.90	1.43	2.96	1.37
180	2.74	1.10	2.87	1.44	2.94	1.36
240	2.72	1.08	2.86	1.41	2.94	1.33

DOC$_i$ = DOC (mg/l) before the incubation; DOC$_f$ = DOC (mg/l) after the incubation

Table A-48 Dissolved organic carbon of TCP for the ratio of Fe^0:H_2O_2:DOC of 10:20:1 at different pHs of 2, 3, and 4

Time, min	**10:20:1 pH=2**		**10:20:1 pH=3**		**10:20:1 pH=4**	
	DOC$_i$	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**	**DOC$_i$**	**DOC$_f$**
0	4.26	4.03	4.30	4.07	4.31	4.10
5	3.69	3.10	3.70	3.14	3.76	3.18
30	3.10	1.94	3.31	2.38	3.38	2.22
60	2.94	1.40	3.05	1.75	3.20	1.71
120	2.66	1.17	2.83	1.45	2.94	1.38
180	2.66	1.17	2.83	1.44	2.92	1.39
240	2.63	1.15	2.84	1.45	2.91	1.36

DOC$_i$ = DOC (mg/l) before the incubation; DOC$_f$ = DOC (mg/l) after the incubation

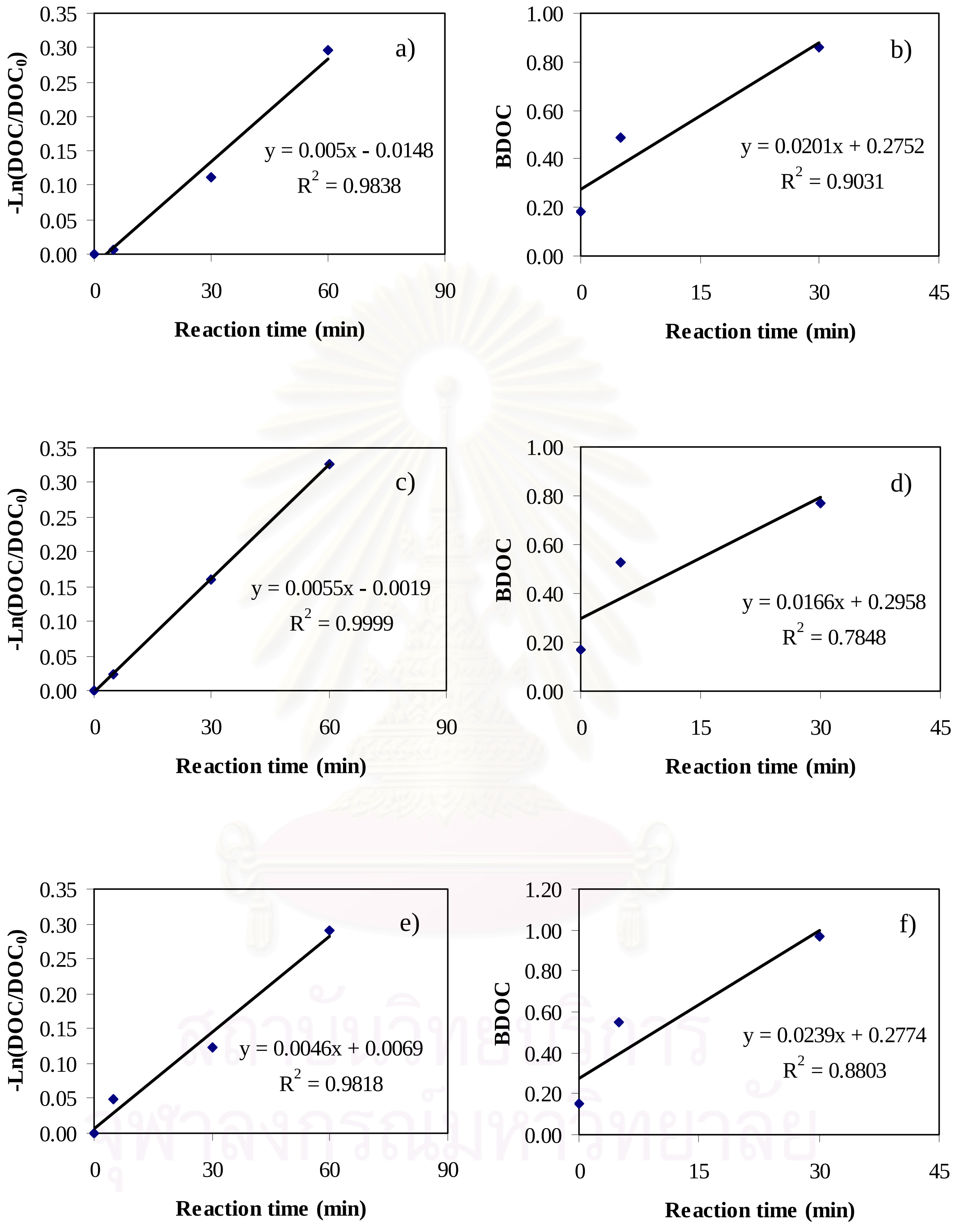


Figure A-1 The kinetic results of mineralization and biodegradability of TCE at Fe^{+2}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

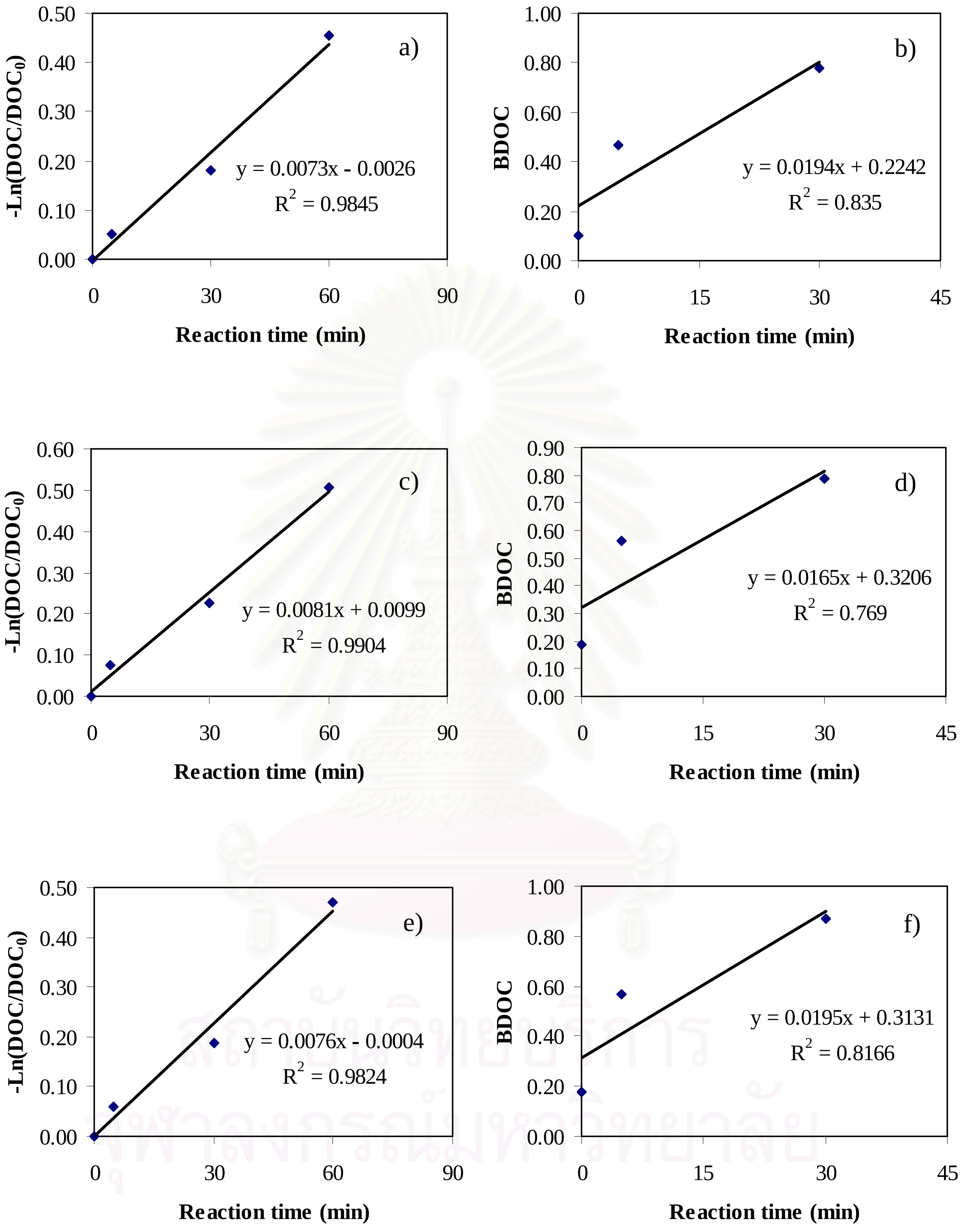


Figure A-2 The kinetic results of mineralization and biodegradability of TCE at Fe^{+2}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

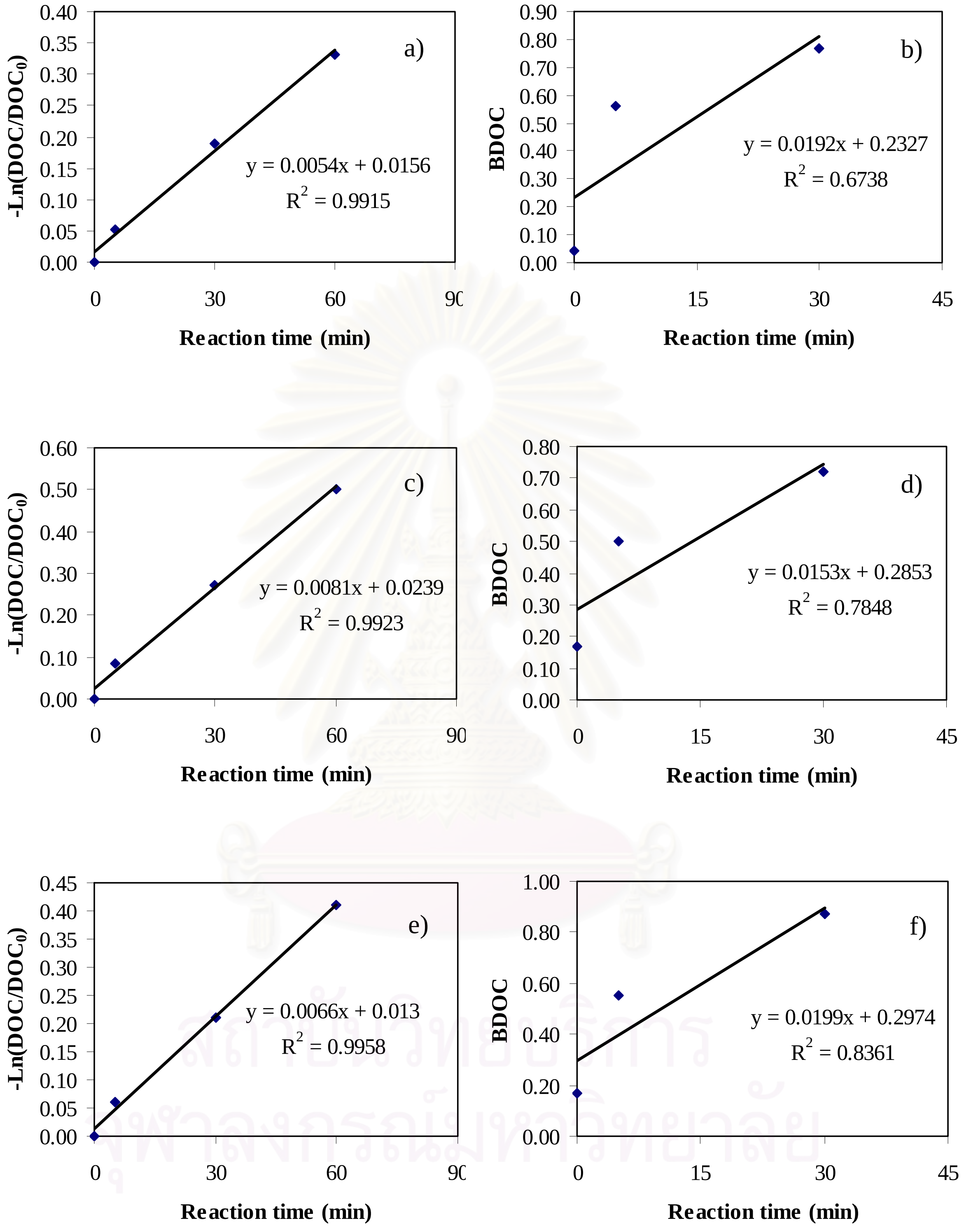


Figure A-3 The kinetic results of mineralization and biodegradability of TCE at Fe^{+2}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

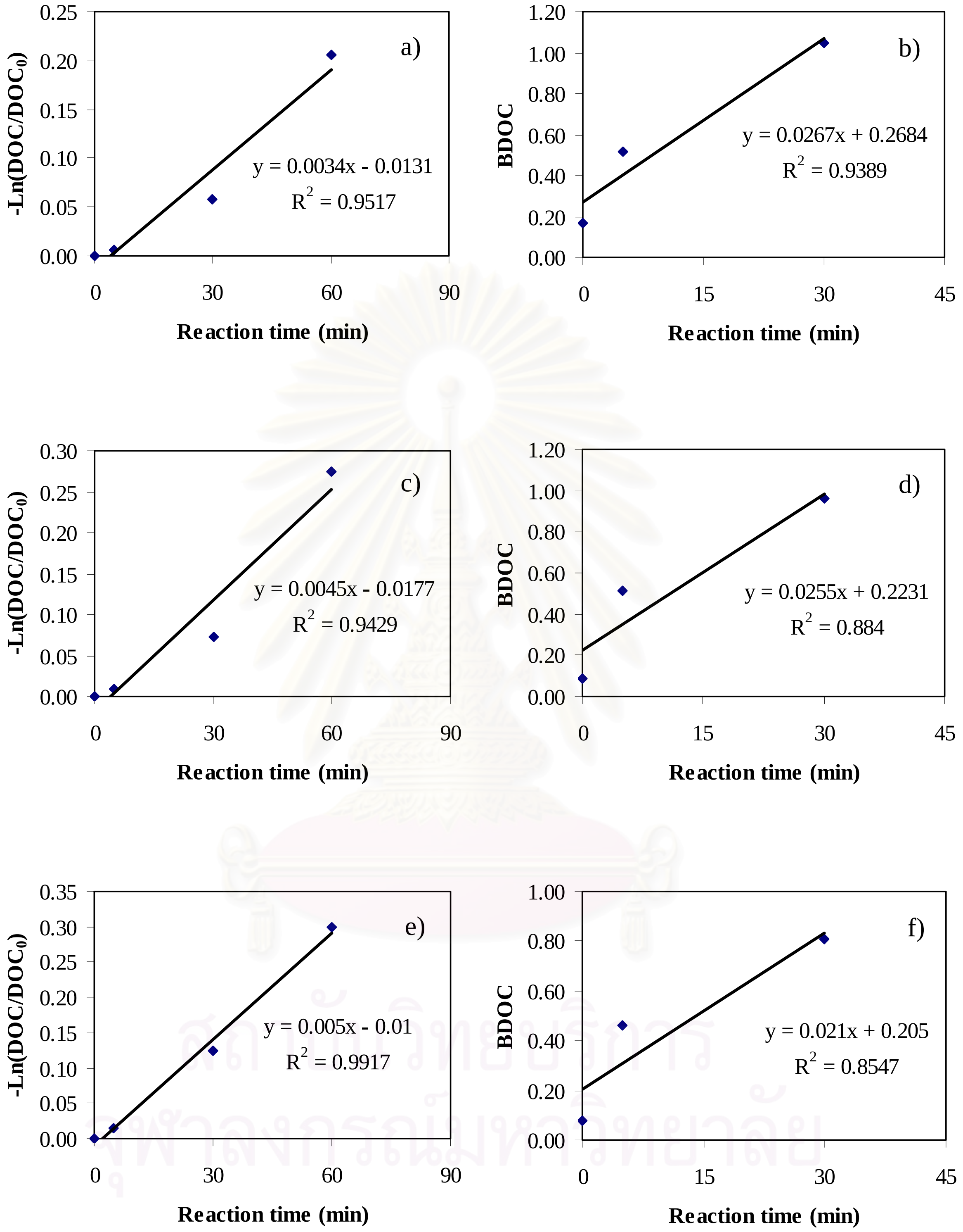


Figure A-4 The kinetic results of mineralization and biodegradability of TCE at Fe^{+3}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

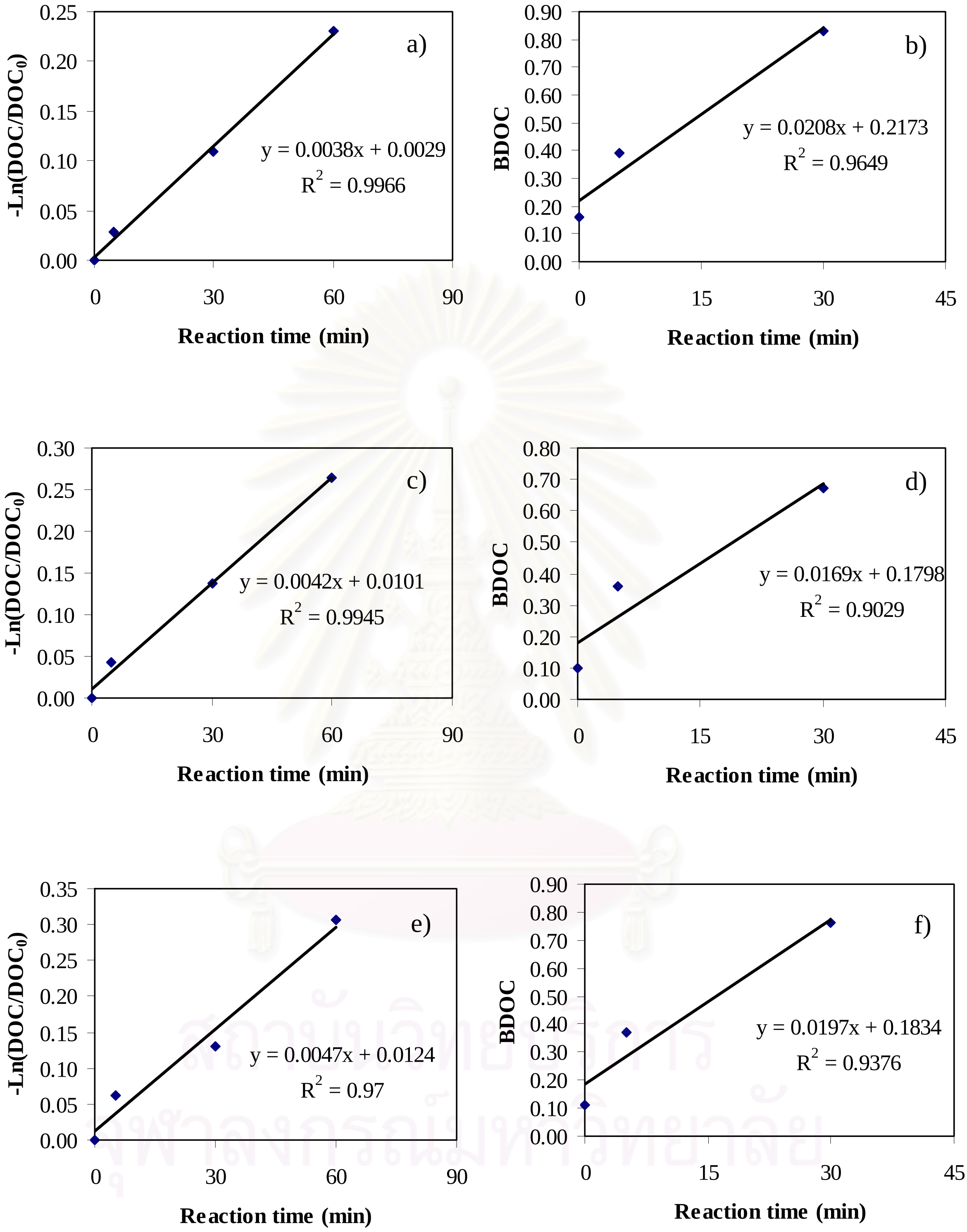


Figure A-5 The kinetic results of mineralization and biodegradability of TCE at Fe^{+3}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

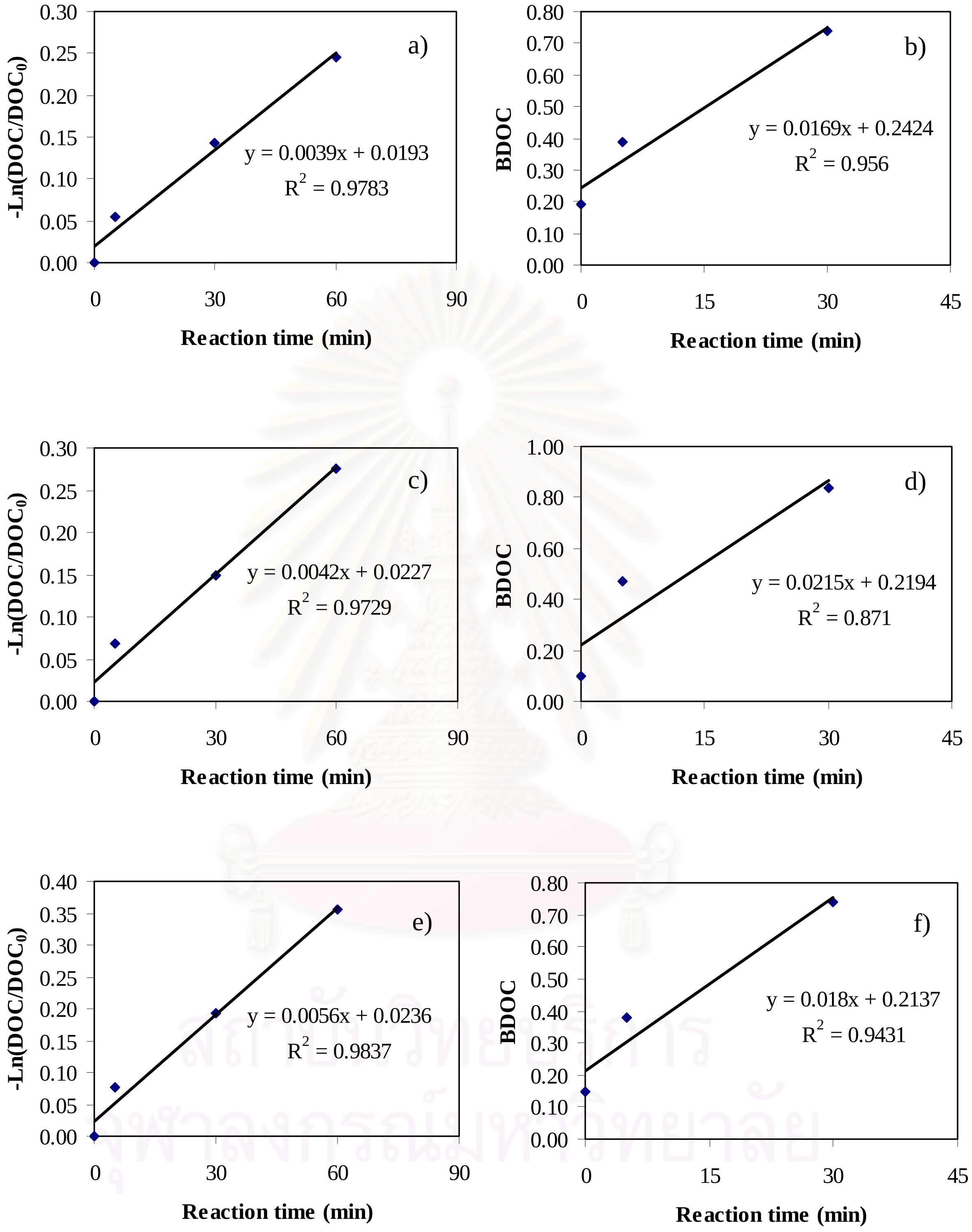


Figure A-6 The kinetic results of mineralization and biodegradability of TCE at Fe^{+3}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

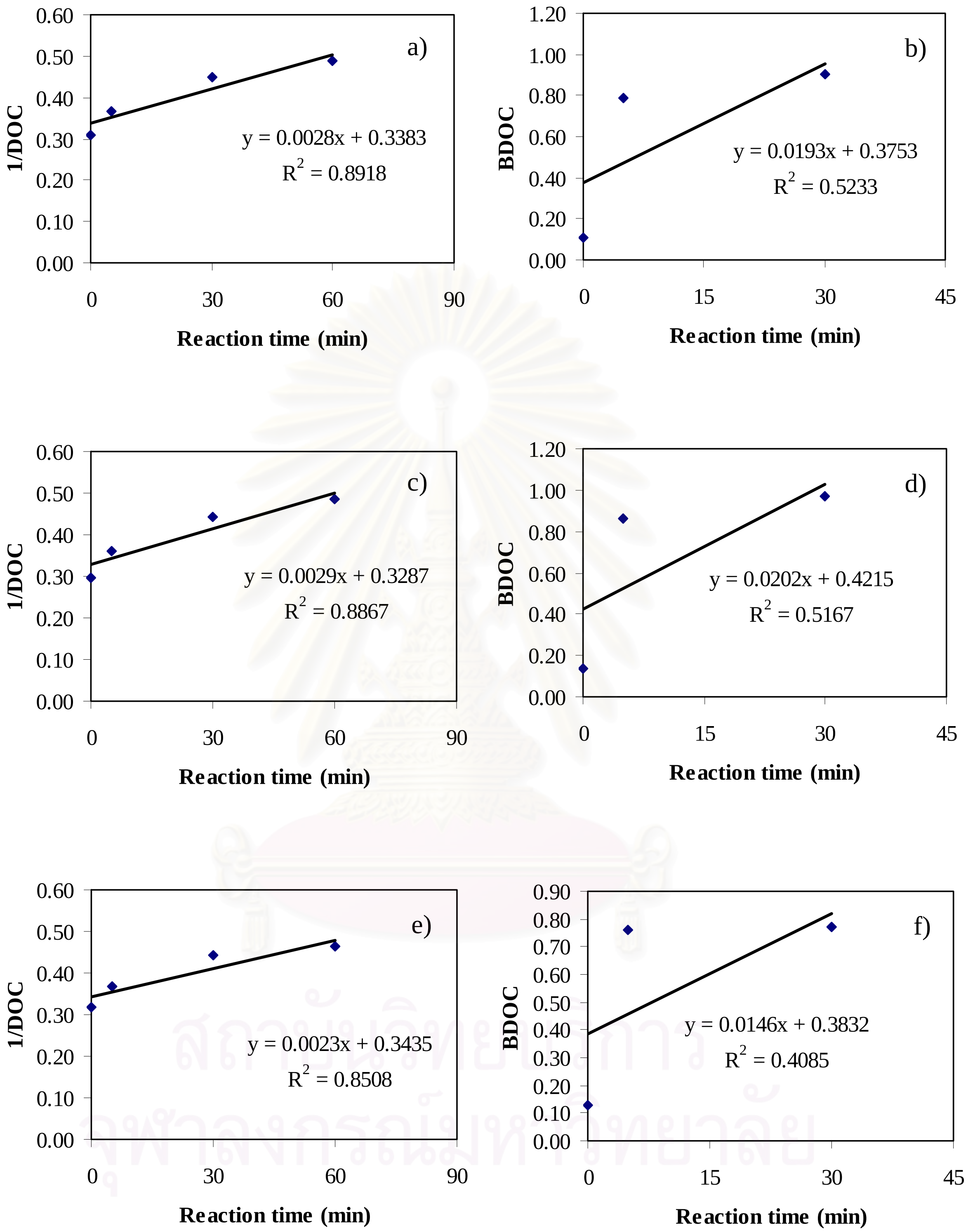


Figure A-7 The kinetic results of mineralization and biodegradability of TCE at Fe^0:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

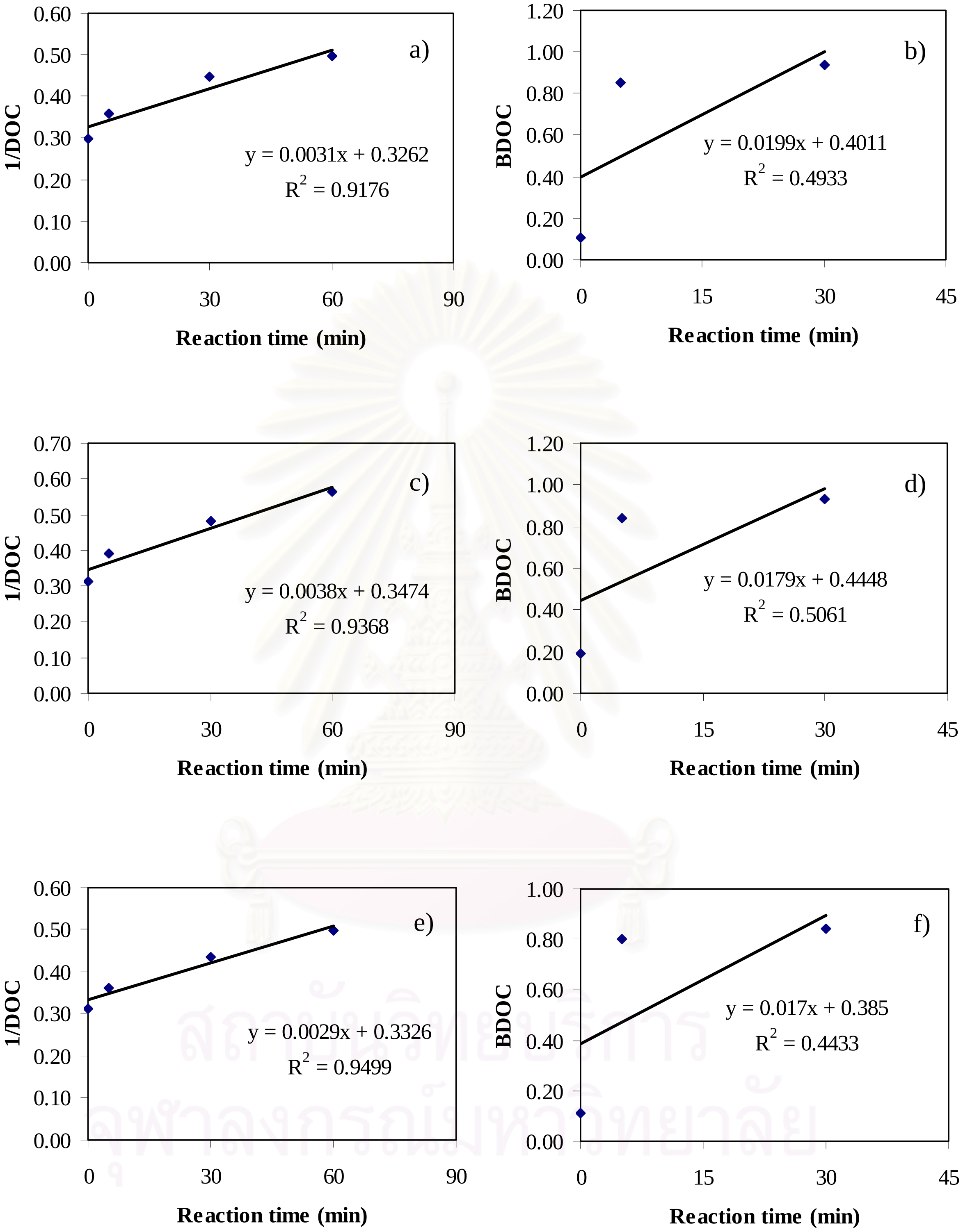


Figure A-8 The kinetic results of mineralization and biodegradability of TCE at Fe^0:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

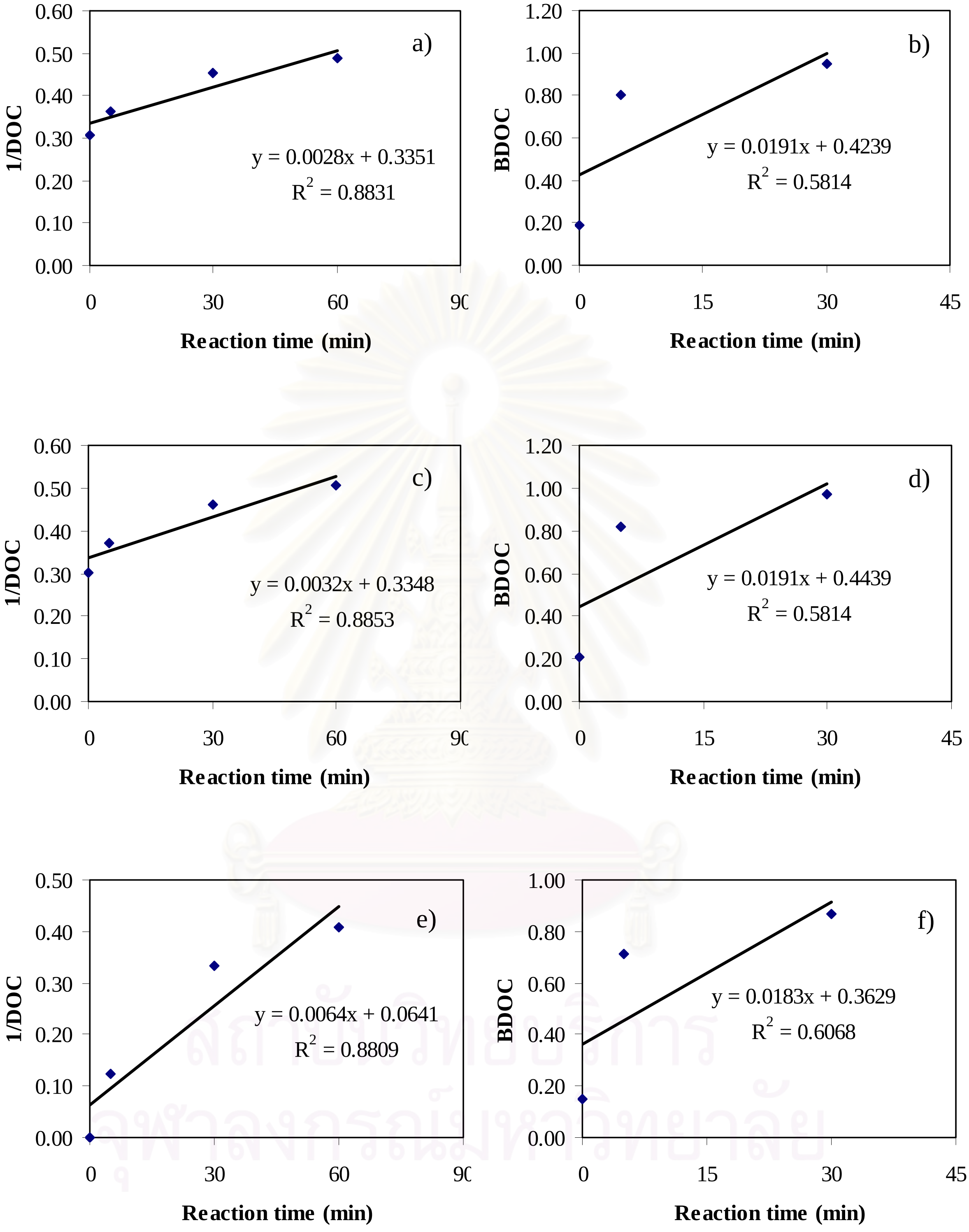


Figure A-9 The kinetic results of mineralization and biodegradability of TCE at Fe^0:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

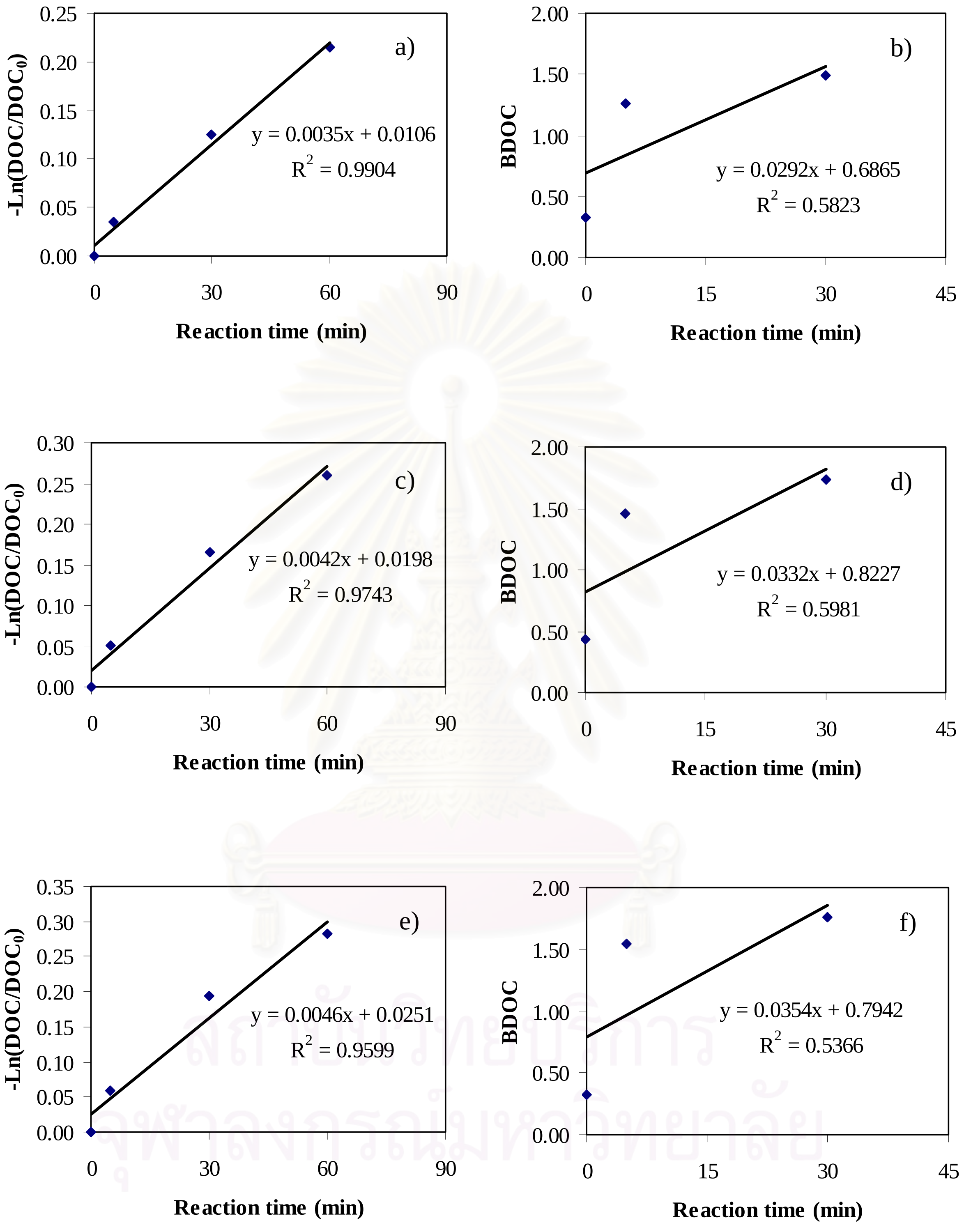


Figure A-10 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^{+2}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

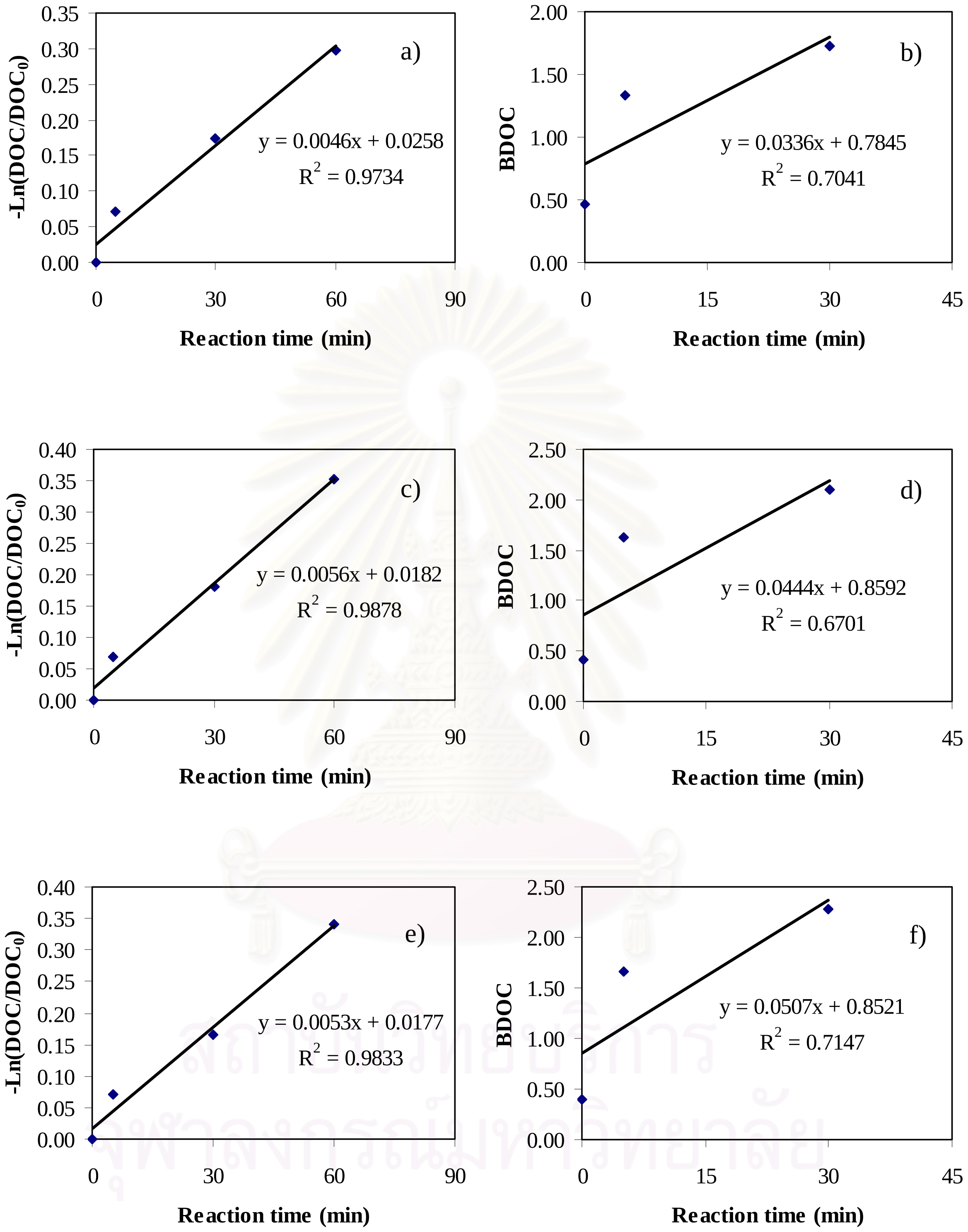


Figure A-11 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^{+2}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

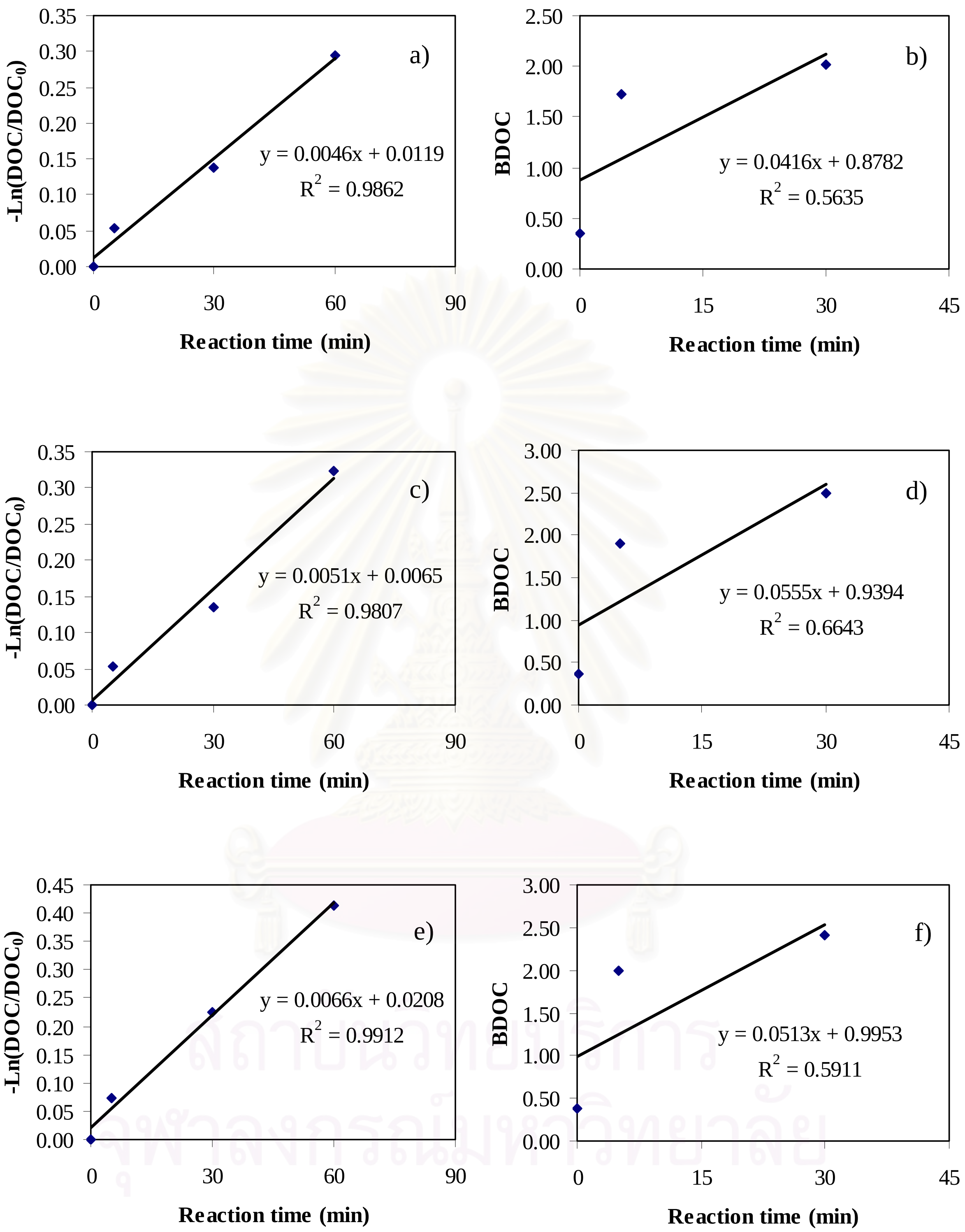


Figure A-12 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^{+2}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

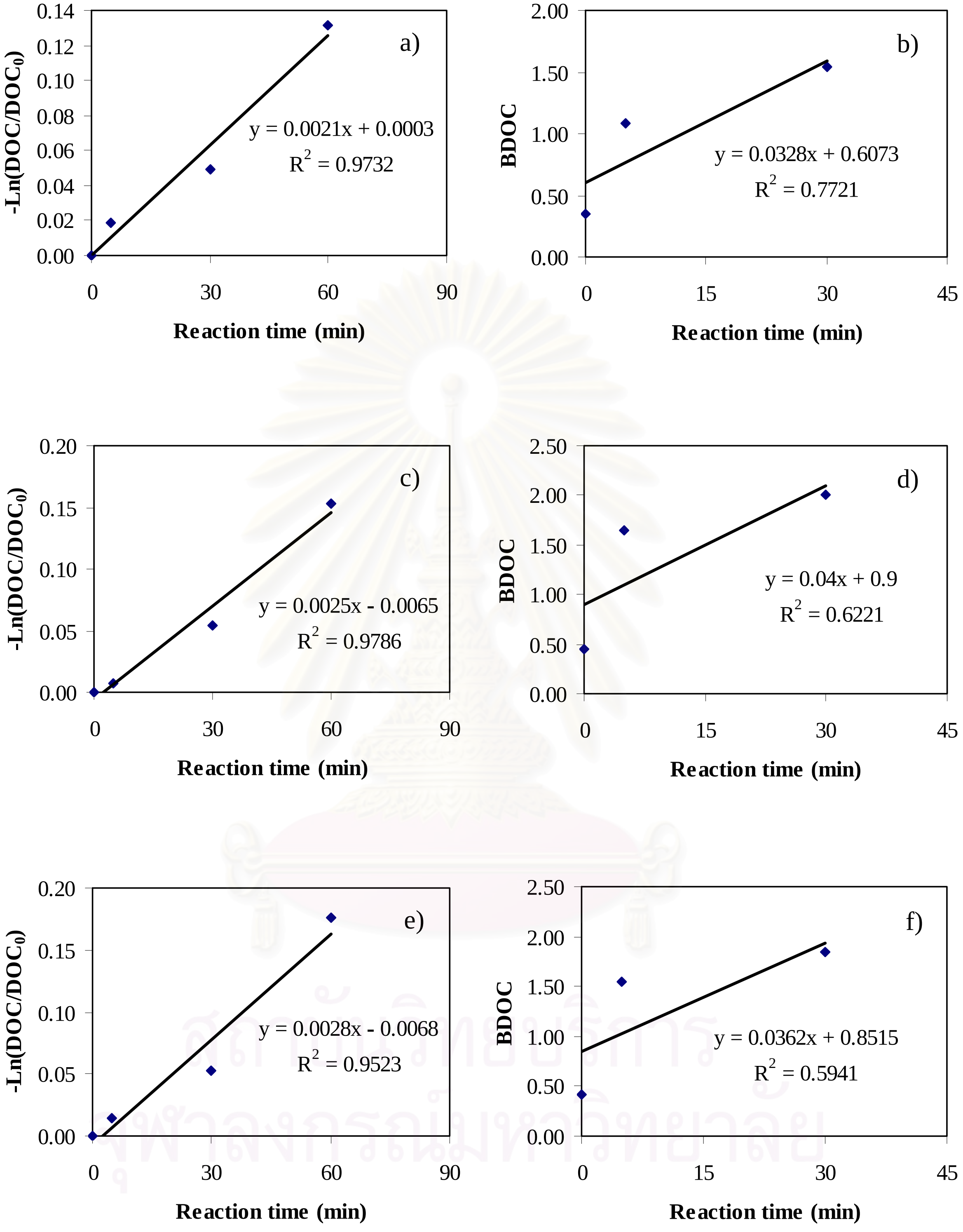


Figure A-13 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^{+3}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

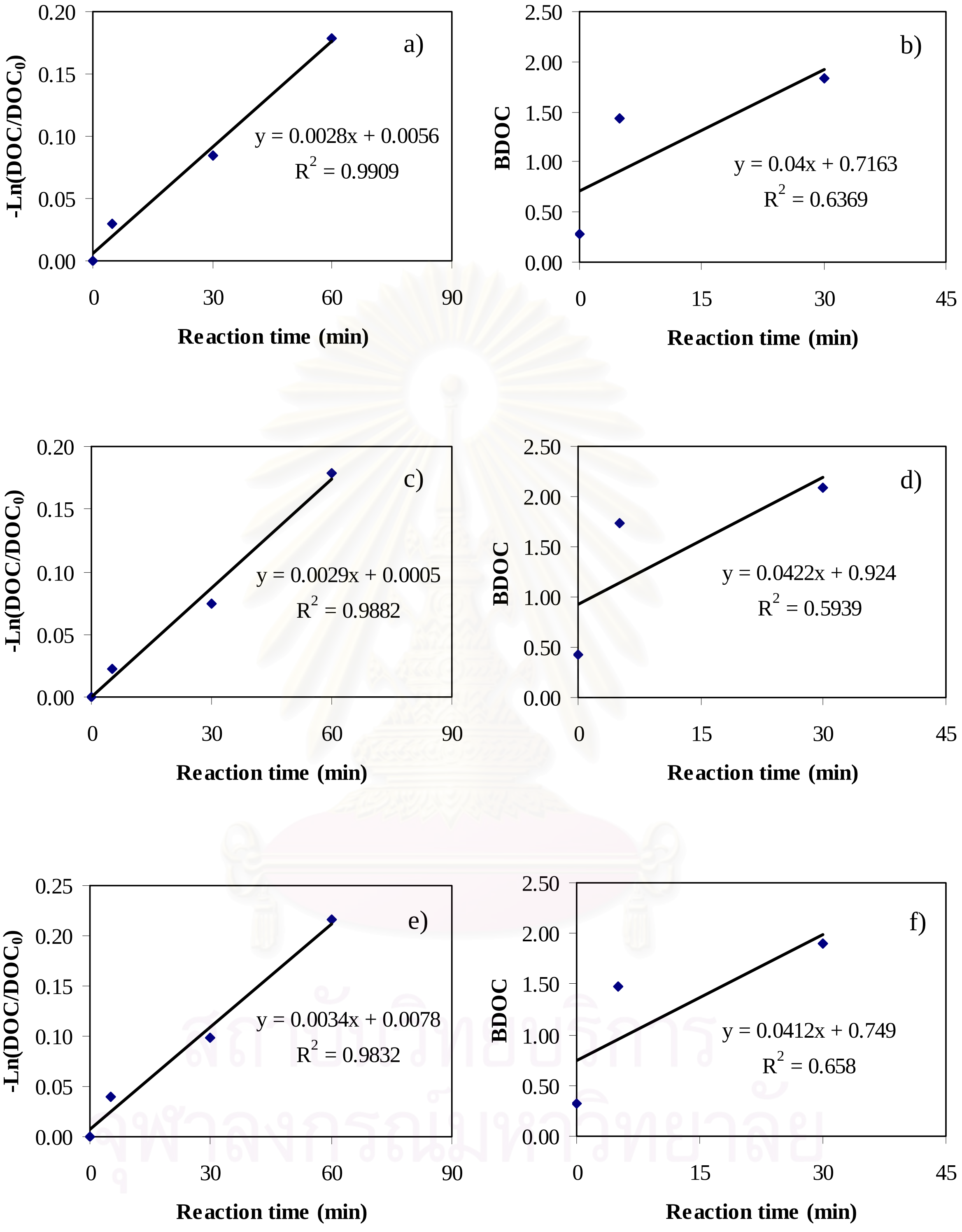


Figure A-14 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^{+3}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

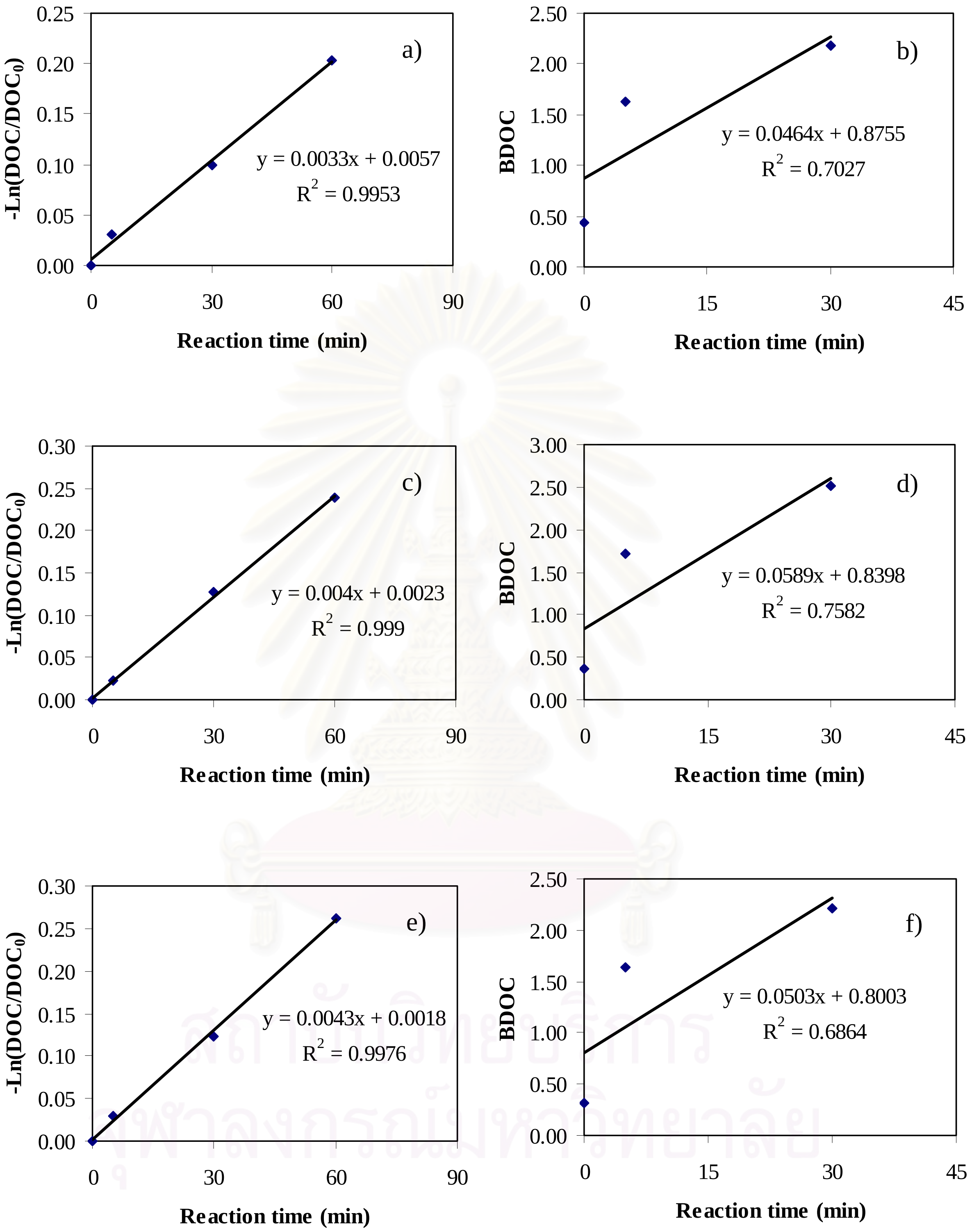


Figure A-15 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^{+3}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

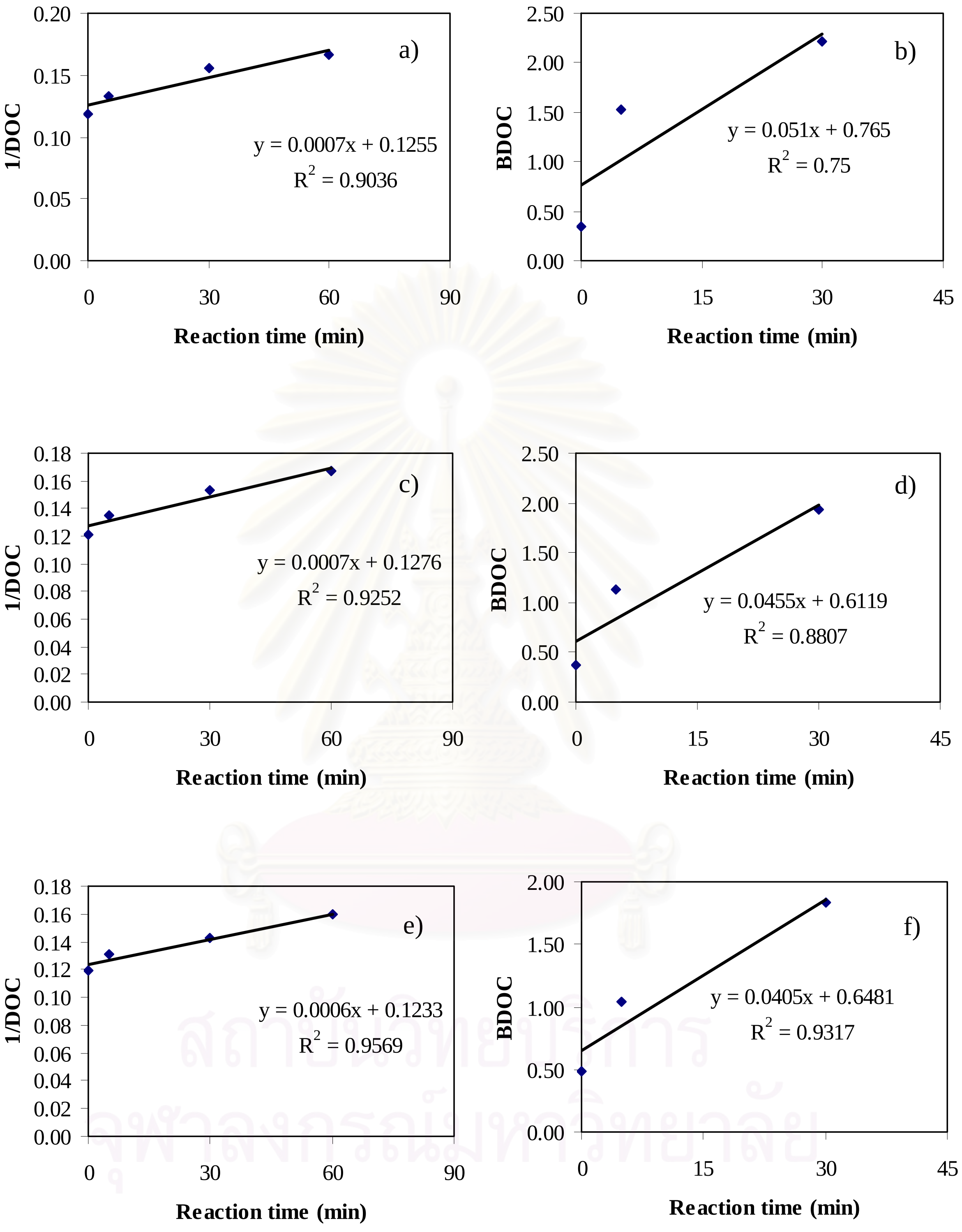


Figure A-16 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^0:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

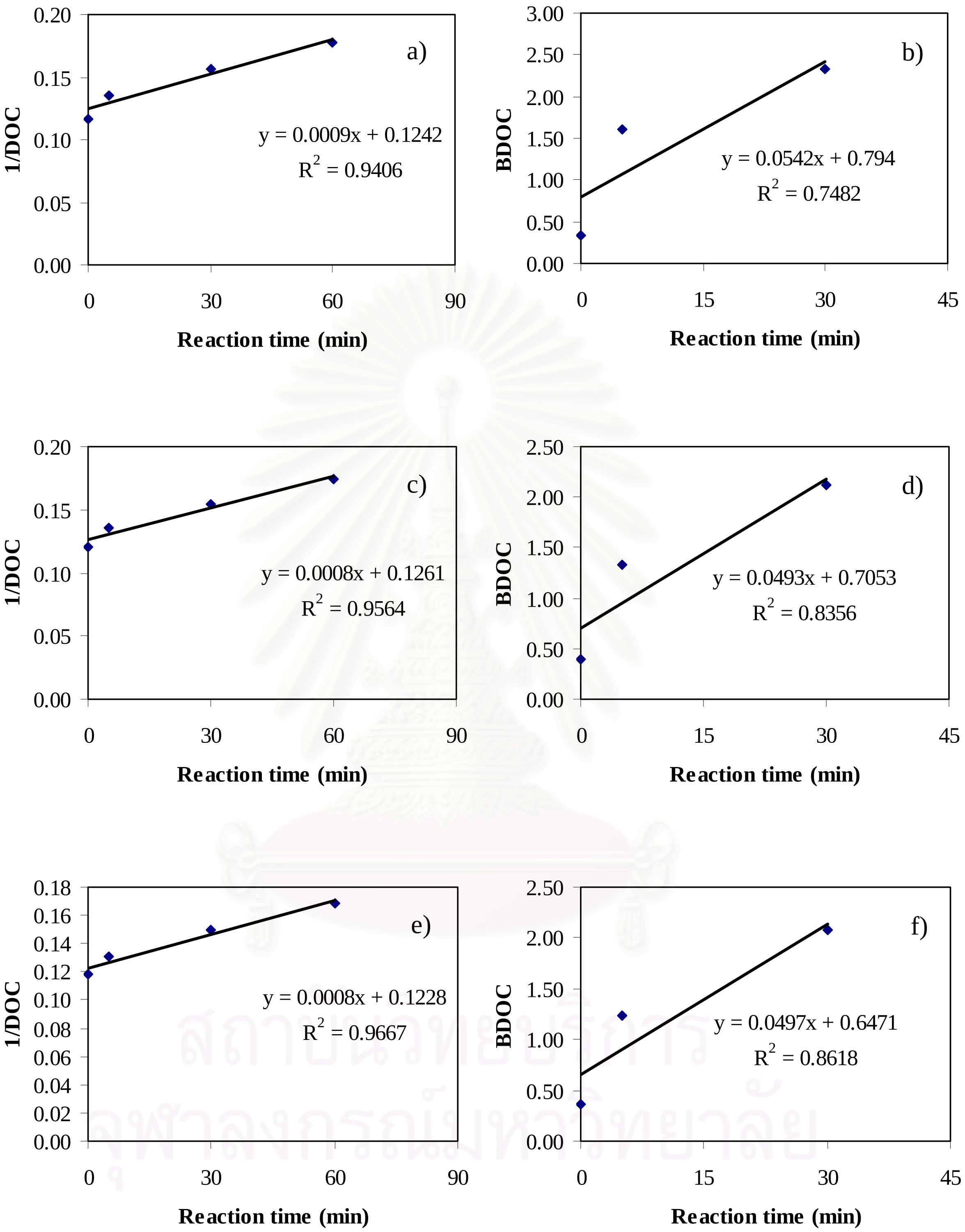


Figure A-17 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^0:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

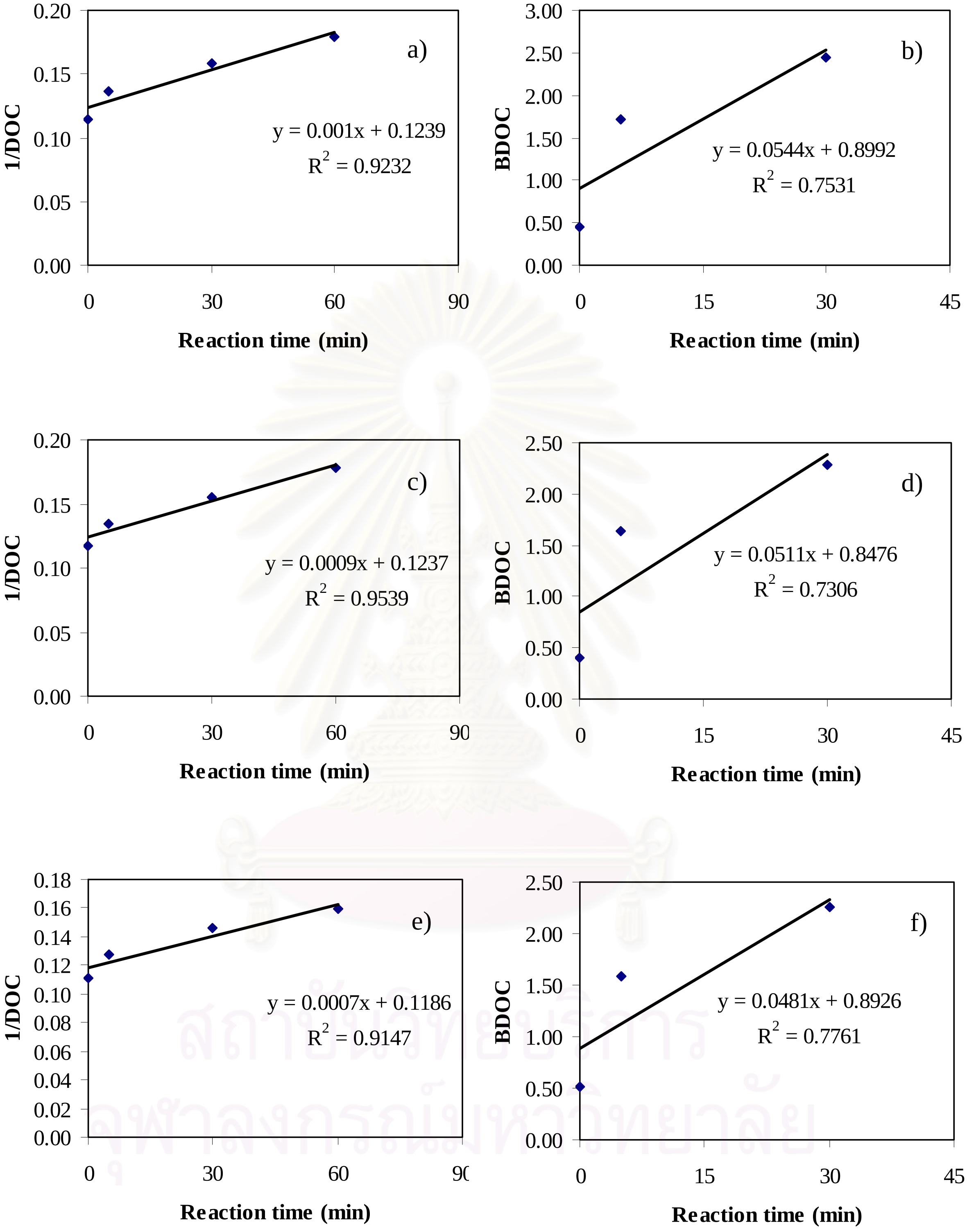


Figure A-18 The kinetic results of mineralization and biodegradability of 2,4-DCP at Fe^0:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

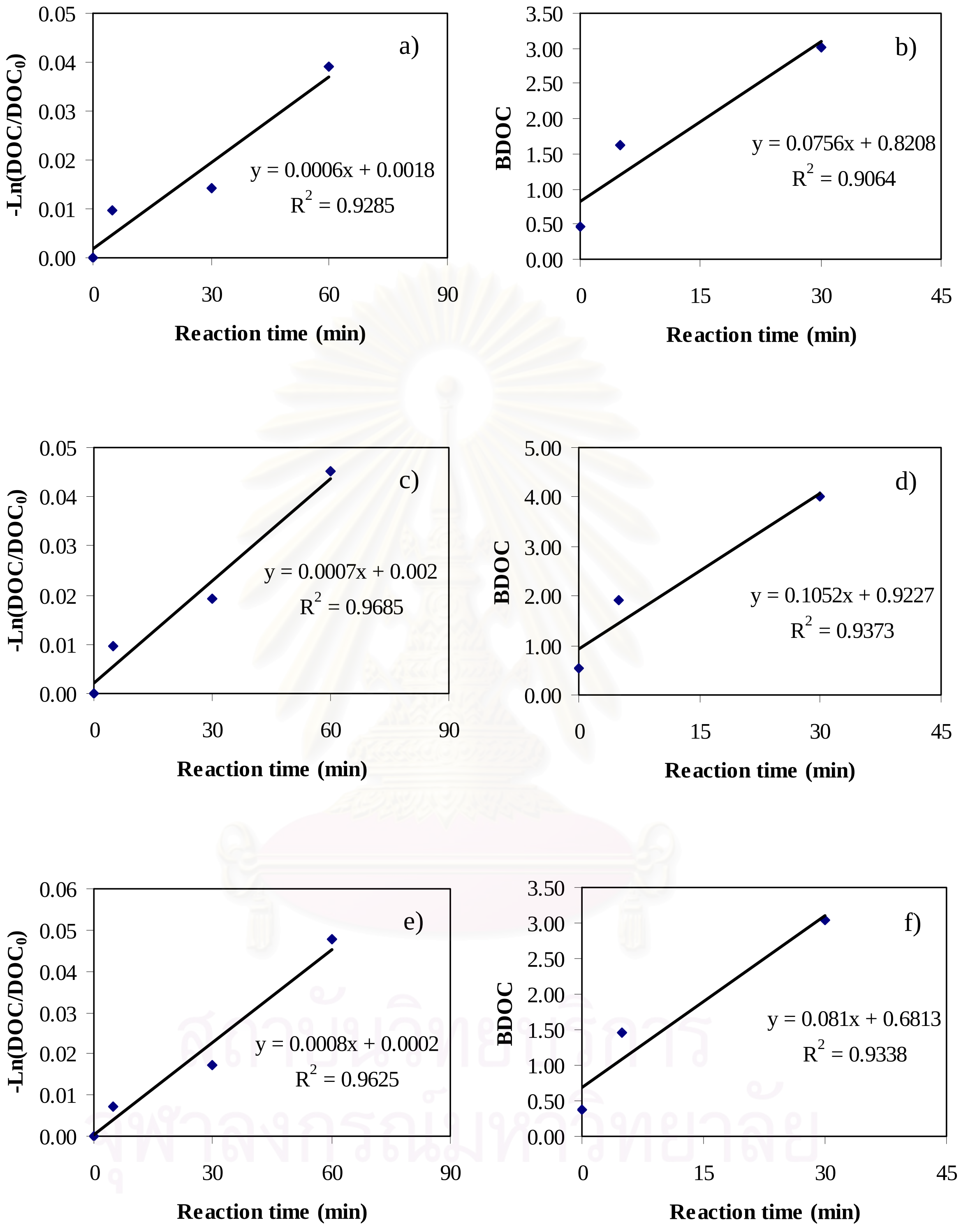


Figure A-19 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+2}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

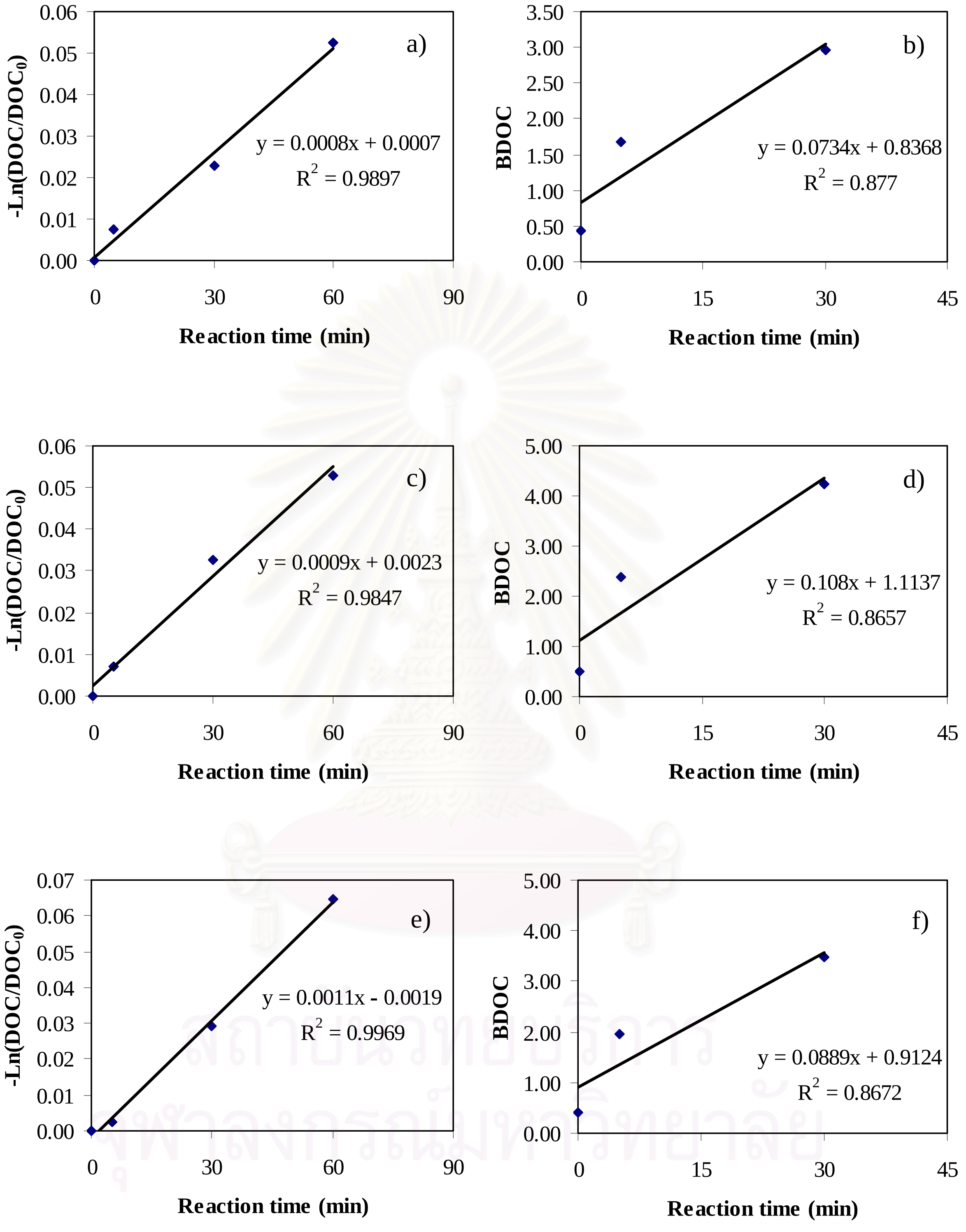


Figure A-20 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+2}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

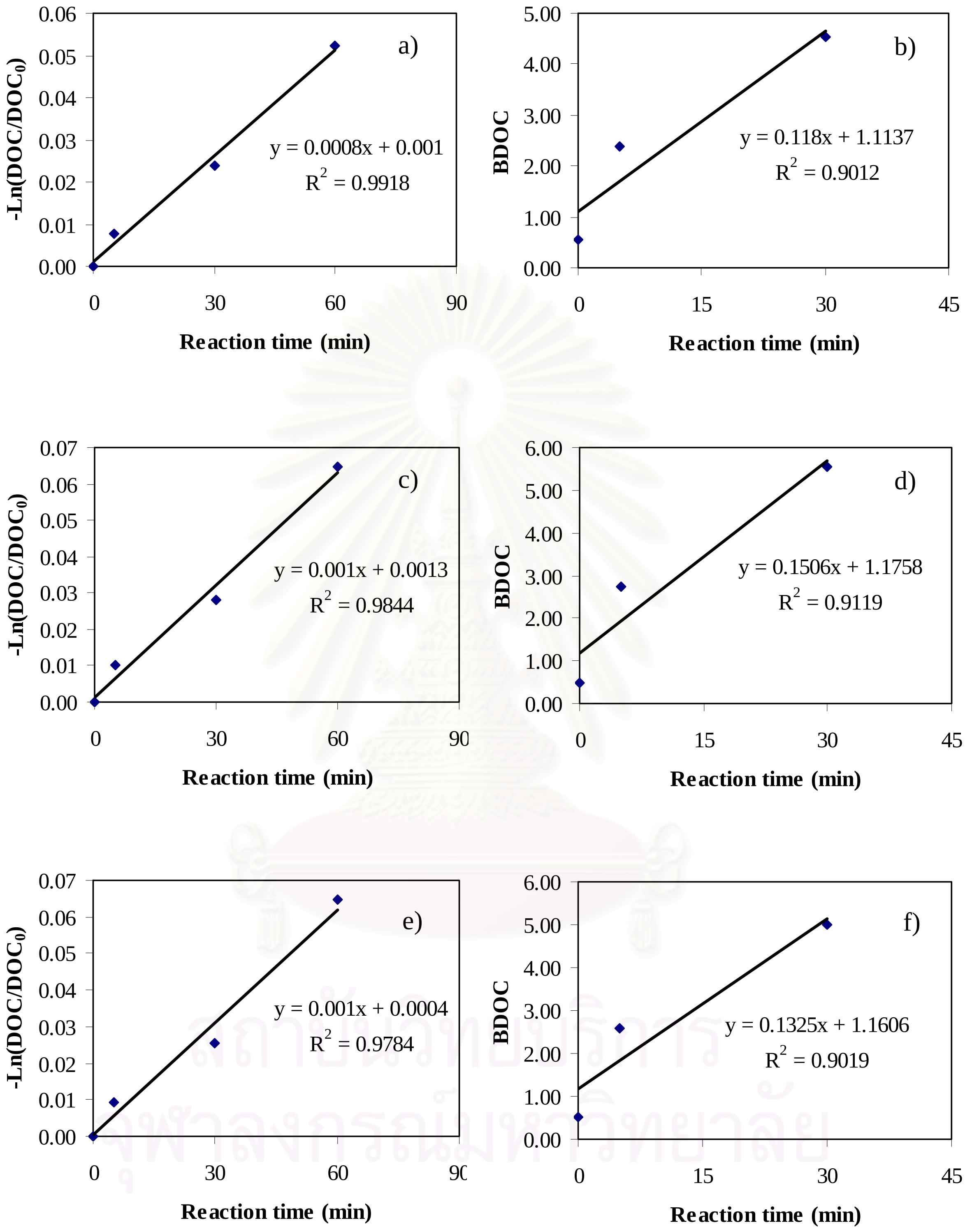


Figure A-21 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+2}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

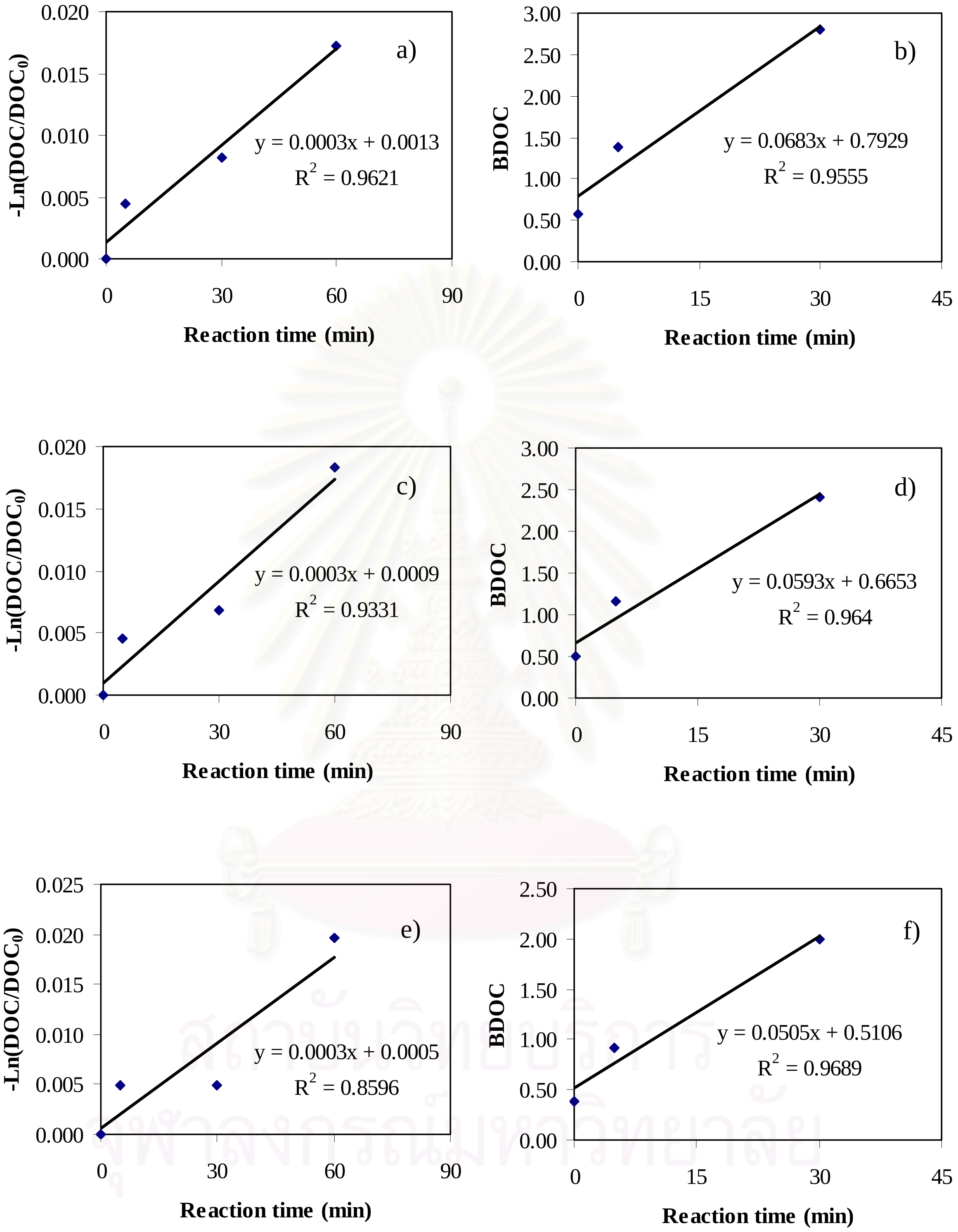


Figure A-22 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+3}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

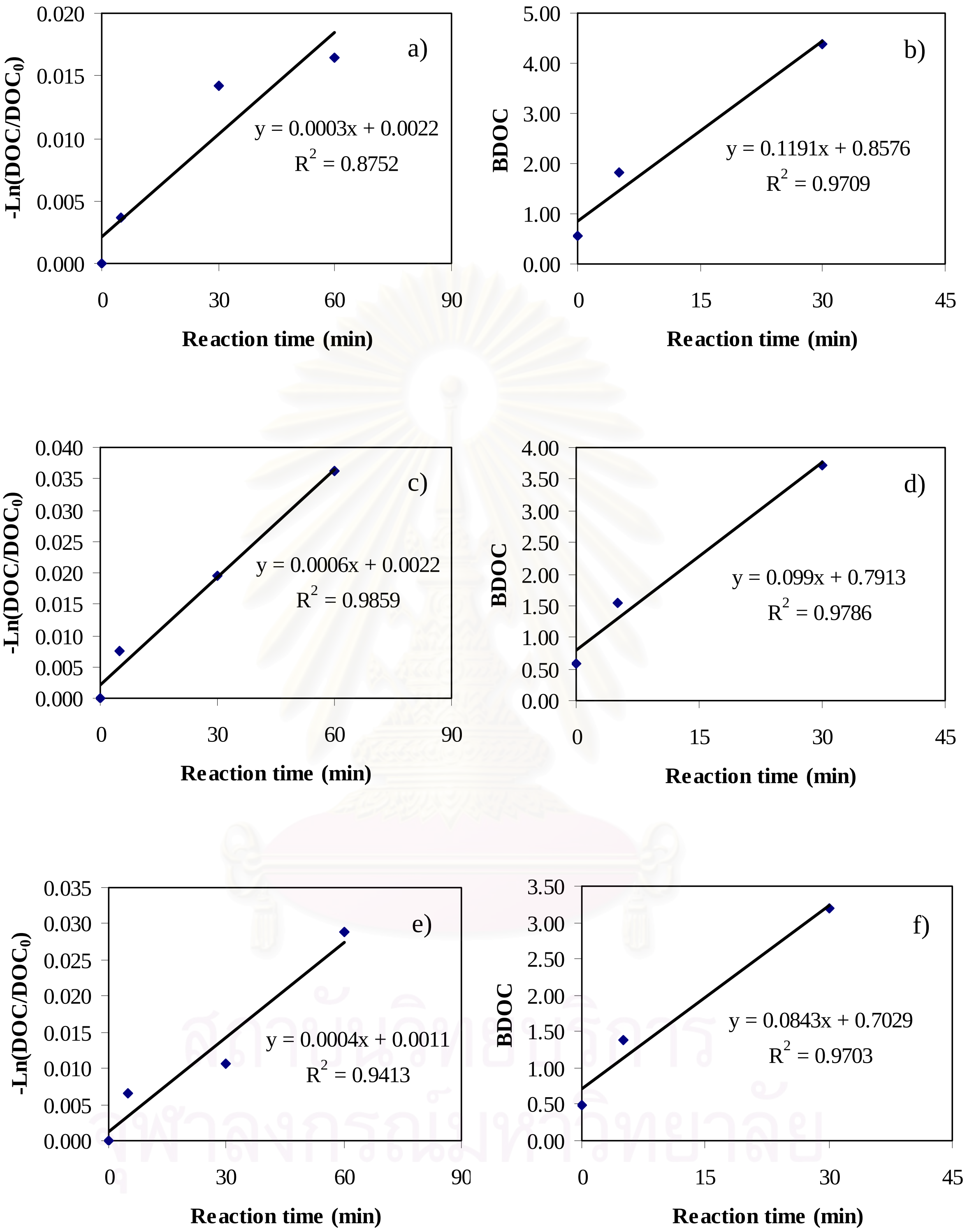


Figure A-23 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+3}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

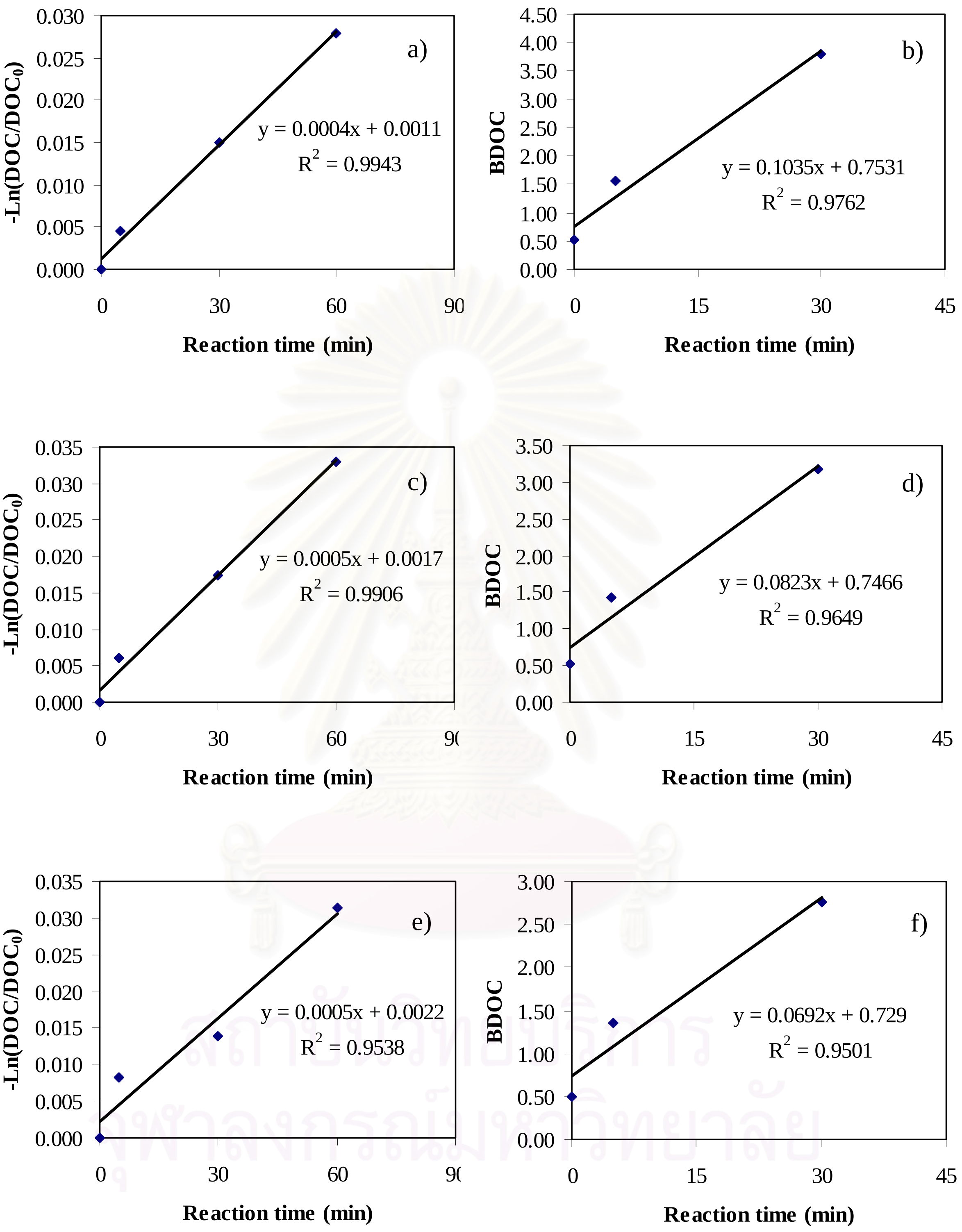


Figure A-24 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+3}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

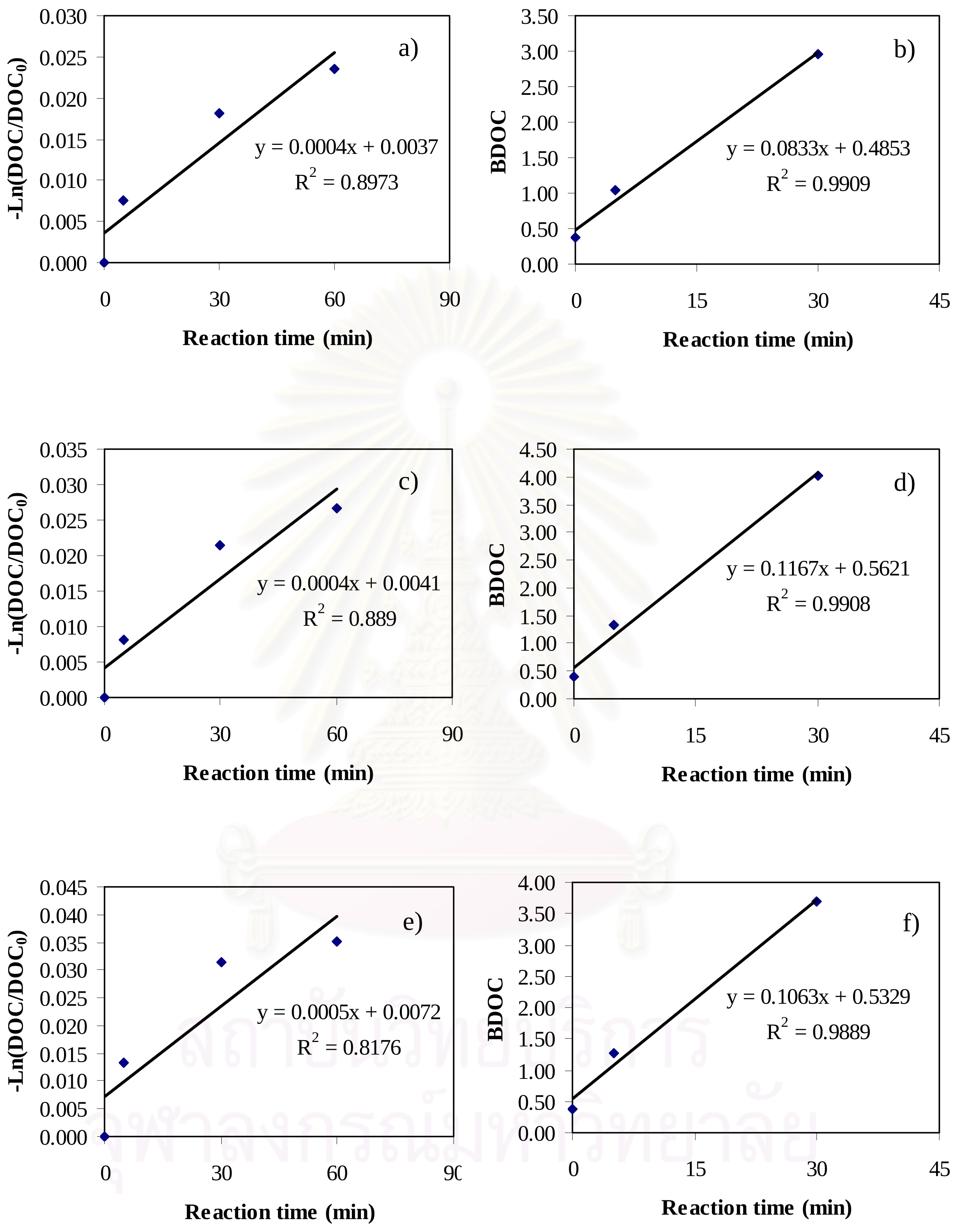


Figure A-25 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^0:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

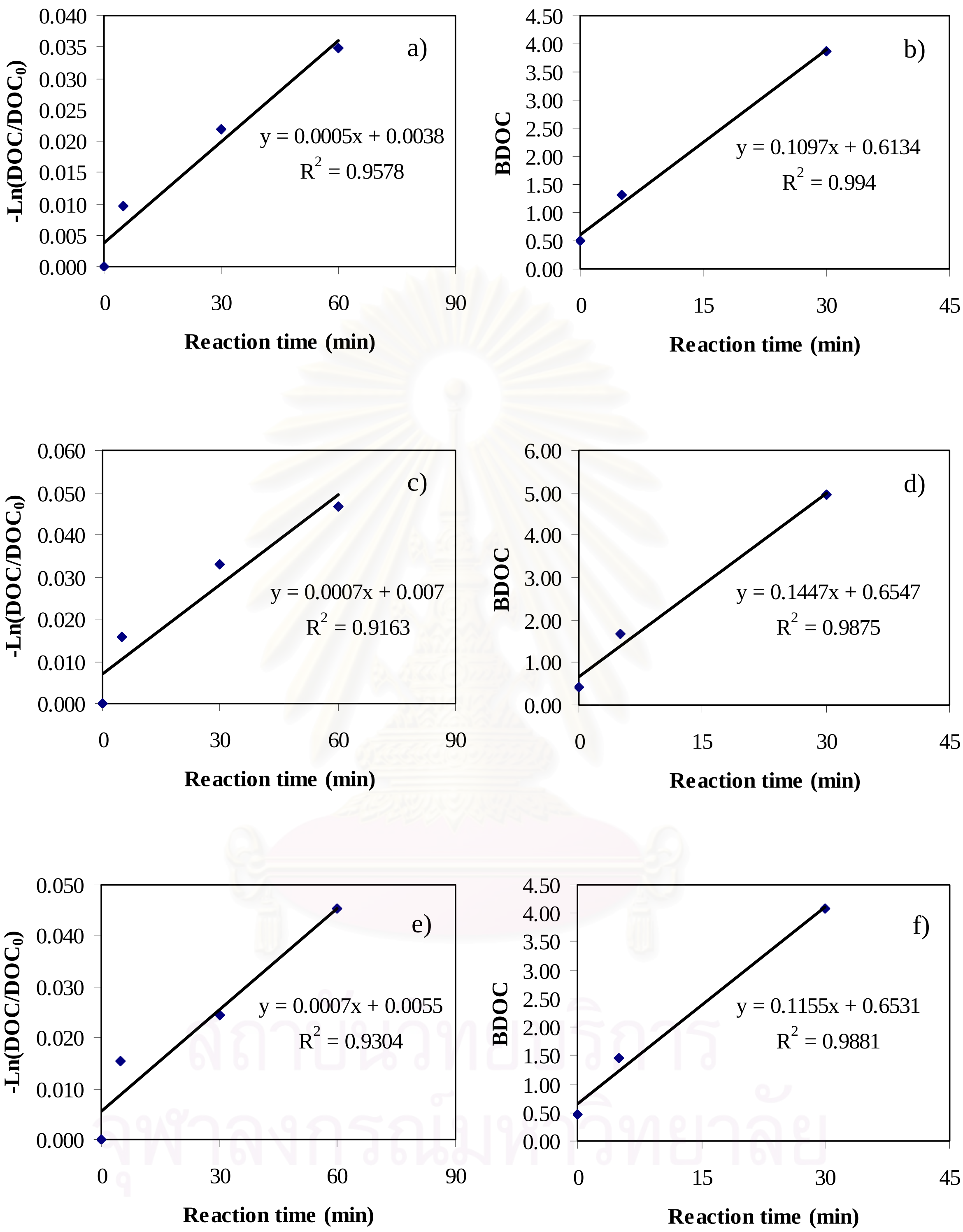


Figure A-26 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^0:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

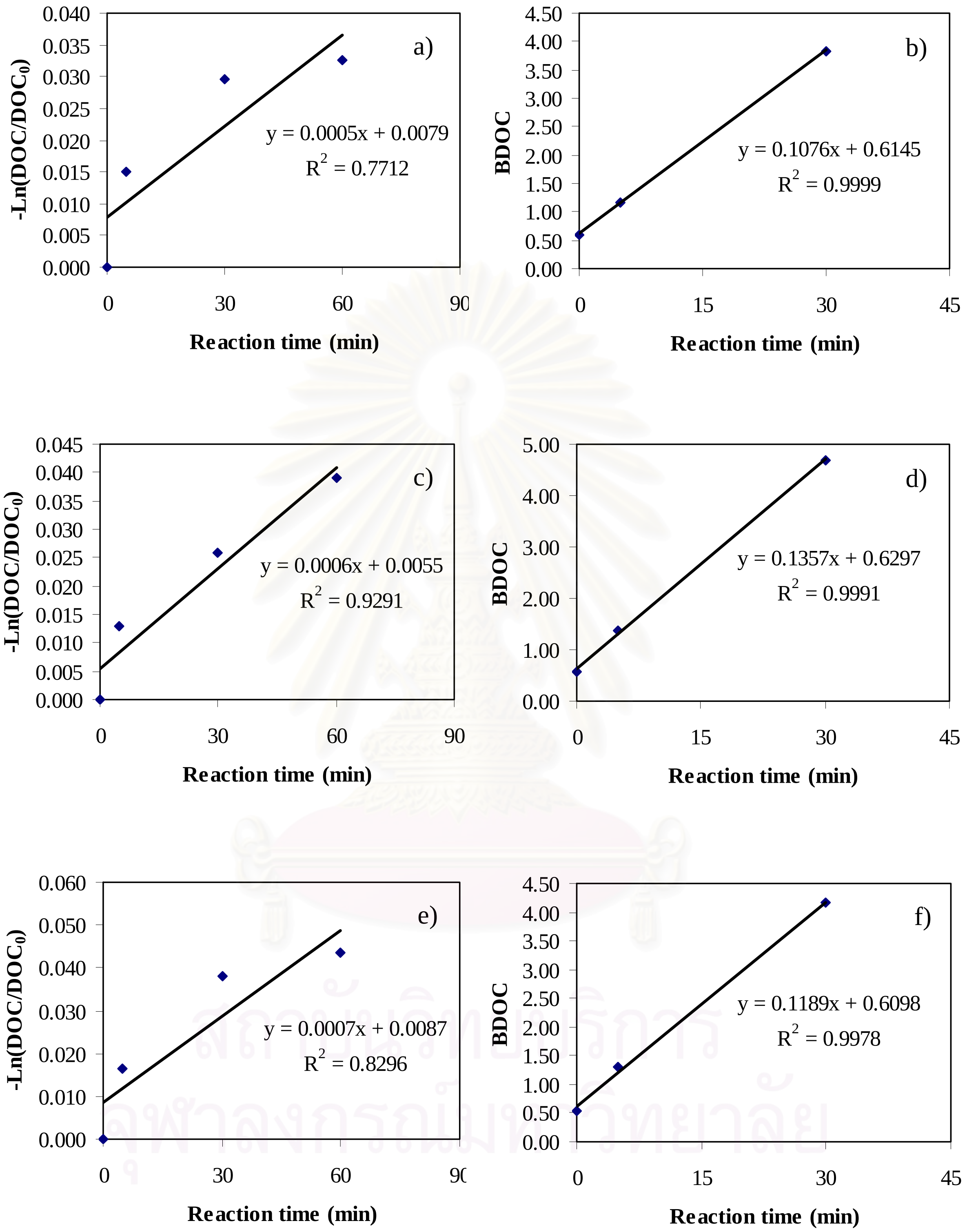


Figure A-27 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^0:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

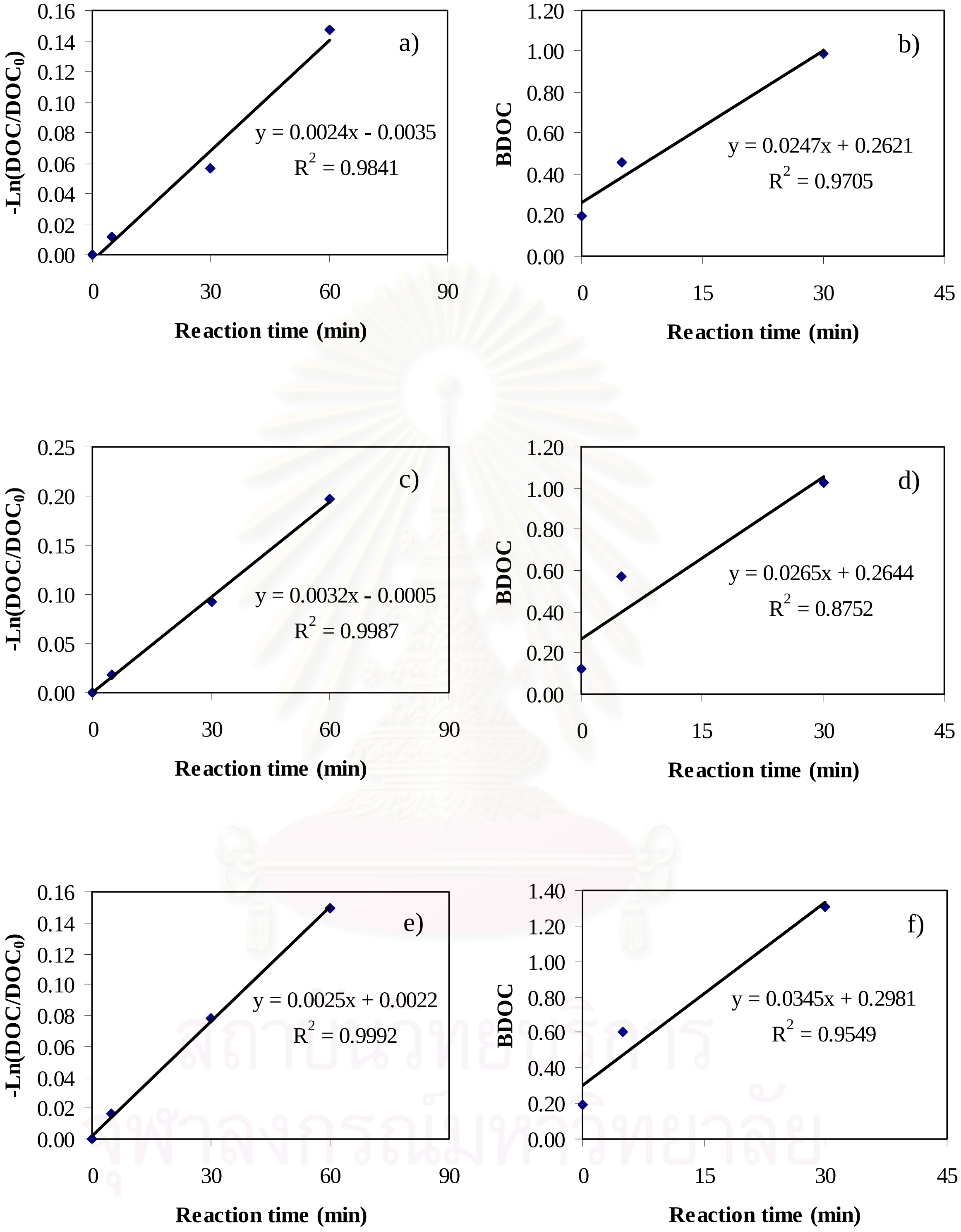


Figure A-28 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+2}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

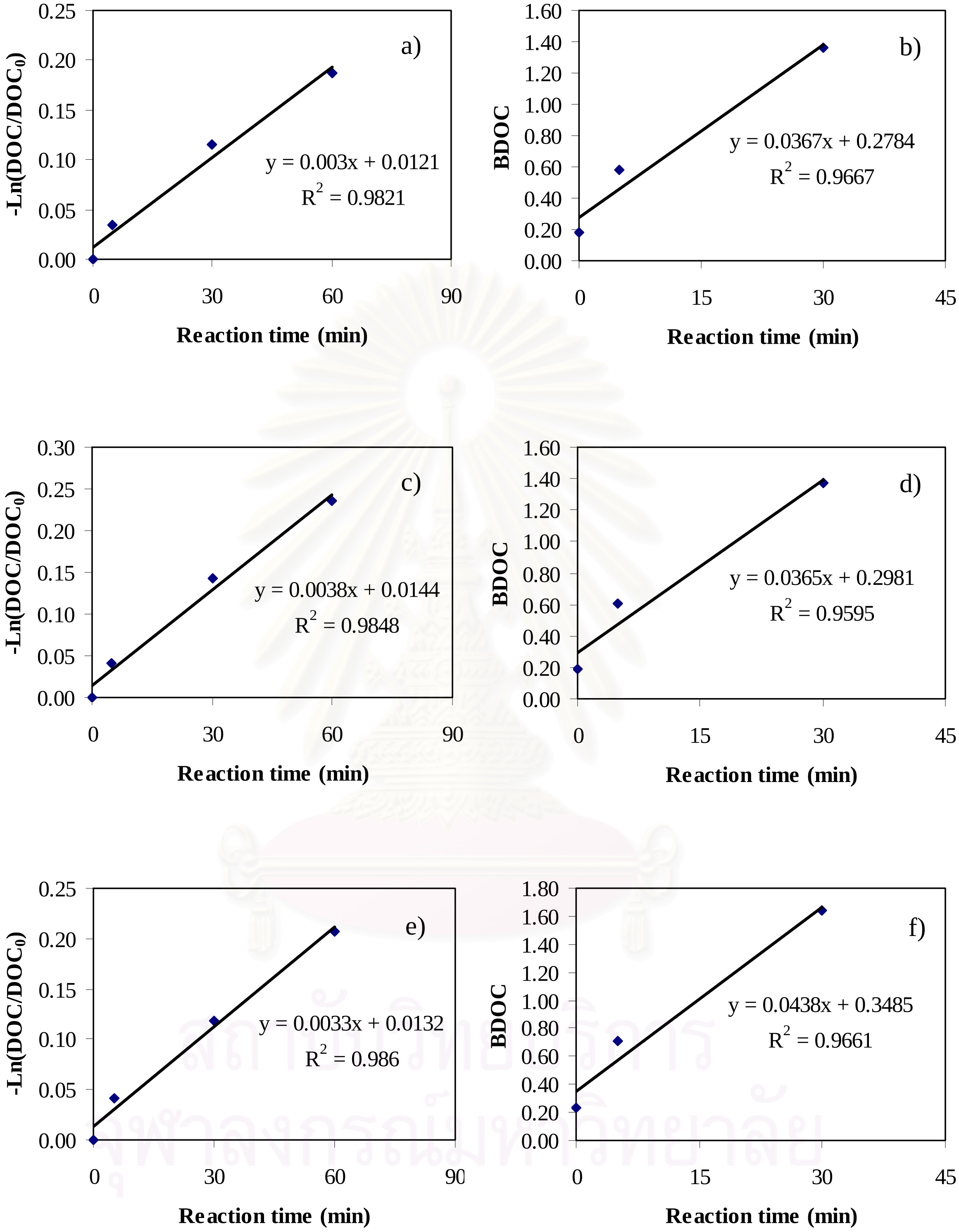


Figure A-29 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+2}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

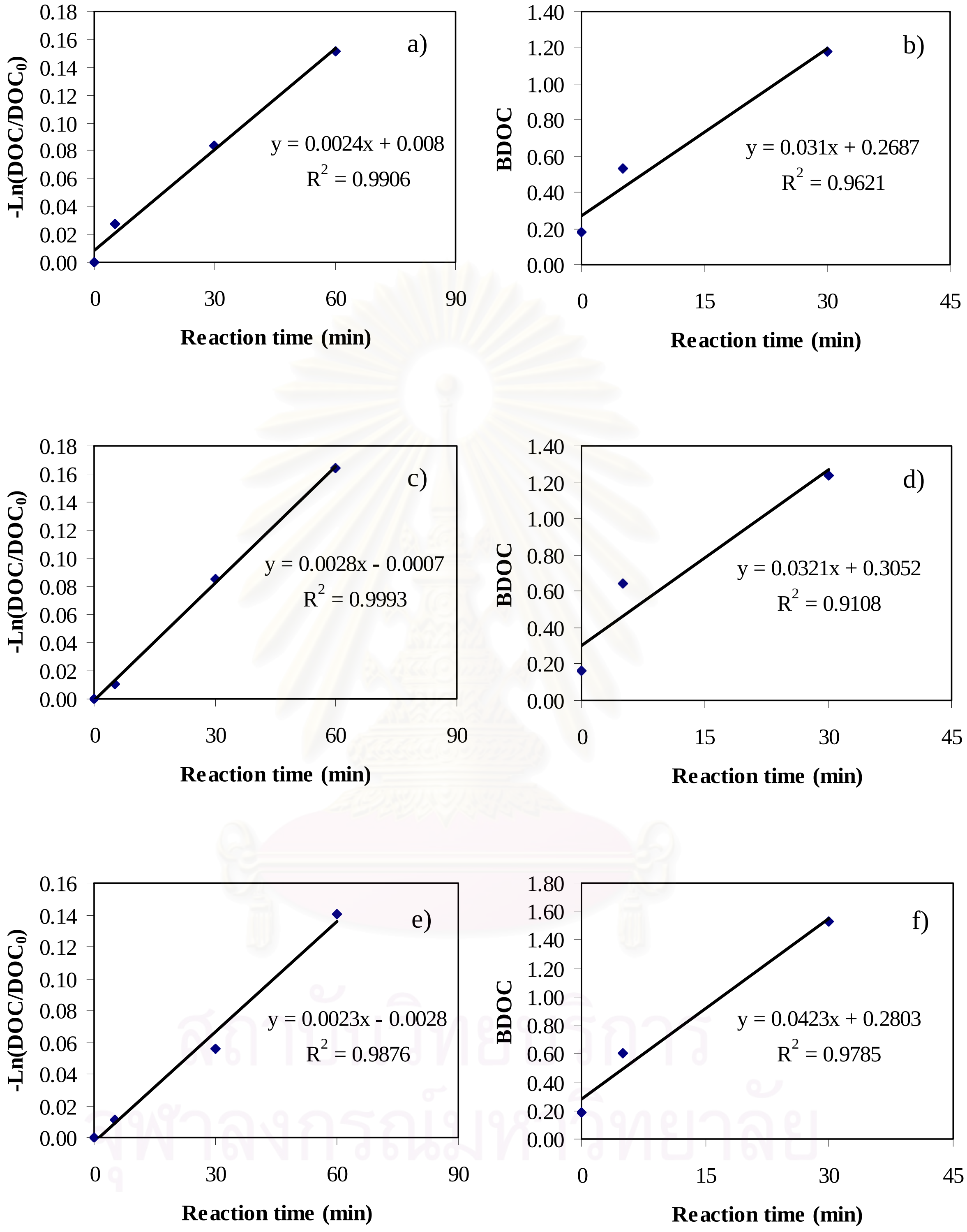


Figure A-30 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+2}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

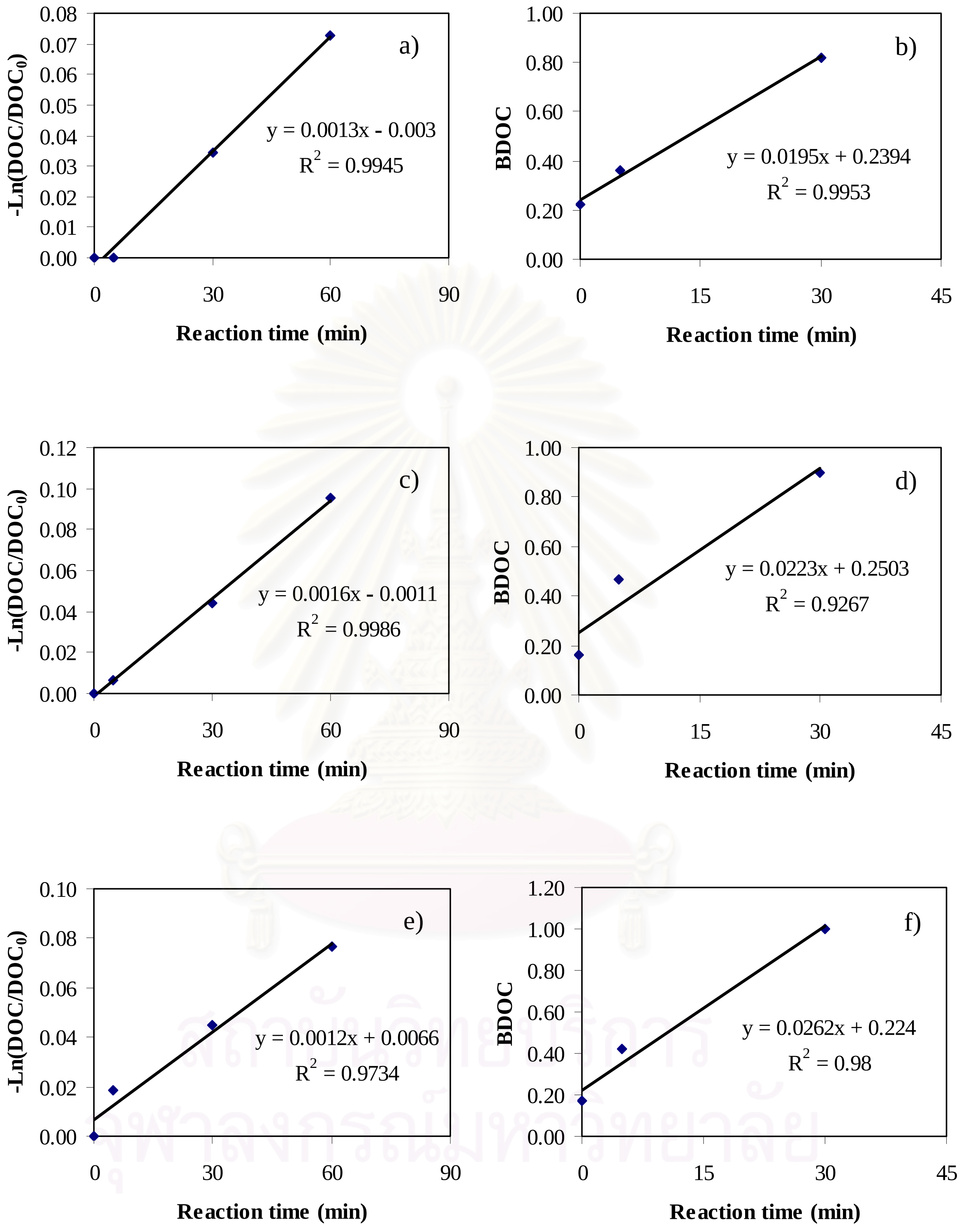


Figure A-31 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+3}:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

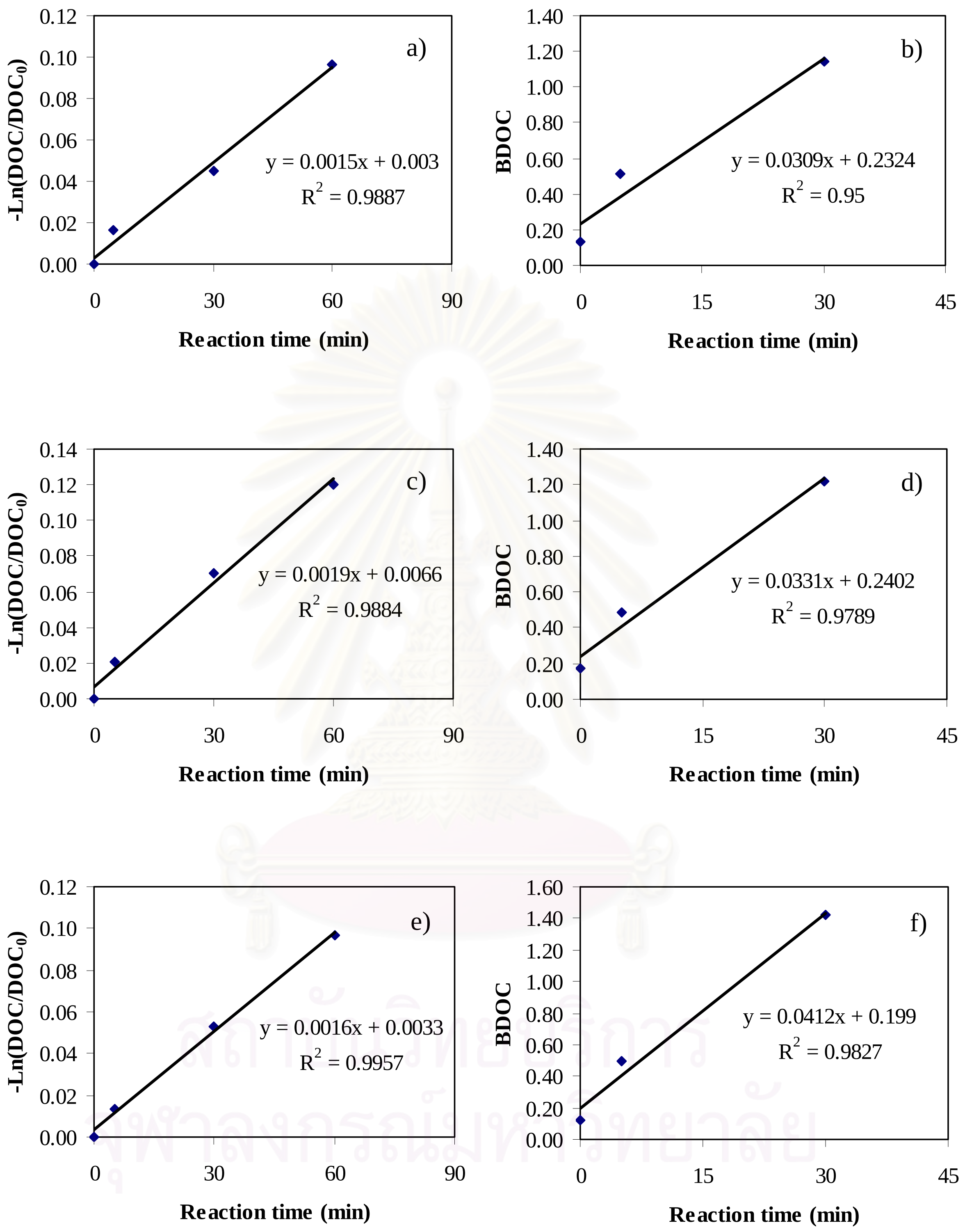


Figure A-32 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+3}:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

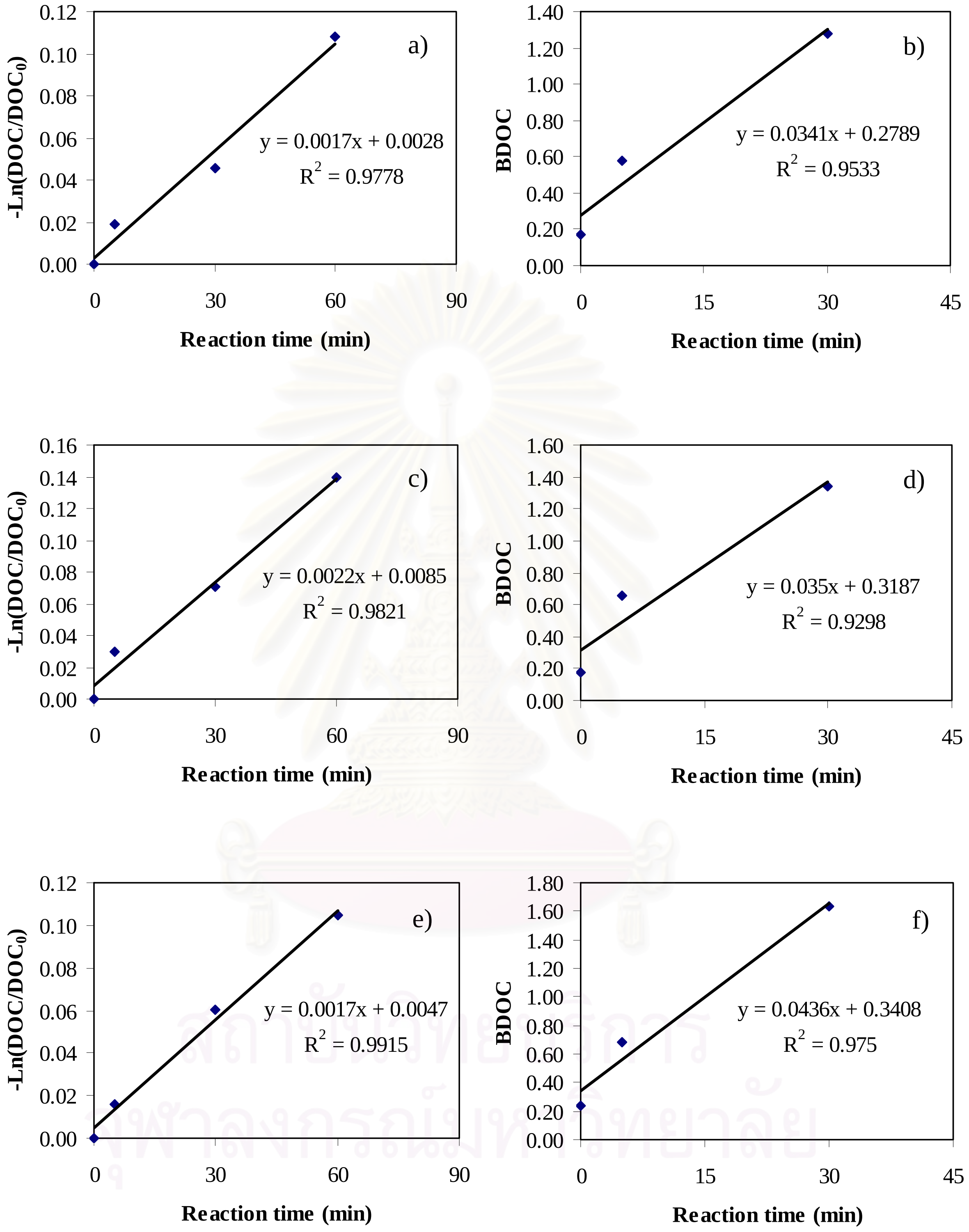


Figure A-33 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^{+3}:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

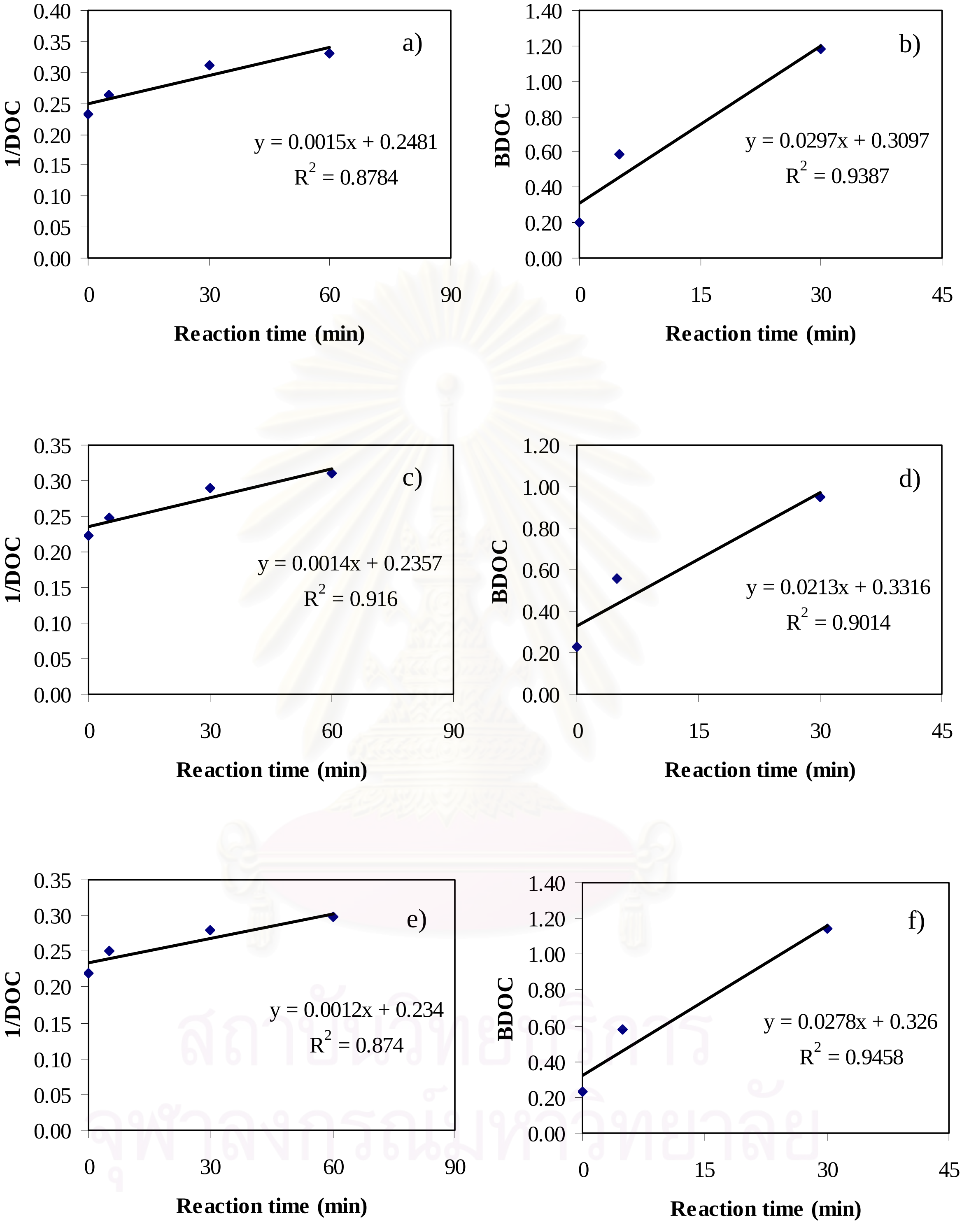


Figure A-34 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^0:H_2O_2:DOC of 5:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

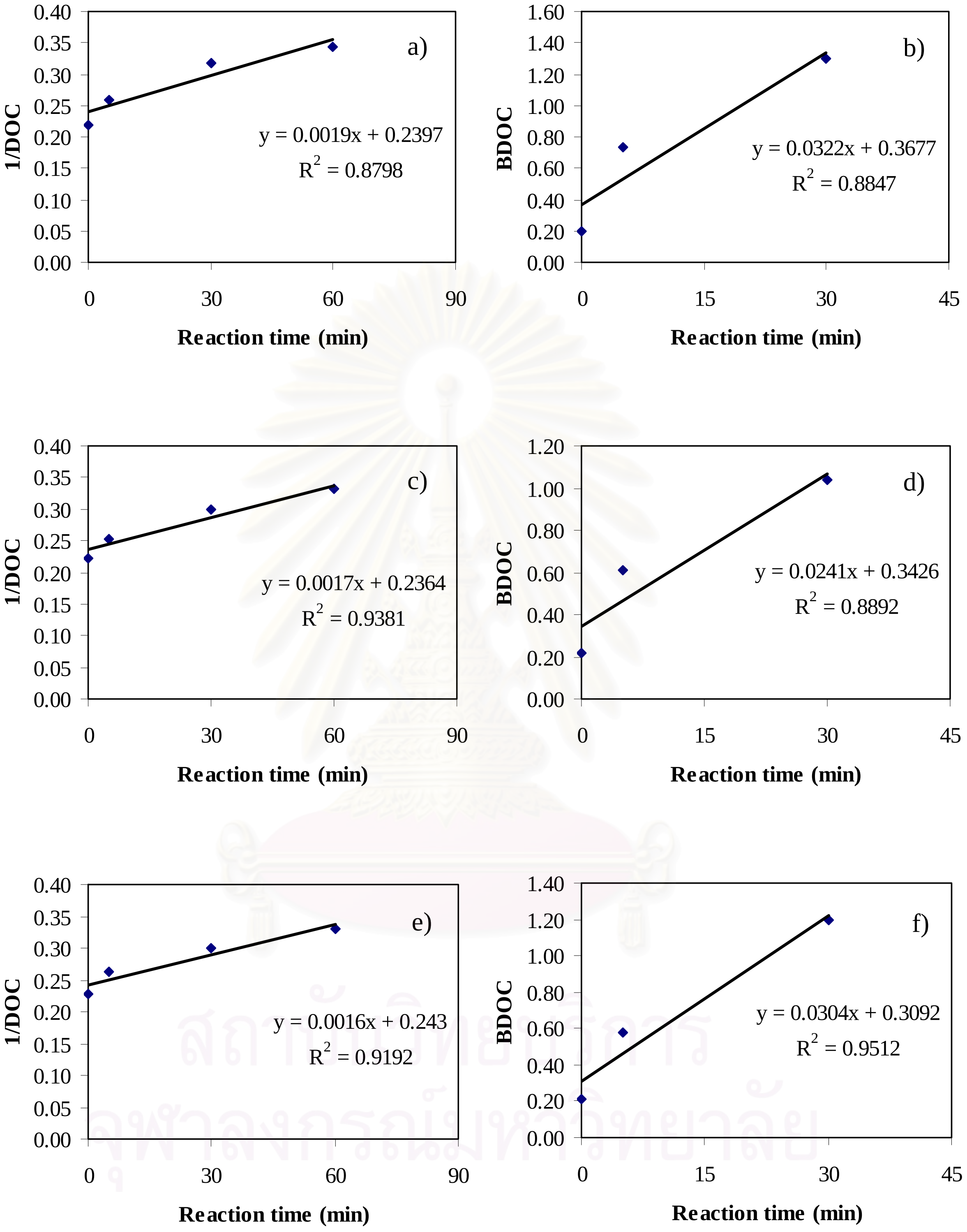


Figure A-35 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^0:H_2O_2:DOC of 10:10:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

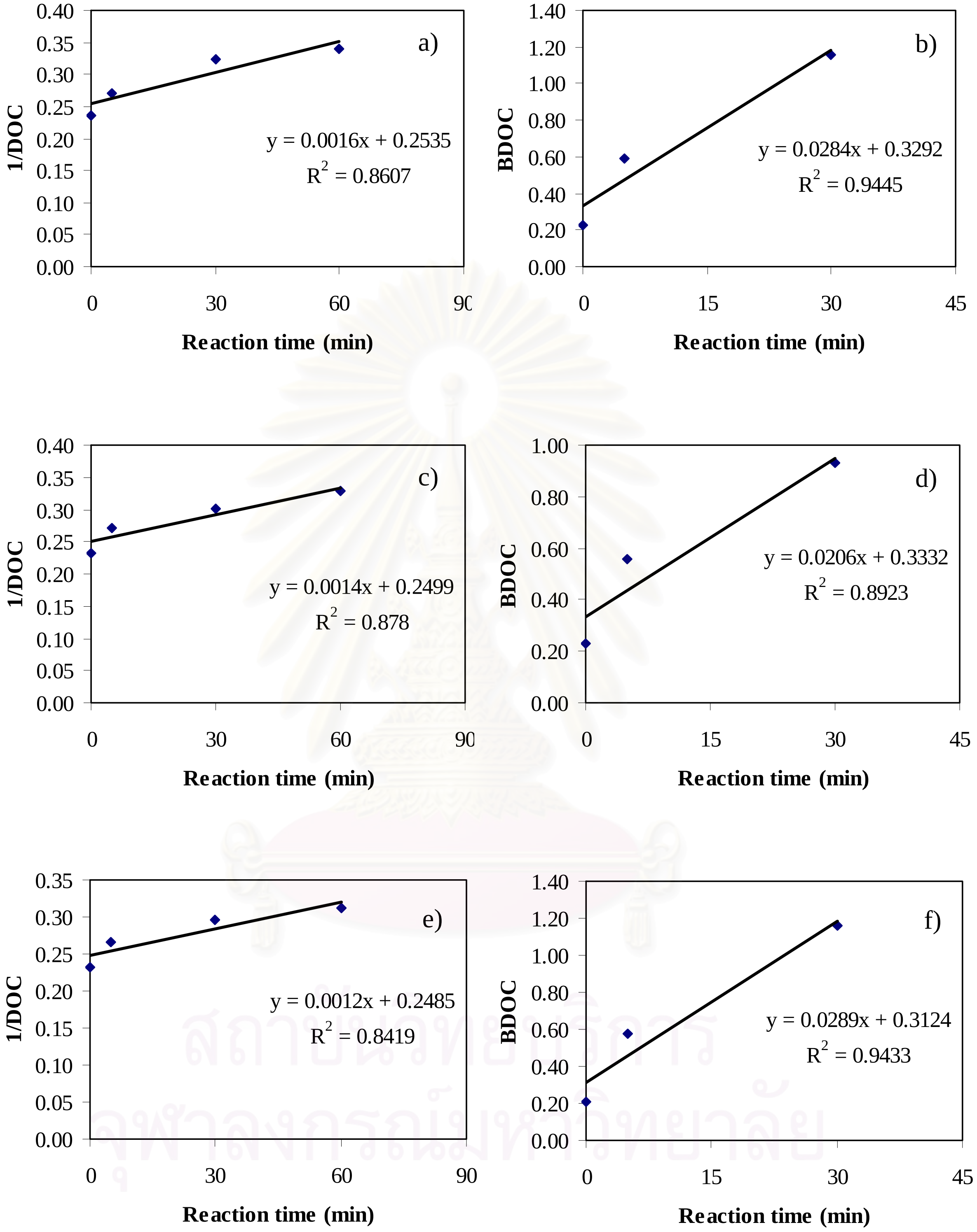


Figure A-36 The kinetic results of mineralization and biodegradability of 1,4-D at Fe^0:H_2O_2:DOC of 10:20:1 ratio and pH of 2 [(a) and (b)]; 3 [(c) and (d)]; and 4 [(e) and (f)]

Figure A-37 Mass spectrum of phosgene

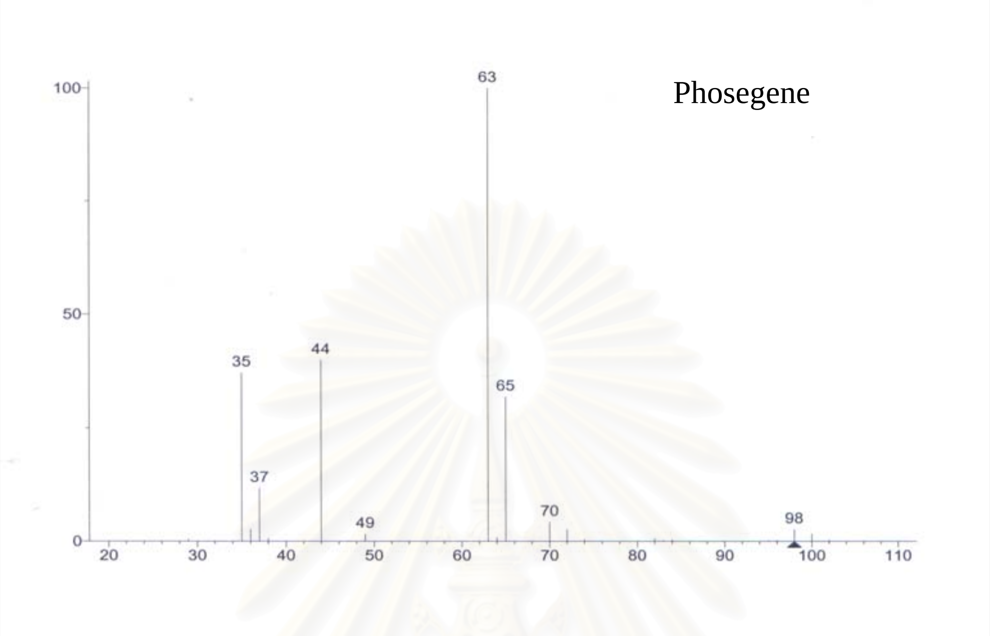


Figure A-38 Mass spectrum of DCAC

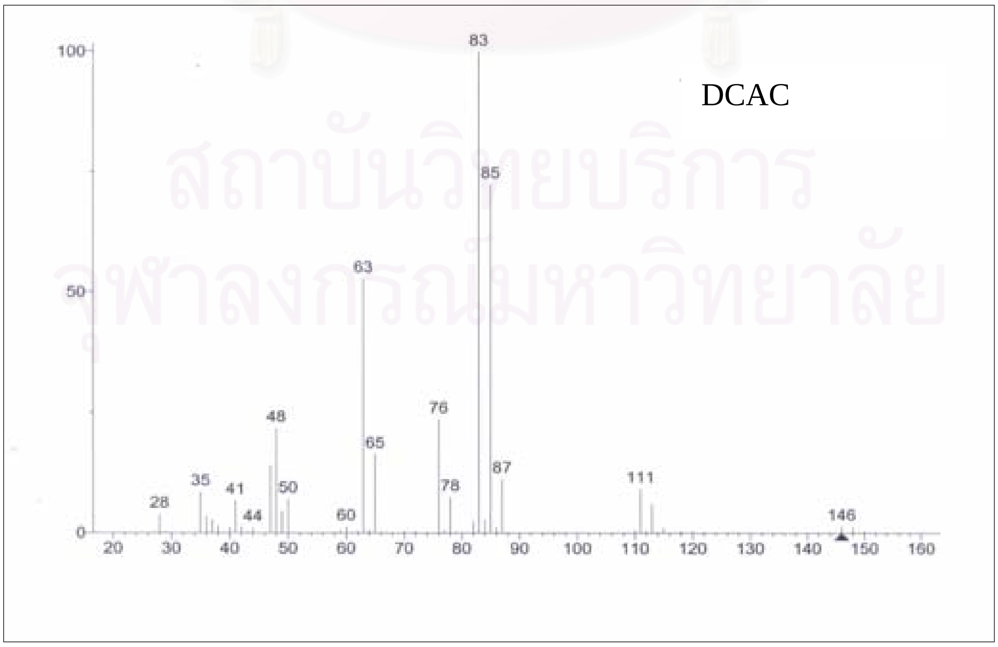


Figure A-39 Mass spectrum of ethene

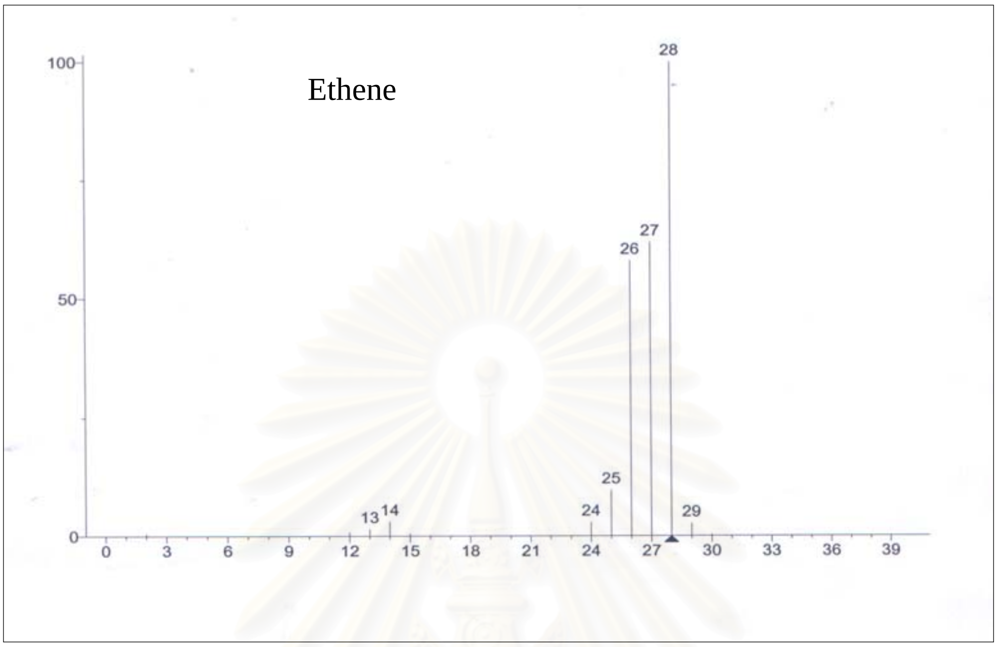


Figure A-40 Mass spectrum of ethane

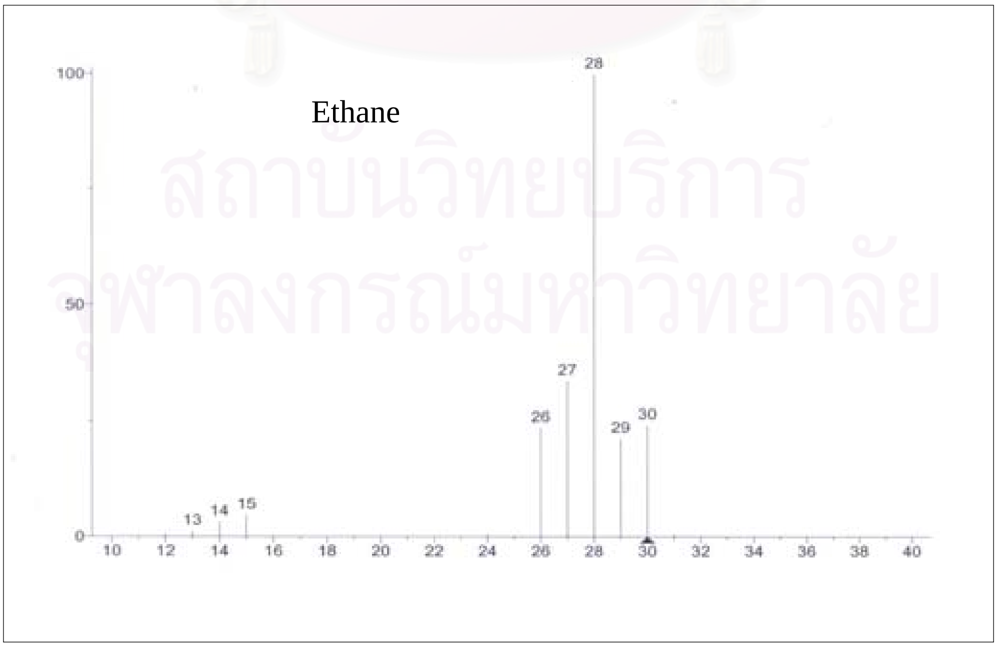


Figure A-41 Mass spectrum of VC

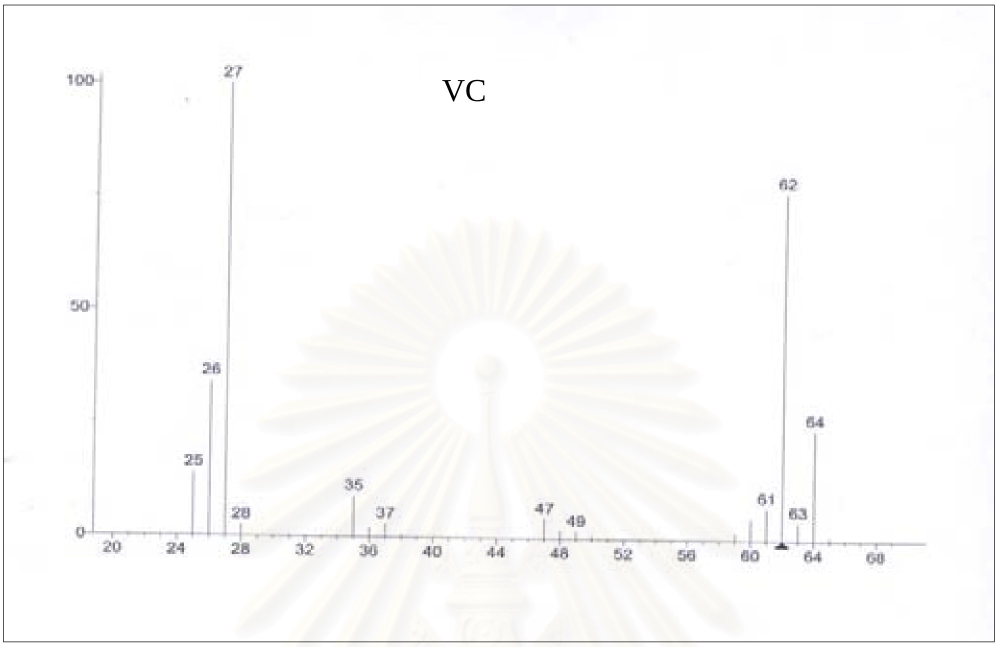


Figure A-42 Mass spectrum of chlorohydroquinone

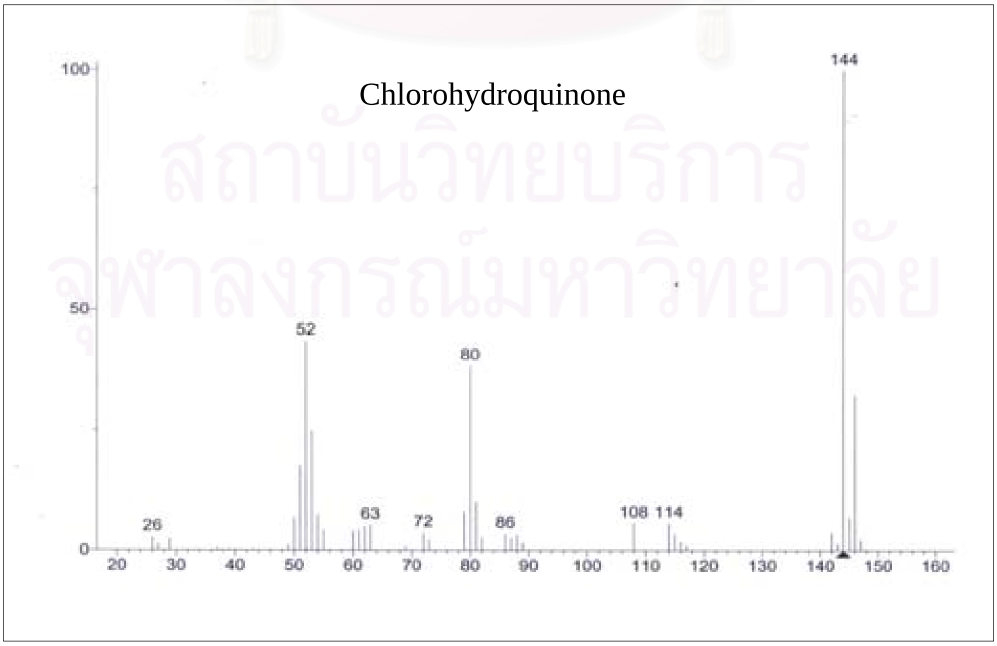


Figure A-43 Mass spectrum of 2-chloro-1,4-benzoquinone

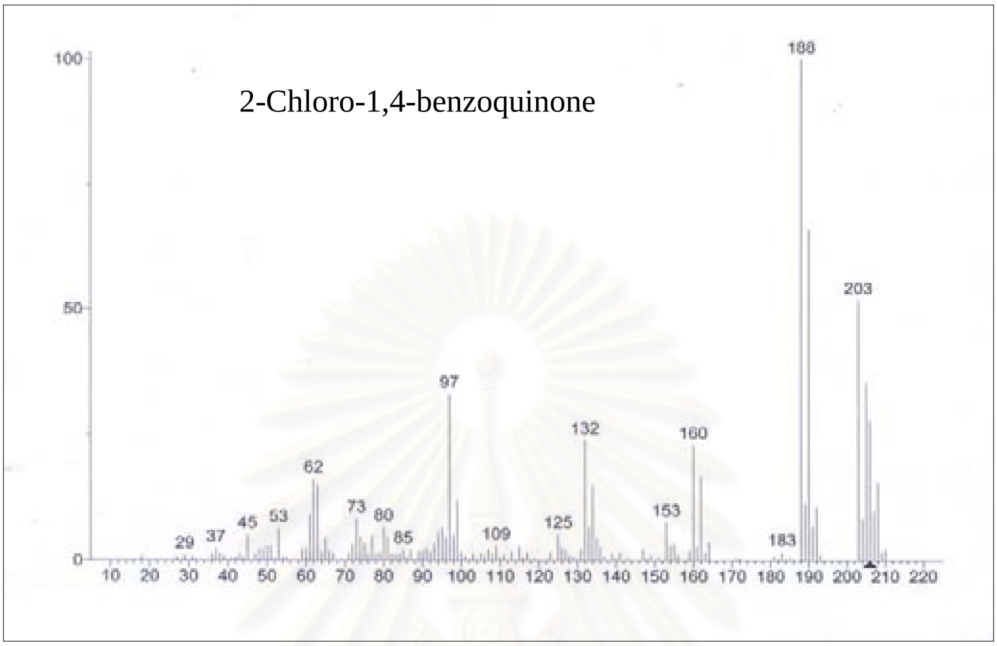


Figure A-44 Mass spectrum of 4,6-dichlororesocinol

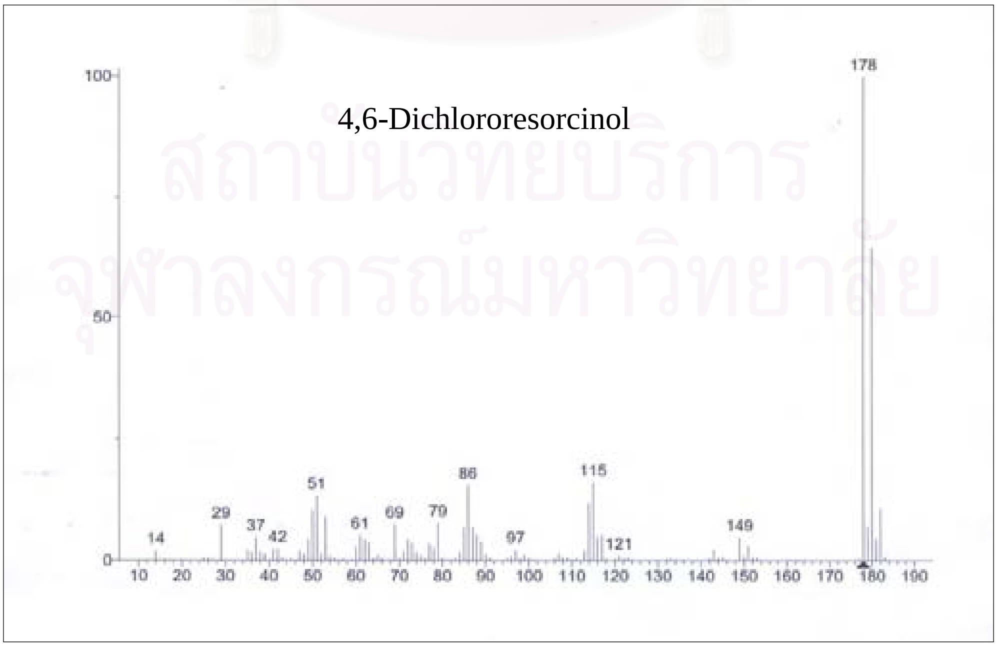


Figure A-45 Mass spectrum of hydroquinone

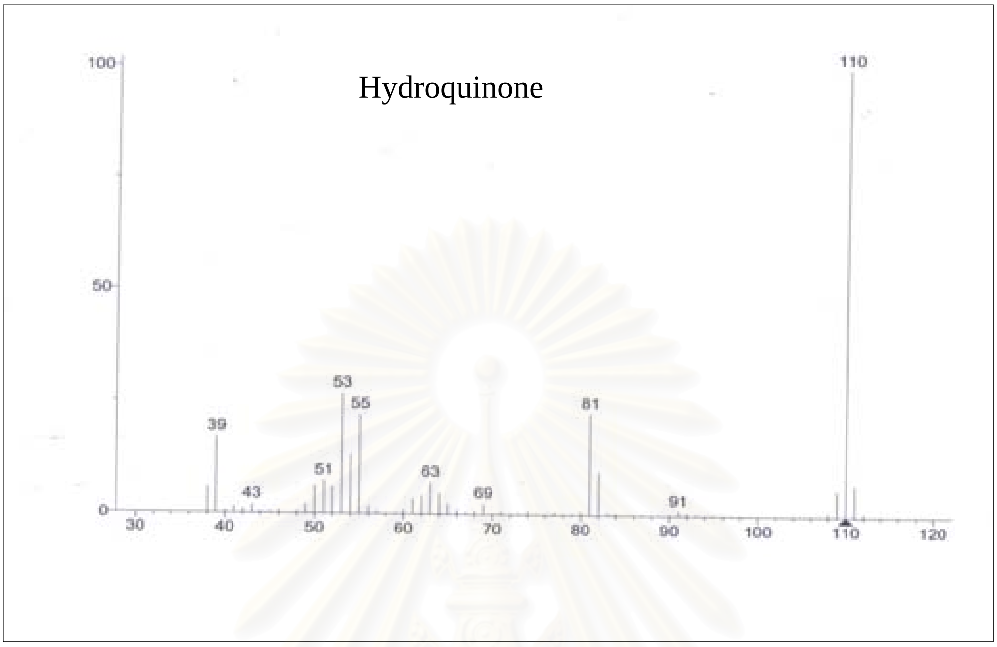


Figure A-46 Mass spectrum of catechol

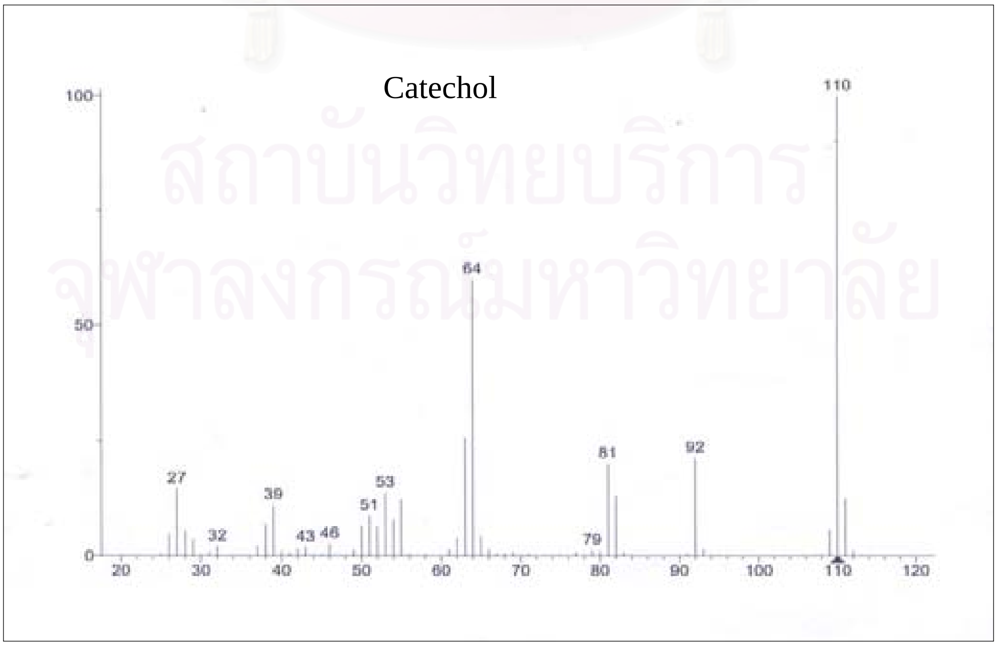


Figure A-47 Mass spectrum of 1,2-ethanediol monoformate

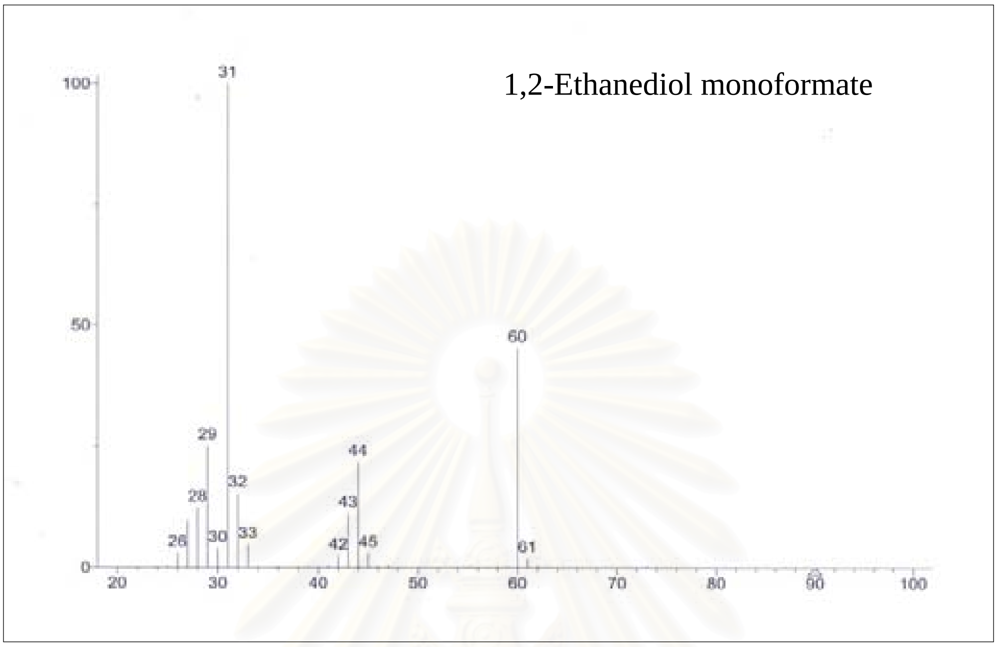


Figure A-48 Mass spectrum of 1,2-ethanediol diformate

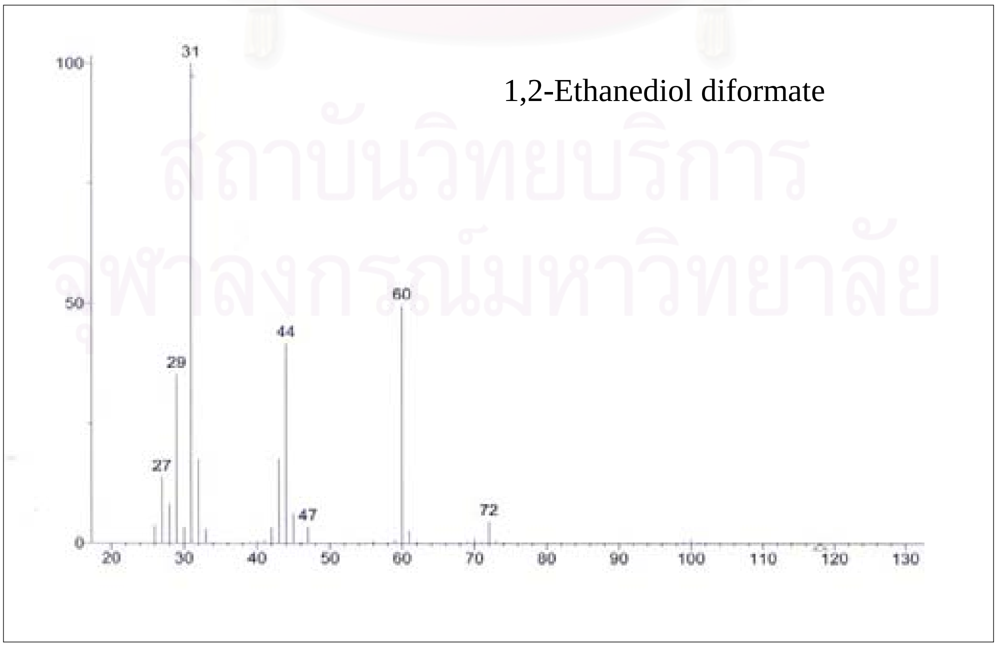


Figure A-49 Mass spectrum of formic acid

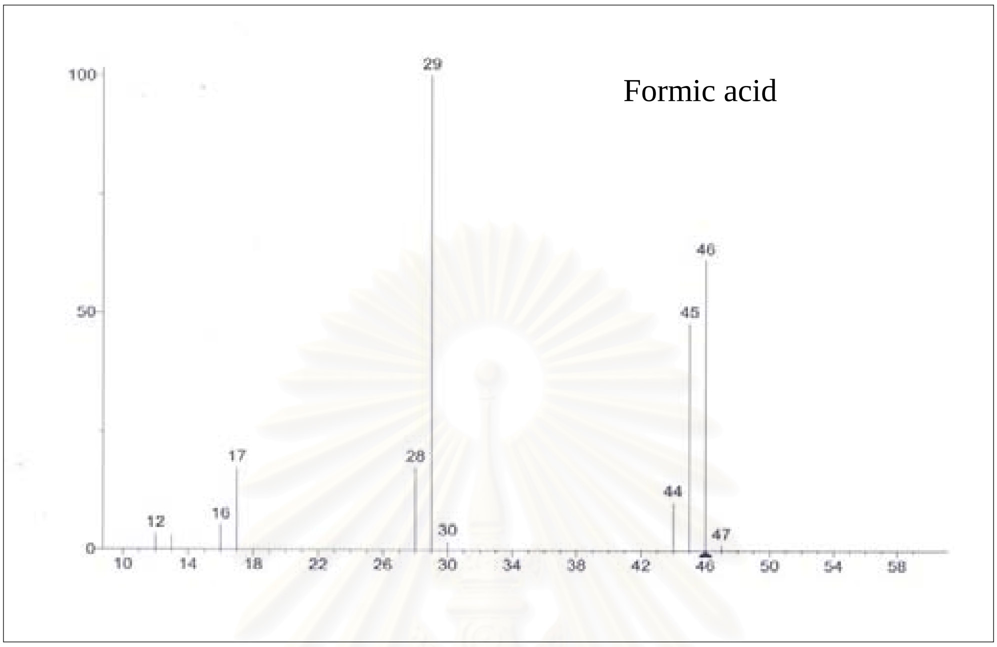


Figure A-50 Mass spectrum of methoxyacetic acid

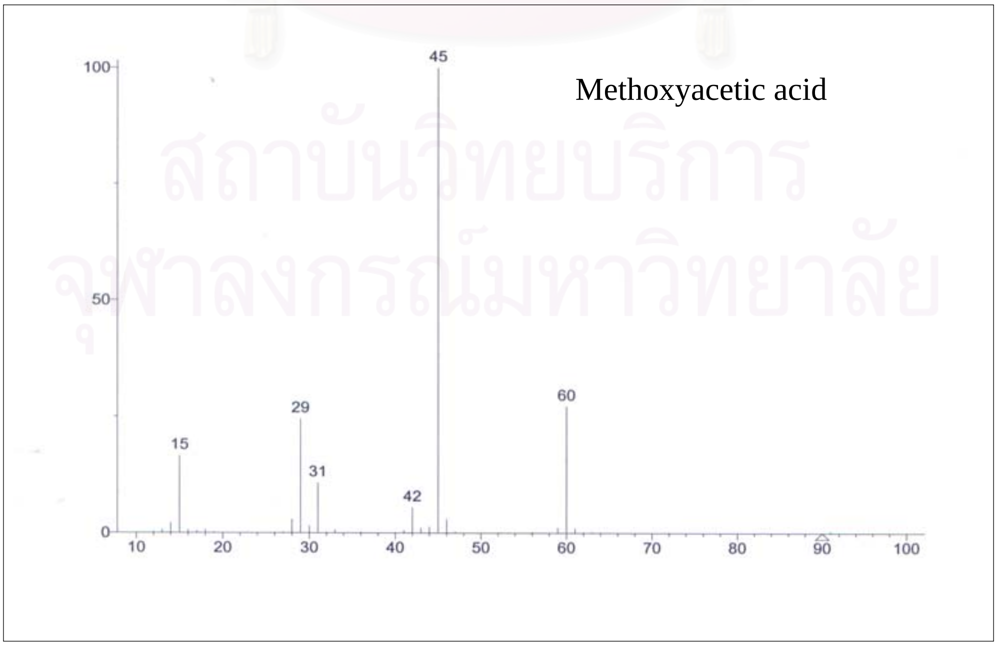


Figure A-51 Mass spectrum of 1,3-dichloto-2-propanone

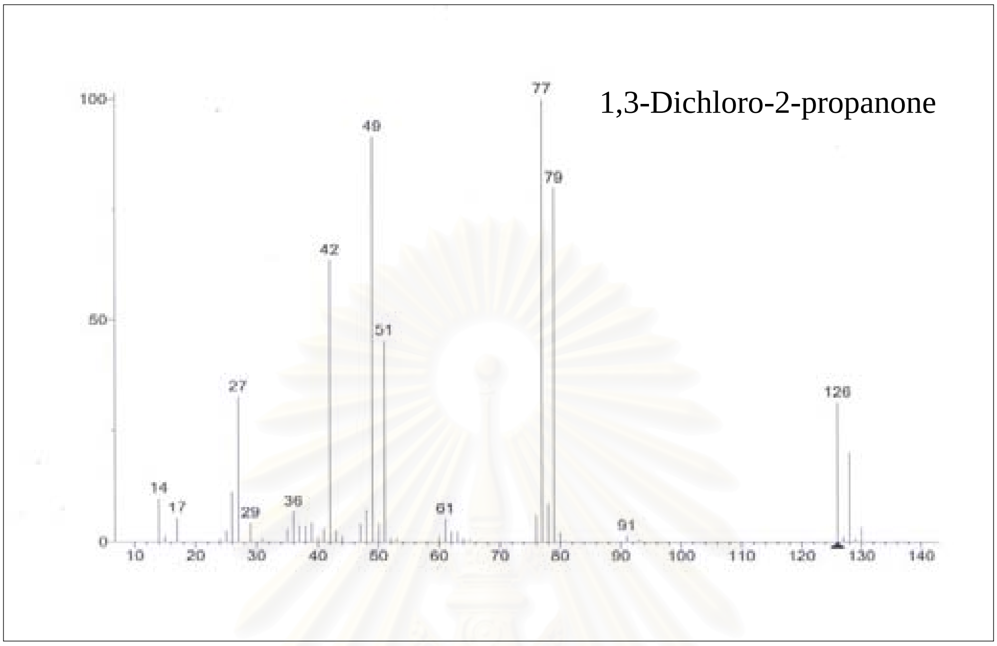


Figure A-52 Mass spectrum of 2,3-dichloto-1-propene

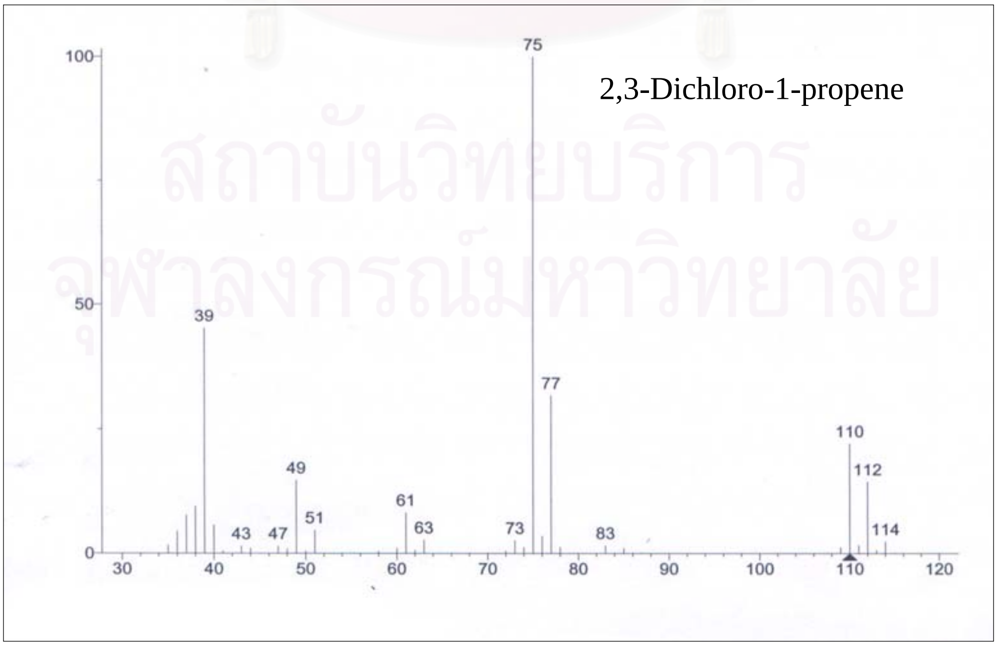


Figure A-53 Mass spectrum of isopropanol

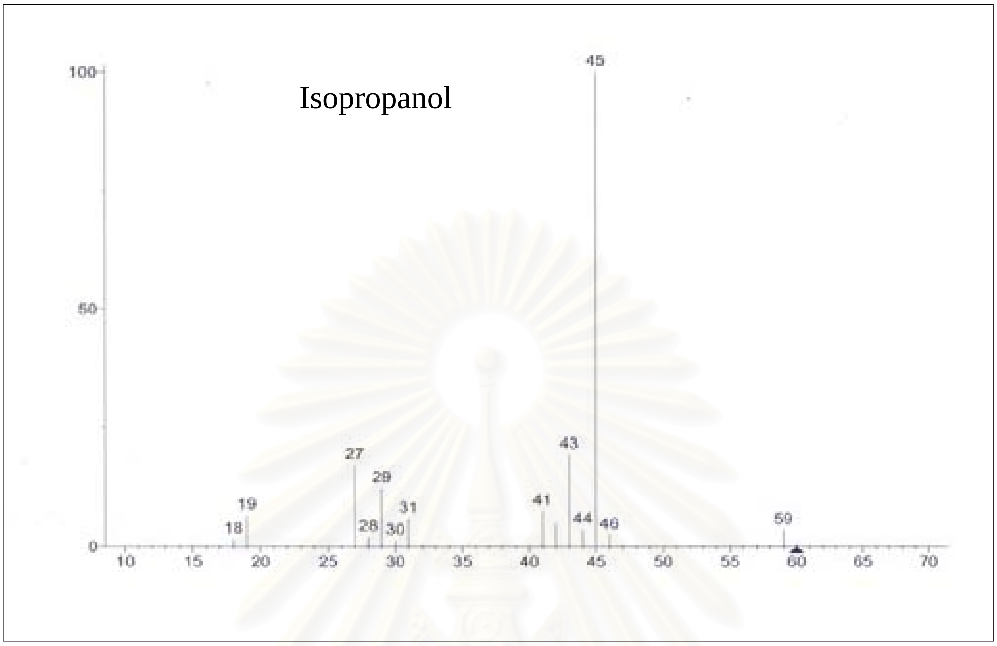
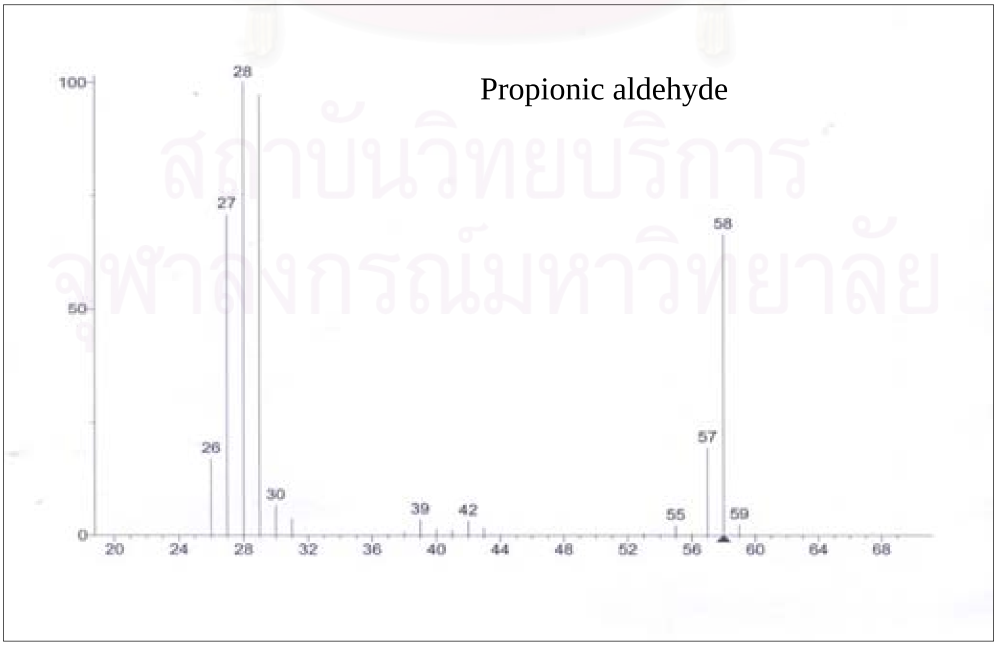


Figure A-54 Mass spectrum of propionic aldehyde



APPENDIX B

Standard Iodometric method (Kingzett, C.T., 1880)

Reagents

1. Potassium iodide solution (1%w/v KI). Dissolve 1.0 grams KI into 100 ml of RO water.
2. Ammonium molybdate solution. Dissolve 9 grams ammonium molybdate in 10 ml 6 N NH_4OH, add 24 grams NH_4NO_3 and dilute to 100 ml with OR water.
3. Sulfuric acid solution (1:4 H_2SO_4). Carefully add one part H_2SO_4 98 % to four parts RO water.
4. Starch indicator
5. Sodium thiosulfate (0.025 N Na_2SO_3. 5 H_2O) solution

Procedure

1. Sample was transfer to 250 ml Erlemeyer flask.
2. Adding RO water to the Erlenmeyer flask until 50 ml. Next, 10ml of 1:4 sulfuric acid solution and 15 ml of 1% w/v of potassium iodide were added. Then 2 drops of ammonium molybdate was added.
3. Titrate with 0.025 N of sodium thiosulfate to faint yellow or straw color. Swirl or stir gentry during titration to minimize iodine loss.
4. Add about 2 ml starch indicator, and continue titration until the blue color just disappear.
5. Repeat steps 2-4 on a blank sample of water.
6. Note ml of 0.025 $Na_2SO_3.5H_2O$ for samples and blanks analysis.

Standardize

1. weight out 2 grams of KI and transfer to 250 ml Erlenmeyer flask. Add RO water to 100 ml
2. Then, 10 ml of 0.025 N of $K_2Cr_2O_7$ and 10 ml of 1+ 9 H_2SO_4 were added. After that, keep the Erlenmeyer flask in dark place for 5 minutes.
3. Add RO water to the Erlenmeyer flask until 200 ml.
4. Tritrate with 0.025 N of sodium thiosulfate. And follow the procedure steps 3-4 as describe earlier.
5. Note ml of 0.025 $Na_2SO_3.5H_2O$ for standardize analysis.

Calculation

$$H_2O_2\ (\text{mg/l}) = \frac{(\text{A-B}) \times (\text{Normality of } Na_2SO_3) \times 17 \times 1{,}000}{\text{ml of sample}}$$

A = ml of Na_2SO_3 for sample

B = ml of Na_2SO_3 for blank

$$N = \text{Normality of } Na_2SO_3 = \frac{10 \times 0.025}{\text{ml of } Na_2SO_3 \text{ for standardize}}$$

BIOGRAPHY

Miss Nawarat Sermsai was born on November 26, 1979 in Chanthaburi province, Thailand. She graduated with a Bachelor’s degree Environmental Engineering from the Faculty of Engineering, King Mongkut,s University of Technology Thonburi in 2003. She studied for her Master’s degree of Science in Environmental Management (Inter-Department), Chulalongkorn University, Thailand from May, 2003 to October, 2005.