การสลายตัวของสารประกอบเชิงซ้อนตะกั่วด้วยวิธีโฟโตออกซิเดชันโดยใช้ไฮโดรเจนเปอร์ออกไซด์

นางสาวดวงกมล จิราโรจน์

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DEGRADATION OF LEAD COMPLEX BY PHOTOOXIDATION IN THE PRESENCE OF HYDROGEN PEROXIDE

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อ.ที่ปรึกษา: อ.ดร.เฟื่องฟ้า อุ่นอบ , 75 หน้า. ISBN 974-17-5133-8.

การศึกษาการสลายตัวของสารประกอบเชิงซ้อนตะกั่วในสารละลายด้วยการฉายแสงอัลตราไวโอเลต โดยใช้ไฮโดรเจนเปอร์ออกไซด์เป็นตัวเร่งปฏิกิริยา แหล่งกำเนิดแสงอัลตราไวโอเลตใช้ medium-pressure mercury lamp ที่ให้แสงในช่วงความยาวคลื่น 254 นาโนเมตร โดยได้ทำการศึกษาอิทธิพลของปัจจัยต่างๆ เพื่อหาสภาวะที่เหมาะสมสำหรับการสลายตัวของสารประกอบเชิงซ้อนตะกั่ว เช่น ความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ ค่าความเป็นกรด-เบสของสารละลาย อัตราส่วนระหว่างความเข้มข้นของสารประกอบเชิงซ้อนตะกั่วต่อไฮโดรเจนเปอร์ออกไซด์ และความเข้มข้นของไนเตรต ผลจากการทดลองแสดงให้เห็นว่าสารประกอบเชิงซ้อนตะกั่วสามารถสลายตัวได้รวดเร็วและสามารถกำจัดตะกั่วออกจากสารละลายได้ในเวลาเดียวกัน ซึ่งสังเกตุได้จากตะกอนที่เกิดขึ้น สภาวะที่เหมาะสมสำหรับการสลายตัวของสารประกอบเชิงซ้อนตะกั่วคืออัตราส่วนระหว่างสารประกอบเชิงซ้อนตะกั่วต่อไฮโดรเจนเปอร์ออกไซด์เป็น 1:20 ที่ค่าความเป็นกรด-เบสเริ่มต้นของสารละลายเป็น 3.0 หลังจากการฉายแสงพบว่ามีผลิตภัณฑ์ต่างๆ เกิดขึ้น เช่น nitrilotriacetic acid, iminodiacetic acid, ออกซาเลตและไนเตรต ส่วนผลของความเข้มข้นของไนเตรตนั้น พบว่าที่ความเข้มข้นต่ำ (0.004 M) ไนเตรตจะไม่ส่งผลต่อการสลายตัวของสารประกอบเชิงซ้อนตะกั่ว แต่ที่ความเข้มข้นสูง (0.04 M) ไนเตรตจะทำให้การสลายตัวของสารประกอบเชิงซ้อนตะกั่วและการกำจัดตะกั่วลดลง ค่า quantum yield ของการสลายตัวของสารประกอบเชิงซ้อนตะกั่วด้วยวิธีโฟโตออกซิเดชัน มีค่า 0.30 นอกจากนี้ได้ศึกษาเปรียบเทียบการสลายตัวของสารประกอบเชิงซ้อนตะกั่วกับสารประกอบเชิงซ้อนของโลหะอื่นๆ เช่นสังกะสีและแคดเมียม พบว่าสารประกอบเชิงซ้อนของสังกะสี และแคดเมียม สามารถสลายตัวได้อย่างรวดเร็วเช่นกัน แต่ปริมาณของสังกะสีและแคดเมียม ในสารละลายยังมีเท่าเดิม ค่า quantum yield ของการสลายตัวของสารประกอบเชิงซ้อนของสังกะสีและแคดเมียมด้วยวิธีโฟโตออกซิเดชัน มีค่าเป็น 0.21 และ 0.22 ตามลำดับ

ภาควิชา......เคมี...... ลายมือชื่อนิสิต..............................
สาขาวิชา......เคมี...... ลายมือชื่ออาจารย์ที่ปรึกษา..............................
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DUANGKAMON JIRAROJ: DEGRADATION OF LEAD COMPLEX BY PHOTOOXIDATION IN THE PRESENCE OF HYDROGEN PEROXIDE. THESIS ADVISOR: FUANGFA UNOB, Ph.D. 75 pp. ISBN 974-17-5133-8.

The degradation of Pb-EDTA in aqueous solution by H_2O_2/UV process was studied. The UV radiation source was a medium-pressure mercury lamp (254 nm). The effect of hydrogen peroxide concentration, initial pH of solution, Pb-EDTA to H_2O_2 molar ratio and nitrate concentration have been investigated. Pb-EDTA can be rapidly degraded by H_2O_2/UV process accompanied by simultaneous lead removal. A precipitation of lead during irradiation has been observed. From the experiments, the optimum conditions are Pb-EDTA: H_2O_2 molar ratio of 1:20 at initial solution pH of 3.0. NTA, IDA, oxalate and nitrate were found as by-products. It was found that the by-products like NTA itself can also be decomposed by photooxidation. The results indicated that nitrate in low concentration (0.004 M) has not effected Pb-EDTA degradation. In contrast, nitrate present at a relatively higher concentration (0.04 M) remarkably reduced Pb-EDTA degradation and lead removal. The quantum yield of the photooxidation of Pb-EDTA was 0.30. The photooxidation of Zn-EDTA and Cd-EDTA have also been studied. It was found that Zn-EDTA and Cd-EDTA were decomposed rapidly but total zinc and cadmium concentration were not reduced. The quantum yield of the photooxidation of Zn-EDTA and Cd-EDTA are 0.21 and 0.22, respectively.

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LIST OF SYMBOLS AND ABBREVIATIONS

AOPs	advanced oxidation processes
CE	capillary electrophoresis
Cd-EDTA	cadmium ethylenediaminetetraacetic acid
FAAS	flame atomic absorption spectrometry
EDDA	ethylenediaminediacetic acid
EDTA	ethylenediaminetetraacetic acid
IDA	iminodiacetic acid
NTA	nitrilotriacetic acid
Pb-EDTA	lead ethylenediaminetetraacetic acid
TTAB	tetradecyltrimetylammonium bromide
UV	ultraviolet
Zn-EDTA	zinc ethylenediaminetetraacetic acid
M	molar
min	minute
mL	milliliter
mM	millimolar
t	time
λ	wavelength
Φ	quantum yield
$h\nu$	ultraviolet radiation
$R_{Ac,\lambda}$	the photonic flux of ferrioxalate actinometer at wavelength λ
$R_{0,\lambda}$	the incident photonic flux of the irradiation source
A_{λ}^{Ac}	the absorbance of ferrioxalate actinometer at wavelength λ
ε	the corresponding molar absorption coefficient
n_B	the number of B produced

CHAPTER I

INTRODUCTION

At present, industries are developed rapidly. As a consequence, the environment is more and more polluted. One of the most found pollutants is lead and lead complexes, widely used in various industries. Eighty percent of lead are used in the production of automotive and industrial lead-acid battery [Atwood, Matlock and Howerton 2002]. Furthermore, the cosmetic, pigment and printing, mining or insecticide industries also use lead as a composition [Odum 2000]. Therefore, lead and lead complexes may be released to the environment. The human body can absorb lead through air, food and water. Lead can accumulate in the body and tissues beginning from intestine and lung [Odum 2002]. A high level of lead causes a sickness or death. It is necessary to remove lead and lead complexes from wastewater before releasing to environment.

1.1 Toxicity of lead and ethylenediaminetetraacetic acid (EDTA)

1.1.1 Toxicity of lead

Lead is physiologically and neurologically toxic to human. It can damage practically all tissues, particularly the kidney and the immune system. Lead poisoning results in disfunction of kidney, liver, reproductive system, brain and central nervous system, causing sickness or death. Lead reaches all other tissues through the blood. Because of its ability to mimic calcium, lead can accumulate in the bone and becomes a stable bone component, particularly in the case of insufficient calcium intake. In adults, lead damages mainly cause peripheral neuropathy, which is characterized predominantly by demyelination of the nerve fibers. High lead levels cause encephalopathy, with the following symptoms: vertigo, insomnia, migraine, irritability and even convulsions, seizures and coma. Lower levels of the metal give rise to lead-induced neuropathy, which mainly affects the brain developing, provokes behavioural problems and cognitive impairment [Odum 2002].

1.1.2 Ethylenediaminetetraacetic acid (EDTA)

Ethylenediaminetetraacetic acid (EDTA) is widely used as a complexing agent in many industries, for example in the production of detergents, textiles, pulp and paper, metal plating, cosmetics industries, medical service, cleaning products[Sillanpää and Sihavonen 1997]. EDTA is often used in large quantity because of its high solubility in water. As a result, the excess of EDTA is left in wastewater. In water, EDTA is slowly degraded by biodegradation process and accumulates in the environment.

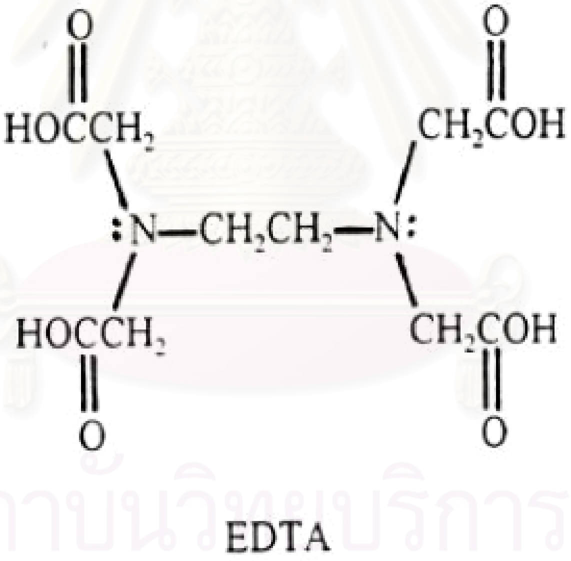


Figure 1.1 EDTA structure

EDTA is a tetraprotic acid denoted as H_4Y [Sheppard and Henion 1997]. The four stepwise dissociation constants of the parent acid to yield H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-} are 1.00×10^{-2}, 2.16×10^{-3}, 6.92×10^{-7}, and 5.50×10^{-11}, respectively [Allen and Chen 1993]. EDTA is a strong chelating agent and their complexes with metals are also stable. One EDTA molecule can only chelate one metal ion [Egli and Bucheli-Witschel 2001]. In the environment, EDTA can form complexes with heavy metals that dissolve in sediments and water. When metals are in EDTA complex form, it can not be removed by traditional wastewater treatment method such as hydroxide precipitation. For this reason, heavy metals in form of metal-EDTA complexes can escape and accumulate in the environmental sources [Allen and Chen 1993; Nowack 2002; Nörtemann 1999].

In this work, we are interested in the degradation of lead-EDTA complex (Pb-EDTA).

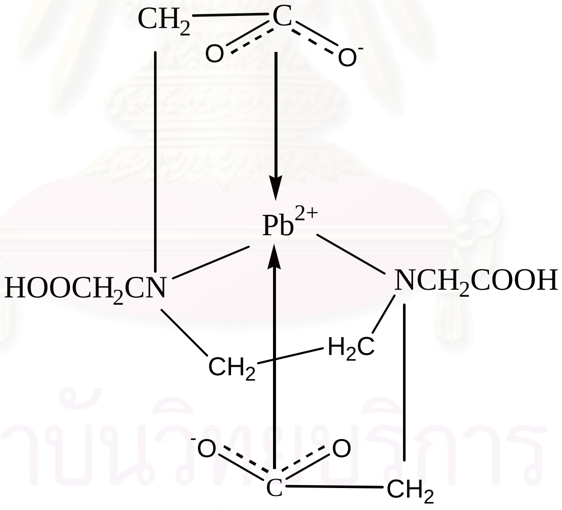


Figure 1.2 Pb-EDTA Structure [Dragan and Fitch 1998]

Pb-EDTA is very stable and soluble in water and sediment [Nowack 2002]. In solution, Pb-EDTA exists in different species depending on pH value, as shown in figure 1.3. For pH values lower than 2.0, the majority of species are free cation (Pb^{2+}) and free ligand (H_4Y). At pH higher than 3.0, complex PbY^{2-} species is mainly present.

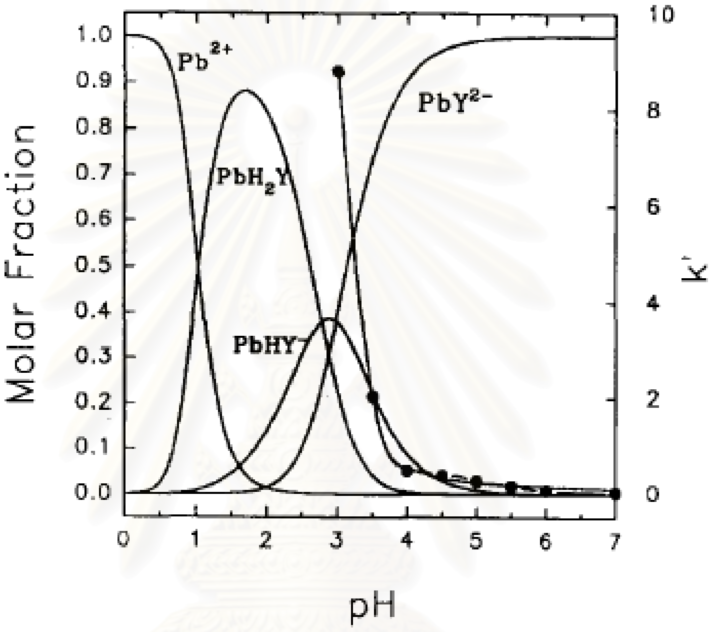
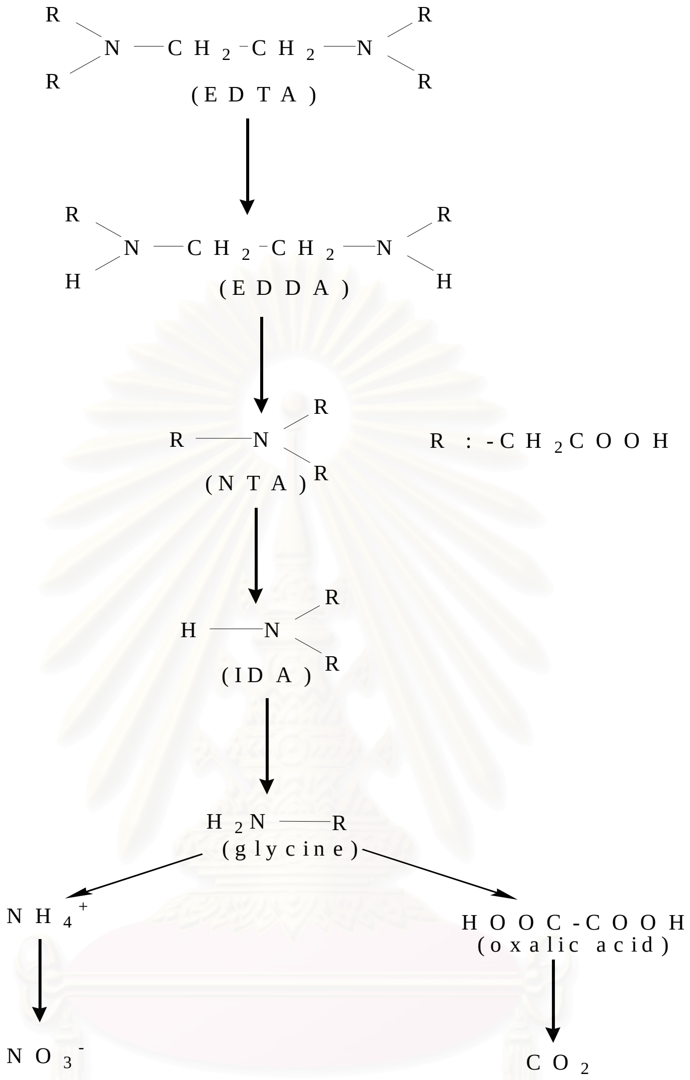


Figure 1.3 Molar fractions of Pb-EDTA species as function of pH [Sarzanini *et al.* 1995]

Pb-EDTA is not biodegradable or removable by traditional techniques, such as precipitation. In the last decades, Advanced Oxidation Processes (AOPs) have been introduced to wastewater treatment. There is a large number of works investigating the decomposition of EDTA in aqueous solution and identification of its by-products. For example, the degradation of EDTA by UV/H_2O_2 process [Ku *et al.* 1998; Peralta-Zamore *et al*. 2002; Nörtemann 1999] gives the by-products as ethylenediaminediacetic acid (EDDA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), glycine, and oxalic acid. The decomposition of EDTA can be represented in scheme 1.1.



Scheme 1.1 The proposed pathway of EDTA decomposition [Ku *et al*. 1998]

1.1.3 Toxicity of EDTA and by-products

In human body, EDTA is not or scarcely metabolized and thus excreted as a chelate complex via urine following glomerular filtration and tubular secretion. World Health Organization (WHO) fixed the acceptable daily intake of EDTA to 2.5 mg/kg body weight [Egli and Bucheli-Witschel 2001]. If the body absorbs EDTA at higher dose levels, it will cause headache, nausea, diarrhea, emaciation, loss of body weight, low blood pressure, convulsion, kidney failure, irregular heart beat, seizures or even death.

EDTA is resistant to biodegradation. In contrast, NTA, one of EDTA degradation by-products, was found to be readily biodegradable [Nörtemann 1999]. It can be degraded principally by microorganism and by carbon-nitrogen cleavage with the formation of intermediates such as IDA, glyoxylate, glycerate, glycine, and ammonia. The eventual metabolic products obtained are carbon dioxide, water, ammonia and nitrate. In human body, NTA is not metabolized but rapidly excreted by the kidney. It is moderately toxic to mammals [Egli and Bucheli-Witschel 2001]. NTA can accumulate in bone and kidney by forming complexes with divalent cations such as calcium. However the concentrations of NTA can decrease rapidly [Budny and Arnold 1973]. There are, so far, no reports about toxicity of other degradation by-products of EDTA.

1.2 Removal of heavy metal

Various physicochemical and biological methods have been studied for heavy metal removal. The most widely used method is the precipitation of heavy metals in the form of hydroxide or sulfide salts. It is applied for the removal of metal ions such as Fe^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, and Zn^{2+} from water [McLaughlin *et al*. 1995]. The examples of research using other methods for removal of heavy metals are listed below.

1. Sorption processes

Lin and Juang [2002] have used the montmorillonite modified with sodium dodecylsulfate (SDS) for heavy metals removal from water. Some natural filter substrates (combination of calcium silicate rock (opoka), zeolite and peat) were also applied in the sorption process [Färm 2002].

2. Ion exchange

Konsowa and Elshazly [2003] used a cation-exchange resin to remove Ni^{2+} from wastewater. And calcium-loaded lignite has also been used as ion exchange media to remove Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, and Fe^{2+} from wastewater [Punčochář *et al*. 2004].

3. Adsorption processes

There were reports of the application of inorganic chemically active adsorbents (ICAAs). The examples of ICAAs studied were ceramic supports immobilized with chelating agents [Deorkar and Tavlarides 1998], a coffee residues binding with clay [Boonamnuayvitaya *et al*. 2004] and a synthetic adsorbent materials, such as an aminodiacetic chelating resin (Lewatit TP 207) [Pagnanelli *et al*. 2004] for heavy metals (Ni^{2+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}) removal.

4. Biosorption processes

An example of this process is the use of polyvinyl alcohol-alginic acid bead for heavy metal removal from wastewater [Yoo *et al*. 2002; Chen *et al* 2001].

5. Photocatalytic digestion method

This method is one of the advanced oxidation processes. TiO_2 photocatalytic process has been used for degradation and removal of heavy metals (Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, and Mn^{2+}) from water [Hasegawa *et al*. 1997; Datye *et al*. 1997; Gutz and Cavicchioli 2001].

1.3 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) rely mainly on the use of short-lived oxidative species (often hydroxyl radicals) generated by photolysis, photocatalysis or radiolysis. AOPs were applied in water purification and wastewater treatment process because of its high efficiency in the destruction of toxic and refractory contaminants. The examples of the use of AOPs in wastewater treatment are the treatment of dye and nitroglycerin in wastewater by H_2O_2/UV process [Shen and Wang 2002; Hempfling 1997] and the photooxidation of 2,4-dinitrotoluene and *p*-hydroxybenzoic acid [Beltran-Heredia *et al*. 2001; Ho 1986]. It was found that the organic substrate can be decomposed by AOPs.

One of the most interesting processes in advanced oxidation processes is photochemical oxidation. In this process, the highly reactive species, such as hydroxyl radicals ($OH^{\bullet}$) are produced as primary oxidant. It was generated by UV irradiation in the presence of an oxidant, such as ozone or hydrogen peroxide. The examples of photochemical oxidation process are Fenton's reagent (Fe^{2+}/H_2O_2), titanium dioxide with UV irradiation (TiO_2/UV), ozone with UV irradiation (O_3/UV), ozone/hydrogen peroxide with UV irradiation (O_3/H_2O_2/UV) [Akgerman and Alnaizy 2000; Weavers *et al*. 2003; Esplugas *et al*. 2002]. In this work, photooxidation in the presence of hydrogen peroxide (H_2O_2/UV) was used to study the degradation of lead-EDTA complex.

Table 1.1 Thermodynamic oxidation potential of common oxidizing agents used in water treatment [Zappi *et al*. 2002].

Species	Comparative oxidation potentials (Volts)
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Hypochlorous acid	1.5
Chlorine	1.4
Oxygen	1.2

By comparing the oxidation potential, the most powerful oxidizing species is the hydroxyl radical, followed by ozone, hydrogen peroxide and potassium permanganate, respectively. Hydroxyl radical is one of the most reactive intermediate chemical species. The relative oxidation potentials of several chemical oxidizing agents used in water treatment are shown in table 1.1.

1.3.1 Hydroxyl radical generation

1.3.1.1 Generation of hydroxyl radicals ($OH^\bullet$) by O_3/UV process

Ozone is a powerful oxidizer having an oxidation potential of about 1.5 times of that of chlorine and oxygen gas, which is the most common oxidizer used in drinking water treatment. The process makes use of UV photons to activate ozone (O_3) molecules, thereby facilitating the formation of hydroxyl radicals. The reaction mechanism starts with activating the ozone molecule by UV to form oxygen radicals, which then combine with water to form $OH^\bullet$ radicals as shown in equation (1.1) and (1.2) [Zhou and Smith 2002; Braun *et al.* 1993].

$$O_3 + h\nu \longrightarrow O_2 + O(^1D) \qquad \text{……(1.1)}$$

$$O(^1D) + H_2O \longrightarrow 2OH^{\bullet} \qquad \text{……(1.2)}$$

The photolysis of ozone dissolved in water leads to the production of hydrogen peroxide as shown in equation (1.3).

$$O(^1D) + H_2O \longrightarrow H_2O_2 \qquad \text{…….(1.3)}$$

The H_2O_2 formed could be further photolyzed to yield two hydroxyl radicals. Alternatively, it could be first dissociated into HO_2^- and then participate in a series of chain reactions along with ozone to produce hydroxyl radicals as occured in the O_3-H_2O_2 process. The efficiency of this process would be enhanced by the high concentration of ozone.

1.3.1.2 Generation of hydroxyl radicals ($OH^{\bullet}$) by O_3/H_2O_2 process

The path for the formation of hydroxyl radicals in this process is similar to those radical production mechanisms associated with the O_3/UV system. Hydrogen peroxide reacts very slowly with the ozone molecule in water while its conjugate base (HO_2^-) can rapidly react with molecular ozone. The mechanism during O_3/H_2O_2 process for the formation of the hydroxyl radical are shown in equation (1.4) – (1.8) [Zappi *et al.* 2002; Zhou and Smith 2002].

$$H_2O_2 + H_2O \longleftrightarrow H_3O^+ + HO_2^- \qquad \text{…..(1.4)}$$

$$O_3 + HO^- \longrightarrow HO_2^- + O_2 \qquad \text{…..(1.5)}$$

$$O_3 + HO_2^- \longrightarrow OH^{\bullet} + O_2^{\bullet -} + O_2 \qquad \text{…..(1.6)}$$

$$O_3 + O_2^{\bullet -} \longrightarrow O_3^{\bullet -} + O_2 \qquad \text{…..(1.7)}$$

$$H_2O + O_3^{\bullet -} \longrightarrow OH^{\bullet} + HO^- + O_2 \qquad \text{…..(1.8)}$$

An advantage over the O_3/UV process is that it can be used in turbid or dark waters because it is a dark AOP that is not dependent on the transmissivity of the influent being treated.

1.3.1.3 Generation of hydroxyl radicals ($OH^\bullet$) by TiO_2/UV process

The TiO_2/UV process is a heterogeneous photocatalytic process. Certain metal oxides used can readily generate hydroxyl radicals on the surface of particles when UV light is absorbed. The mechanism of the process is shown in equation (1.9) – (1.13) [Zhou and Smith 2002].

$$TiO_2 + h\nu \longrightarrow TiO_2\,(e^- + h^+) \qquad \text{......(1.9)}$$

$$TiO_2\,(h^+) + H_2O \longrightarrow OH^\bullet + TiO_2 + H^+ \qquad \text{.....(1.10)}$$

$$TiO_2\,(e^-) + O_2 \longrightarrow O_2^- + TiO_2 \qquad \text{..... (1.11)}$$

$$O_2^- + TiO_2\,(e^-) \longrightarrow O_2^{2-} \qquad \text{.....(1.12)}$$

$$O_2^{2-} + H^+ \longrightarrow HO_2^- \qquad \text{....(1.13)}$$

TiO_2 particles generate valence-band holes (h^+) and conduction-band electrons (e^-) by UV irradiation. The valence-band holes (h^+) are very reactive and can directly react with organic substrates absorbed on the surface or indirectly via the hydroxyl radical formed. The conduction-band electrons (e^-) react with organic substrates in water via O_2^-, O_2^{2-} and HO_2 generated.

1.3.1.4 Generation of hydroxyl radicals ($OH^\bullet$) by H_2O_2/UV process

The advantages of the use of hydrogen peroxide, comparing to other oxidizing agents used in wastewater treatment process, include the ease to transport and store, infinite solubility in water, no mass transfer problems associated with gases, two hydroxyl radicals are formed for each molecule of H_2O_2 photolyzed, minimal cost of capital and operating and simple operation procedure [Braun *et al.* 1993; Cassano *et al.* 2001].

When hydrogen peroxide (H_2O_2) is decomposed under UV irradiation, it yields two hydroxyl radicals ($OH^{\bullet}$). Then, the radicals will react with the substrates present in the solution. The mechanism of the decomposition of hydrogen peroxide is shown in equation (1.14) – (1.19) [Braun *et al*. 1993; Zappi *et al*. 2002; Cassano *et al*. 2001; Zhou and Smith 2002].

Initial: $H_2O_2 \xrightarrow{h\upsilon} 2\ OH^{\bullet}$ ….(1.14)

Propagation: $H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O$ ….(1.15)

$H_2O_2 + HO_2^{\bullet} \longrightarrow OH^{\bullet} + H_2O + O_2$ ….(1.16)

Termination: $2\ OH^{\bullet} \longrightarrow H_2O_2$ ….(1.17)

$2\ HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$ ….(1.18)

$OH^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O + O_2$ ….(1.19)

Furthermore, hydrogen peroxide is also decomposed by a dismulation reaction (1.20) without UV irradiation at the pH of its pK_a value (~11.6) [Braun *et al*. 1993].

$$HO_2^{-} + H_2O_2 \longrightarrow OH^{\bullet} + H_2O + O_2 \quad ….(1.20)$$

1.3.2 Hydroxyl radical reactions

In the reactions of hydroxyl radicals in the presence of an organic substrate. There are three different mechanisms:

1. Hydrogen abstraction

$$OH^{\bullet} + RH \longrightarrow R^{\bullet} + H_2O$$

2. Electrophilic addition

$$OH^{\bullet} + PhX \longrightarrow HOPhX^{\bullet} \qquad X=\text{halide}$$

3. Electron transfer

$$OH^{\bullet} + RX \longrightarrow RX^{\bullet+} + OH^{-}$$

The mechanisms mentioned above may lead to organic substrate degradation. The hydroxyl radicals can be consumed by reaction with the contaminants, inorganic constituents present in the influent matrix, or the parent oxidizers themselves. All reactions that do not result in the degradation of the desired contaminants are called “scavenging reactions”. The examples of these scavengers are bicarbonate, carbonate and nitrate. Scavengers can violently reduce the efficiency of oxidation of the desired substrate by reducing number of hydroxyl radicals via the reactions (1.21) and (1.22) [Braun *et al*. 1993; Zappi *et al*. 2002].

$$OH^{\bullet} + HCO_3^{-} \longrightarrow OH^{-} + HCO_3^{\bullet} \quad \text{……(1.21)}$$
$$OH^{\bullet} + CO_3^{2-} \longrightarrow OH^{-} + CO_3^{\bullet-} \quad \text{..…..(1.22)}$$

An excessive amount of hydrogen peroxide will also reduce the efficiency of oxidation. The scavenging reactions are shown in equations (1.23) and (1.24)

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \quad \text{……(1.23)}$$
$$H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O \quad \text{……(1.24)}$$

1.4 Related research

In the last decades, photochemical processes have been used in many chemical reactions and water treatment. In most cases, these processes have been applied for the destruction of organic pollutants. Braun *et al.* have reviewed the degradation of organic pollutants by AOPs, such as H_2O_2/UV, O_3/UV, O_3/H_2O_2/UV, TiO_2/UV, and vacuum ultraviolet processes, for wastewater treatment. In all processes, it was found that the organic concentration and total organic carbon (TOC) were decreased within a few minutes after irradiation.

In 1986, Ho investigated the photooxidation of 2,4-dinitrotoluene in aqueous solution in the presence of hydrogen peroxide. It was found that 2,4-dinitrotoluene was degraded by H_2O_2/UV process and its final products were carbon dioxide, nitric acid and water. The complete degradation was obtained after 3 hours of exposure and no organic compound was left.

Martyanov *et al.* [1997], Dutta *et al.*[1997] and Akgerman and Alnaizy [2000] studied the oxidative degradation of phenol and phenolic compounds by photooxidation. The results indicated that at initial phenol concentrations of approximately 200 ppm, phenol completely disappeared in less than 1 hour at 27° C. In addition, they found that approximately 20% of phenol were mineralized to carbon dioxide and water. The rest was converted to the reaction intermediates.

Chaudhuri *et al.* [1999] and Apak *et al.* [2000] studied the kinetics of H_2O_2/UV oxidation of chlorinated phenols, such as chlorophenols (CPs): 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. The authors found that the optimal substrate: H_2O_2 molar ratio is 1:6 with a reaction time of 1 hour. The photooxidation order in terms of the initial CPs destruction was: $Cl_3Ph \geq Cl_2Ph > ClPh$ and the compounds were converted into harmless inorganic chlorides.

In 2001, Cassano *et al.* and Emmelin *et al.* [2001] investigated the photochemical degradation of aciflurfen and 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution. It was found that 2,4-D was converted to innocuous final products and after 6 hours of operation, for 30 ppm 2,4-D, 70% of compound were reduced.

As mentioned earlier, the photochemical process (H_2O_2/UV) has been demonstrated as a powerful technique for the treatment of toxic and refractory compounds. Apart from H_2O_2, the other oxidants have also been used in wastewater treatment or in combination with H_2O_2 photochemical process. In 2002, Zhao *et al.* studied the photooxidation of azo dye in aqueous dispersions of H_2O_2/α-FeOOH. The results indicated that the reaction process involved the in situ generation of highly reactive hydroxyl radicals. In addition, azo dye can be degraded in the presence of H_2O_2/α-FeOOH under UV radiation at neutral pH.

In the same year, Esplugas *et al.* [2002] investigated iron (III) photooxidation of phenol and nitrobenzene in aqueous solution. The reaction rate was shown to follow a first-order kinetic with respect to the substrate concentration and the kinetic constant depends on the Fe(III)/organic ratio.

Recently, Zappi *et al.* [2002] compared the use of advanced oxidation processes (AOPs) for the treatment of acetone contaminated water. The H_2O_2/UV, O_3/UV, and O_3/H_2O_2/UV processes were studied. It was found that the three AOPs removed over 99% of acetone in less than 30 minutes. In addition, an increase in ozone concentration enhanced the rate of acetone degradation.

Furthermore, AOPs have been used for the decomposition of complexing agents, such as EDTA, and metal complexes, such as metal-EDTA and metal-DTPA. Ku *et al.* [1998] and Peralta-Zemora *et al.* [2002] investigated the decomposition of EDTA in aqueous solution by H_2O_2/UV and H_2O_2-assisted photochemical process. It was found that EDTA was decomposed into by-products such as NTA, ammonia and nitrate ions. Almost complete decomposition of EDTA by H_2O_2/UV process could be accomplished in 1 hour and less than 10 minutes by H_2O_2-assisted photochemical process.

The oxidation of metal complexes, such as metal-EDTA and metal-DTPA, have been studied by Datye *et al.* [1997], Hasegawa *et al.* [1997], Ku *et al.* [1998] and Gunten *et al.* [2001]. In their experiments, they investigated the decomposition of Cu-EDTA, Ni-EDTA, Zn-EDTA, Co-EDTA, Fe-EDTA, and Mn-EDTA by TiO_2/UV process. It was found that Cu-EDTA and Fe-EDTA were degraded readily by the photocatalytic reaction and the amounts of iron and TOC in the solution decreased rapidly. Zn-EDTA was also completely decomposed after the irradiation for at least 1 hour. The amounts of zinc and

TOC in the solution were also reduced rapidly. Although Co-EDTA and Ni-EDTA were degraded almost completely after 2 hours of irradiation, the amounts of metal and TOC were decreased more slowly than other metals. In the part of Mn-EDTA, it is degraded more than 40% after 5 hours of reaction time. Furthermore, they studied the decomposition of Cu-EDTA in aqueous solution by H_2O_2/UV process. The highest decomposition of complex was obtained at Cu-EDTA: H_2O_2 molar ratio of 1:30 and pH value of solution as 3.0. And they observed the decomposition of EDTA giving the intermediate such as NTA, ammonia, and nitrate ions. The metal-DTPA complex, such as Ca-DTPA, Zn-DTPA, and Fe-DTPA could be easily decomposed by ozonation and DTPA was degraded to ethylenediaminetriacetate (ED3A) and diethylenetriamine-tetraacetate (DTTA) as major products.

By the literature review, the AOPs have been rarely used for the treatment of metal complexes. So we are interested in the degradation of metal complexes especailly Pb-EDTA by the H_2O_2/UV process.

1.5 The Quantum yield and photonic flux

Quantum yield (Φ) is the number of defined events which occur per photon absorbed by the system or the amount of product formed per amount of photon absorbed [Wishart and Nocera 1998]. It can be calculated as equation (1.25).

$$\Phi_X = \frac{\text{number of X formed}}{\text{number of photons absorbed}} \quad \text{..........................(1.25)}$$

X = product

There are two pieces of information required before a quantum yield can be determined. First, the number of photon absorbed must be known. Second, the number of moles of products must be measured. To determine the number of photon absorbed, one has to know the photonic flux (F) of the light source used. The photonic flux is the emission of photon from the lamp per unit of time (moles photon/min or Einstein/min). It indicates the number of photon passing into the sample.

In this work, we use potassium ferrioxalate [$K_3Fe(C_2O_4)_3$] [Parker and Hatchard 1956], as chemical actinometer for the determination of the photonic flux. The photochemical reaction of the actinometer can be presented as [Bossmann *et al.* 1998]:

$$[(Fe(C_2O_4)_3]^{3-} + h\nu \longrightarrow [(Fe(C_2O_4)_2]^{2-} + C_2O_4^{\bullet -} \quad \ldots\ldots(1.26)$$

$$[(Fe(C_2O_4)_3]^{3-} + C_2O_4^{\bullet -} \longrightarrow [(Fe(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2 \quad \ldots\ldots(1.27)$$

When ferrioxalate actinometer (Ac) is the only substance that absorbs light at the wavelength of irradiation, λ, the rate at which photons are absorbed by Ac ($R_{Ac,\lambda}$) is then given by [Serpone and Salinaro 1999]:

$$R_{Ac,\lambda} = R_{0,\lambda}(1-10^{-A_\lambda^{Ac}}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.28)$$

$R_{Ac,\lambda}$ = the photonic flux of ferrioxalate actinometer at wavelength λ
$R_{0,\lambda}$ = the incident photonic flux of the irradiation source
A_λ^{Ac} = the absorbance of ferrioxalate actinometer at wavelength λ

Practically, the concentration of actinometer solution should be high enough to keep $A_\lambda^{Ac} \geq 2$ during the entire irradiation period, so that $R_{Ac,\lambda} \approx R_{0,\lambda}$.

$R_{0,\lambda}$ is given by:

$$R_{0,\lambda} = \frac{n_B}{\Phi_B t(1-10^{-A_\lambda^{Ac}})} \text{..........................(1.29)}$$

$$R_{0,\lambda} = \frac{n_B}{\Phi_B t(1-10^{-\varepsilon[A]l})} \text{............................(1.30)}$$

n_B = the number of moles of Fe^{2+} produced from ferrioxalate actinometer

Φ_B = the quantum yield of ferrioxalate actinometer (Φ_B =1.24 at 254 nm)

t = time of irradiation (min)

ε = the corresponding molar absorption coefficient

The number of moles of Fe^{2+} formed are determined by UV/Vis spectrophotometry. The yield of Fe^{2+} is determined by measuring the absorbance of the intense red complex between Fe^{2+} and 1,10-phenanthroline ($[Fe(phen)_3]^{2+}$) at 510 nm.

1.6 Objective

In this work, we study the degradation of lead-EDTA using UV irradiation in the presence of hydrogen peroxide. The effects of parameters such as hydrogen peroxide concentration, Pb-EDTA:H_2O_2 molar ratio, pH of solution, and nitrate concentration have been investigated. Finally, the by-products from the degradation of the complex have also been identified.

CHAPTER II

EXPERIMENTAL

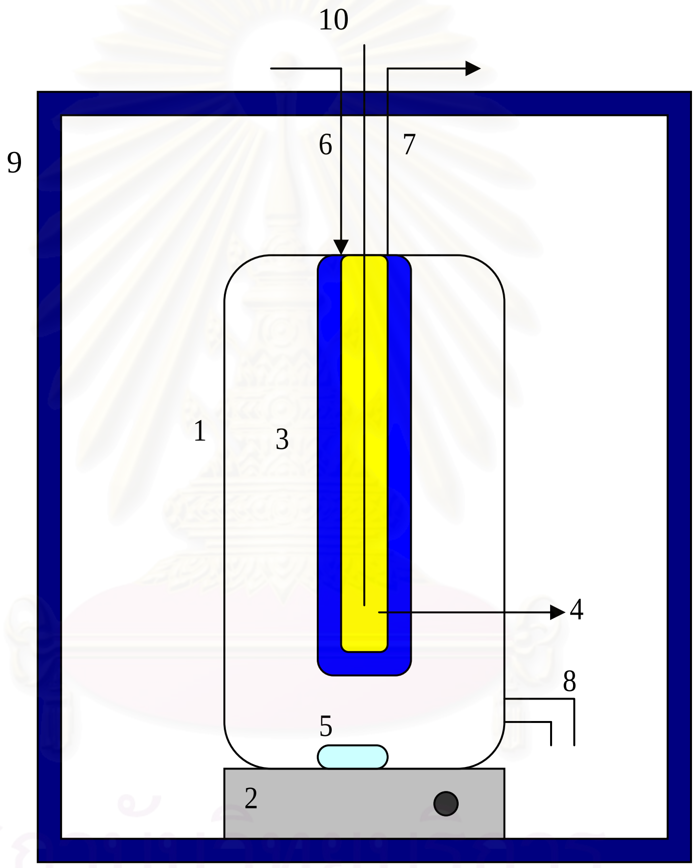
2.1 Chemicals

Lead chloride ($PbCl_2$) was purchased from Merck and ethylenediaminetetraacetic acid disodium salt dihydrate ($Na_2 \cdot EDTA$) was purchased from Fluka. Nitrilotriacetic acid (NTA), ethylenediaminediacetic acid (EDDA) and iminodiacetic acid (IDA) were obtained from Aldrich. Hydrogen peroxide 30% (w/w), cadmium sulfate, lead standard solution 1000 ppm, nitric acid (HNO_3), sulfuric acid (H_2SO_4), methanol and hydrochloric acid (HCl) were obtained from Claro. Cobalt(II)nitrate ($Co(NO_3)_2$), zinc chloride ($ZnCl_2$), oxalic acid, acetone, sodium acetate and *tri*-sodium orthophosphate (Na_3PO_4) were purchased from Fisher. Sodium hydrogen carbonate ($NaHCO_3$), sodium hydroxide (NaOH), sodium nitrate ($NaNO_3$), cadmium sulphate ($Cd(SO_4)_2$), phthalic acid, tetradecyltrimetylammonium bromide (TTAB), sodium nitrate, ammonium ferrous sulphate and potassium oxalate monohydrate were supplied by Fluka. All materials were analytical grade.

The preparation of Pb-EDTA complex: complex solutions of 0.002 M Pb-EDTA were prepared by dissolution of 0.5564 g $PbCl_2$ in 500 mL of 0.004 M EDTA solution and diluted to 1000 mL in volumetric flask with deionized water.

2.2 Photochemical process

Experiments were carried out in a reactor as schematically demonstrated in figure 2.1. A 450 W medium-pressure mercury lamp (220-600 nm), from Hanovia. The lamp was introduced into the reactor and kept separate from the aqueous solution by a quartz cooling jacket. The temperature of the water circulated in the cooling jacket was 21 ± 0.5 ^{0}C regulated and controlled by a recirculating chiller. In a typical photochemical experiment, 1000 mL of substrate aqueous solution (complex of PbEDTA) and hydrogen peroxide (H_2O_2) were filled in the reactor. Afterwards, the UV-lamp was introduced into the reactor. The solution was stirred by a magnetic bar throughout the experiments in order to keep the solution homogeneous. The reaction run lasted 20 minutes and samples were collected every 2 minutes. Total sampling volume was kept under 5% of total solution volume. The pH of the solution was measured with a HANNA instruments pH 211 Microprocessor pH meter and adjusted to the desired value by addition of sodium hydroxide (NaOH) or hydrochloric acid (HCl). Each experiment was performed twice.



1. Photoreactor
2. Magnetic stirrer
3. Quartz cooling jecket
4. UV lamp
5. Stir bar
6. Water inlet
7. Water outlet
8. Sampling port
9. Box
10. Connection to power supply

Figure 2.1 The reactor

2.3 Analytical determinations

2.3.1 Determination of Pb-EDTA and by-products concentration

The concentration of PbEDTA and its reaction by-products (NTA, EDDA and IDA) were determined by capillary electrophoresis (CE). CE experiments were performed with a P/ACE^{TM} MDQ capillary electrophoresis system. An uncoated fused-silica capillary used was 57 cm in length (50 cm to detector) × 75 μm in diameter and an indirect UV detection was set at 214 nm. Thermostatted at 25^{o}C, the samples and standards were introduced into the capillary using the pressure injection (0.5 psi) for 6 seconds. The separation voltage was set at –25 kV. The background electrolyte (BGE) consisted of 1×10^{-2} M phthalic acid and 5×10^{-4} M TTAB, pH~ 7.0. The BGE, sample, and standard solutions were filtered through a 0.45 μm membrane filter and degassed before use. Before the analysis each day, the capillary was rinsed with 0.1 M NaOH for 15 min, and then BGE for 15 min. Between each run, the capillary was flushed with 0.1 M NaOH for 3 min and then BGE for 3 min. After the analysis each day, the capillary was rinsed with 0.1 M NaOH for 10 min and then water for 10 min. Each experiment was performed twice.

Limit of detection (LOD) and limit of quantitation (LOQ) were determined by injection of diluted standard solution (PbEDTA, NTA, EDDA, and IDA) until the signal to noise ratios of 3 for LOD and 10 for LOQ were obtained.

2.3.2 Determination of lead concentration

Flame Atomic Absorption Spectrometry (FAAS) was used for determining the total lead concentration in sample solutions. FAAS analysis was performed with a Perkin-Elmer (Analyst 100) flame atomic absorption spectrometer. Atomic absorption measurements were carried out using air/acetylene flame (air flow ~ 4mL/min, acetylene flow ~ 2 mL/min). Detection wavelength was set at 283.3 nm using slit width of 0.7 nm.

The calibration curve was established using the lead standard solutions prepared by dilutions of 1000 ppm standard solution. Standards and samples were diluted with 0.1 M HNO_3 Each experiment was run in triplicate using read time of 5 seconds.

Limit of detection (LOD) and limit of quantitation (LOQ) were difined as the analyte concentrations giving a signal equal to three and ten times of standard deviation of blank signal, respectively. The linear range of experiment was 6 to 20 mg L^{-1}.

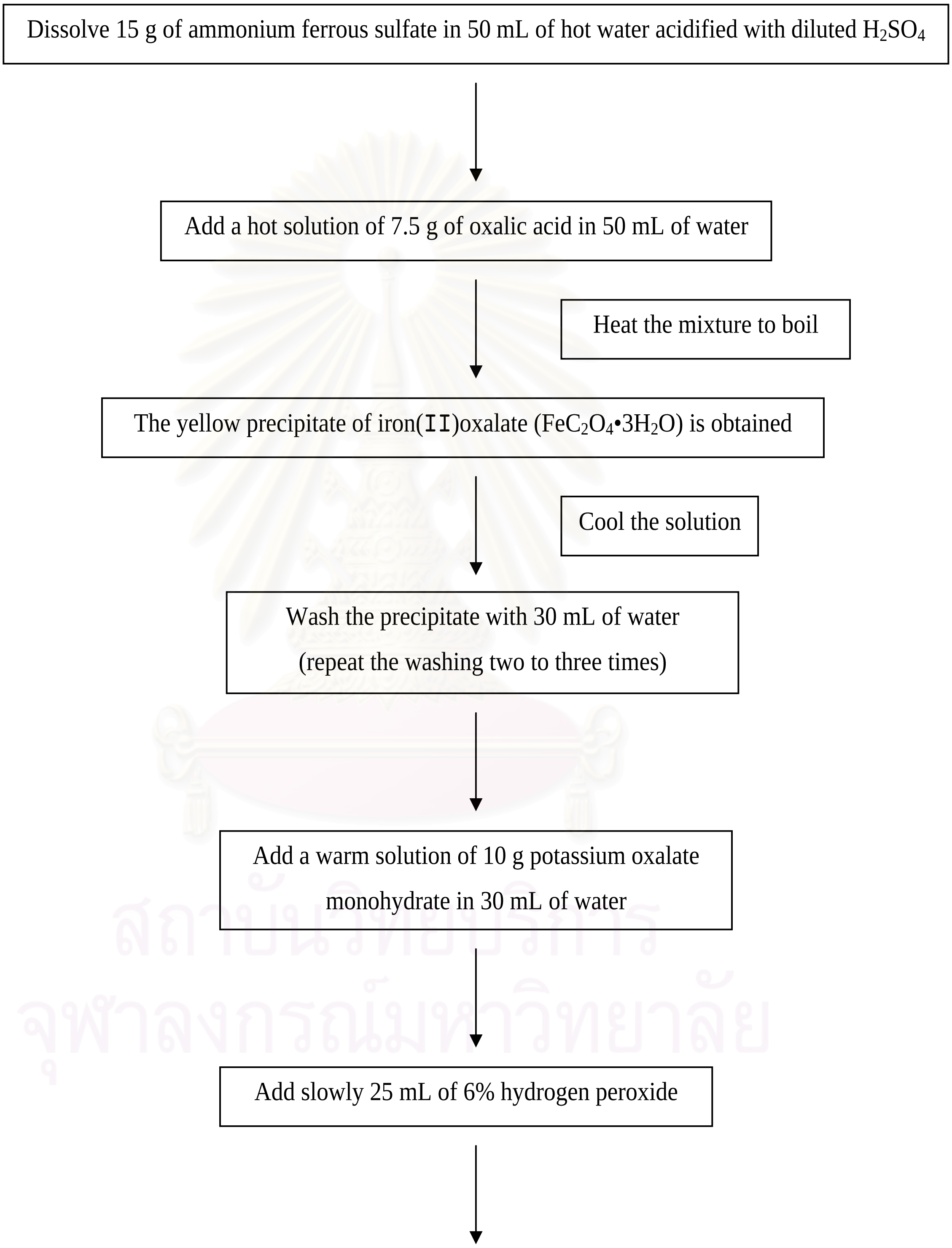
2.3.3 Determination of hydrogen peroxide concentration

The concentration of hydrogen peroxide (H_2O_2) in sample solutions was determined by UV-Visible Spectrophotometry (UV-Vis). The UV-Visible Spectrophotometry experiments were performed with a HP 8453 UV-Visible Spectrophotometer. The detection wavelength was 258 nm. Each sample was mixed with cobalt(II)nitrate (4 g L^{-1}, 0.2 mL), *tri*-sodium orthophosphate (10 g L^{-1}, 0.2 mL) and sodium hydrogen carbonate (1 M, 4 mL). The final volume was made up to 10 mL in the volumetric flask with deionized water.

The standard solutions of hydrogen peroxide were diluted from hydrogen peroxide 30% (w/w) and prepared in the same way as samples. The linear range of experiment was 0.01 to 0.04 mM.

2.3.4 Determination of photonic flux and quantum yield

2.3.4.1 Preparation of potassium ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$)



Dissolve 15 g of ammonium ferrous sulfate in 50 mL of hot water acidified with diluted H_2SO_4

Add a hot solution of 7.5 g of oxalic acid in 50 mL of water

Heat the mixture to boil

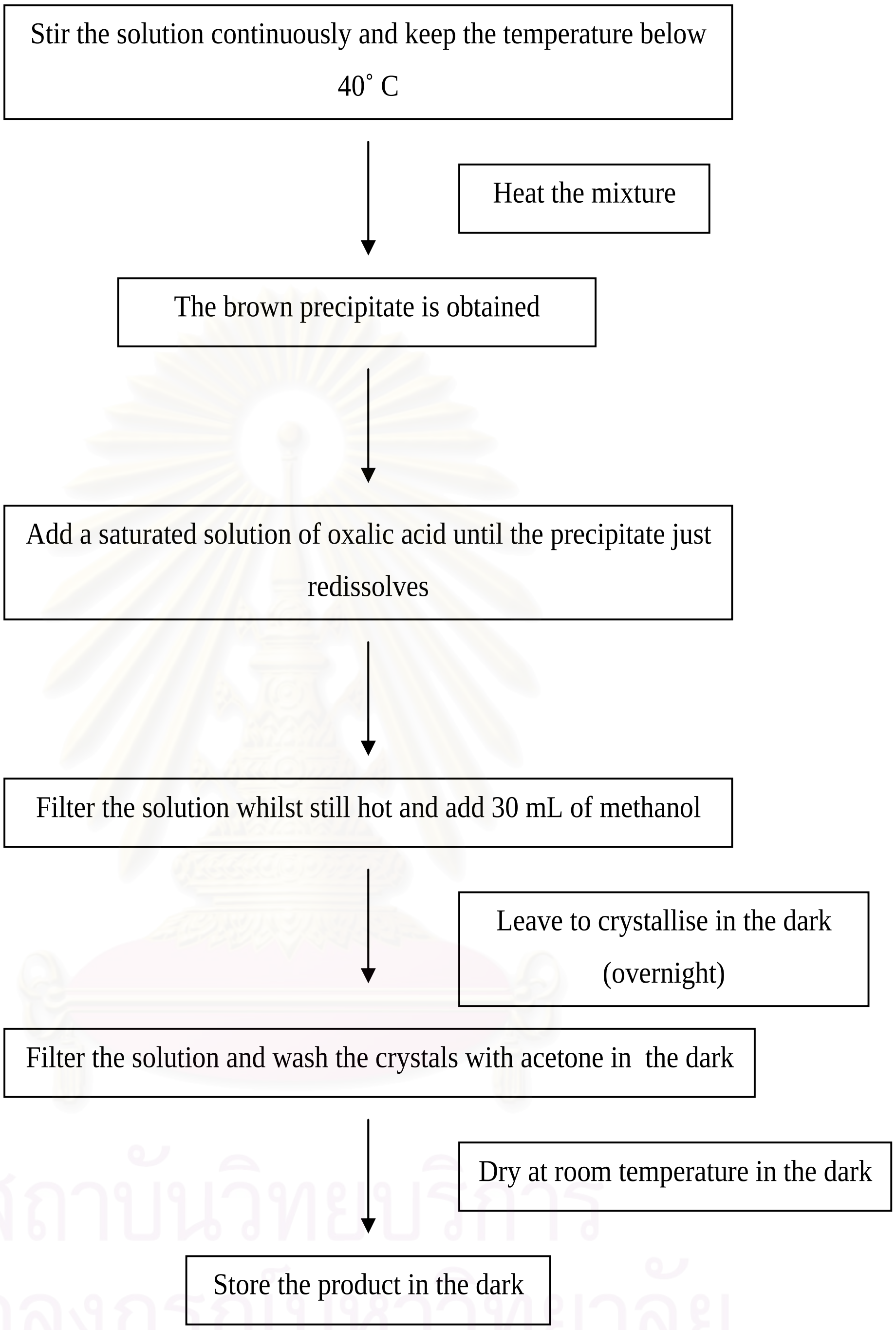
The yellow precipitate of iron(II)oxalate ($FeC_2O_4 \cdot 3H_2O$) is obtained

Cool the solution

Wash the precipitate with 30 mL of water
(repeat the washing two to three times)

Add a warm solution of 10 g potassium oxalate monohydrate in 30 mL of water

Add slowly 25 mL of 6% hydrogen peroxide



Scheme 2.1 Pathway of preparation of potassium ferrioxalate

2.3.4.2 Preparation of a calibration curve for ferrous iron

Solutions required are: (a) 0.4 mM Fe^{2+} in 0.1 N H_2SO_4, (b) 0.1% 1,10-phenanthroline monohydrate in water, (c) buffer solution (0.6 N sodium acetate and 0.36 N H_2SO_4).

Solution (a) was mixed with 0.1 N H_2SO_4 to make the total acidity equivalent to 10 ml of 0.1 N H_2SO_4. Add 2.5 mL of solution (b) and 6.25 mL of solution (c). The final volume was made up to 25 mL in volumetric flask with deionized water, mix and allow to stand for at least ½ hour. The solution was analysed by UV-Vis spectrophotometry at 510 nm. The linear range of ferrous iron concentration was 0.02 to 0.1 mM.

2.3.4.3 Determination of photonic flux

Solution of 0.006 M $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ in 0.1 N H_2SO_4 (1000 mL) were irradiated for 20 min in the reactor used in photooxidation experiments. Collect the sample every 2 min. After the photooxidation, 2.5 mL of solution (b) and solution (c) equal to half the volume of sample taken were added to each sample. The final volume was made up to 25 mL in volumetric flask with deionized water, mix and allow to stand in the dark for at least ½ hour. The sample (Fe^{2+}) was analysed by UV-Vis spectrophotometry at 510 nm. Each experiment was performed twice.

Each sample of Fe^{2+} concentration was calculated to the photonic flux by $R_{0,\lambda}$ (equation 1.23, chapter I) and calculated the average of photonic flux.

2.4 Parameters studied and conditions used

2.4.1 Influence of hydrogen peroxide concentration

Three concentrations of hydrogen peroxide (0.02, 0.04, and 0.08 M) were used in the photooxidation of Pb-EDTA (2 mM, initial pH=3.0). The Pb-EDTA:H_2O_2 molar ratio was 1:10, 1:20, and 1:40. The photooxidation experiments lasted 20 min and samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Pb-EDTA and by-products concentration, FAAS for total Pb concentration and UV-Vis spectrophotometry for hydrogen peroxide concentration.

2.4.2 Influence of initial pH of solution

Solution of 2 mM Pb-EDTA and 0.04 M hydrogen peroxide were used in this study. The Pb-EDTA:H_2O_2 molar ratio was 1:20. We observed the photooxidation at different initial pH value: 1.5, 3.0, 6.0, and 8.0. The pH value was adjusted by using 1 M NaOH or 1 M HCl. The photooxidation experiments lasted 20 min each run and samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Pb-EDTA and by-products concentration, FAAS for total Pb concentration and UV-Vis spectrophotometry for hydrogen peroxide concentration.

2.4.3 Optimization of conditions used

The concentration of Pb-EDTA was reduced to 1.3 mM. The photooxidation experiments were carried out using 0.02 M hydrogen peroxide. The Pb-EDTA:H_2O_2 molar ratio was 1:15. The initial pH of the mixture was 3.0. The photooxidation experiments lasted 20 min each run and samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Pb-EDTA and by-products concentration, FAAS for total Pb concentration and UV-Vis spectrophotometry for hydrogen peroxide concentration.

2.4.4 Influence of nitrate concentration

Solution of 2 mM Pb-EDTA, 0.04 M hydrogen peroxide with initial pH of solution as 3.0 were used in this study. Sodium nitrate was added to obtain 0.004 and 0.04 M of nitrate in solution before irradiation. The molar ratio of nitrate:H_2O_2 was 1:10 and 1:1. The photooxidation experiments lasted 20 min each run and samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Pb-EDTA and by-products concentration, FAAS for total Pb concentration and UV-Vis spectrophotometry for hydrogen peroxide concentration.

2.4.5 Effect of irradiation time on Pb-EDTA and by-products degradation

Solution of 2 mM Pb-EDTA, 0.04 M hydrogen peroxide with initial pH of solution as 3.0 was used in this study. The Pb-EDTA:H_2O_2 molar ratio was 1:20. We observed the photooxidation at different irradiation time: 30 min. Samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Pb-EDTA and by-products concentration, FAAS for total Pb concentration and UV-Vis spectrophotometry for hydrogen peroxide concentration.

2.5 Comparison with other metal-EDTA complexes

2.5.1 Zn-EDTA degradation

Solution of 2 mM Zn-EDTA and 0.04 M hydrogen peroxide were used in this study. $ZnCl_2$ was used instead of $PbCl_2$. The Zn-EDTA:H_2O_2 molar ratio was 1:20 and the initial pH of solution was 3.0. The photooxidation experiments lasted 20 min each run and samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Zn-EDTA and by-products concentration, FAAS for total Zn concentration and UV-Vis spectrophotometry for hydrogen peroxide concentration

2.5.2 Cd-EDTA degradation

Solution of 2 mM Cd-EDTA and 0.04 M hydrogen peroxide were studied. $CdSO_4$ was used instead of $PbCl_2$. The Cd-EDTA:H_2O_2 molar ratio was 1:20 and the initial pH of solution was 3.0. The photooxidation experiments lasted 20 min each run and samples were collected every 2 min. The experiment was duplicated. The samples were analysed by CE for Cd-EDTA and by-products concentration, FAAS for total Cd and UV-Vis spectrophotometry for hydrogen peroxide concentration

2.6 Limit of detection (LOD) and limit of quantitation (LOQ)

LOD was defined as the analyte concentration yielding a signal-to-noise ratio of 3. LOQ was defined as the analyte concentration producing a signal-to-noise ratio of 10. The LOD and LOQ of these studies are summarized in table 2.1

Table 2.1 Limit of detection (LOD) and limit of quantitation (LOQ)

Element	Technique	LOD	LOQ
Pb-EDTA	CE	0.03^a	0.09^a
NTA	CE	0.10^a	0.70^a
IDA	CE	0.06^a	0.10^a
Lead	FAAS	0.044^b	1.809^b
Zinc	FAAS	0.010^b	0.193^b
Cadmium	FAAS	0.002^b	1.218^b

a; mM

b; mg L^{-1}

CHAPTER III

RESULTS AND DISCUSSION

In this chapter, we present the result of the degradation of Pb-EDTA by H_2O_2/UV process. The influence of the parameters used in the degradation of Pb-EDTA, such as hydrogen peroxide concentration, initial pH of solution and Pb-EDTA concentration are described. Finally, the degradation of Zn-EDTA and Cd-EDTA are studied comparing to Pb-EDTA.

3.1 Direct photolysis and photooxidation essay

At the beginning, we have studied the influence of the UV radiation in the degradation of both hydrogen peroxide and Pb-EDTA. The results are shown in figures 3.1 – 3.3. The results show that in the absence of UV radiation, hydrogen peroxide having initial concentration of 0.02 M did not disappear during the interval of time studied. In contrast, a photolysis of hydrogen peroxide led to a remarkable decrease of hydrogen peroxide in solution. This may result in hydroxyl radical formation.

It was found that Pb-EDTA was not degraded in the presence of oxidizing agent as hydrogen peroxide (molar ratio as 1:10). The initial pH of the solutions studied were around 3.0. It is possible that hydrogen peroxide does not dissociate to hydroxyl radicals, a more powerful oxidizing agent, without UV radiation at this pH [Braun *et al.* 1993; Ku *et al.* 1998]. Therefore, Pb-EDTA did not disappear. From figure 3.2 and 3.3, the direct photolysis of Pb-EDTA led to a small reduction of complex concentration. The total lead concentration did not change. On the other hand, a rapid reduction of Pb-EDTA and total lead in solution were observed when H_2O_2/UV process was used. This shows that the photooxidation in the presence of hydrogen peroxide is an efficient method for Pb-EDTA degradation and lead removal.

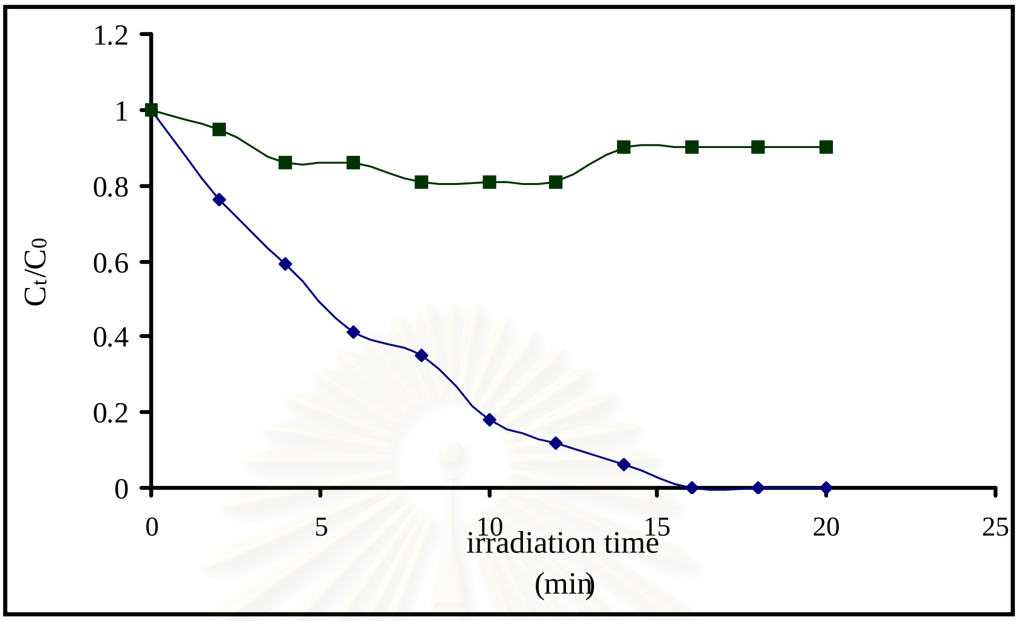


Figure 3.1 The change of hydrogen peroxide concentration with irradiation time; initial concentration 0.02 M. (♦) hydrogen peroxide with UV radiation, (■) hydrogen peroxide without UV radiation

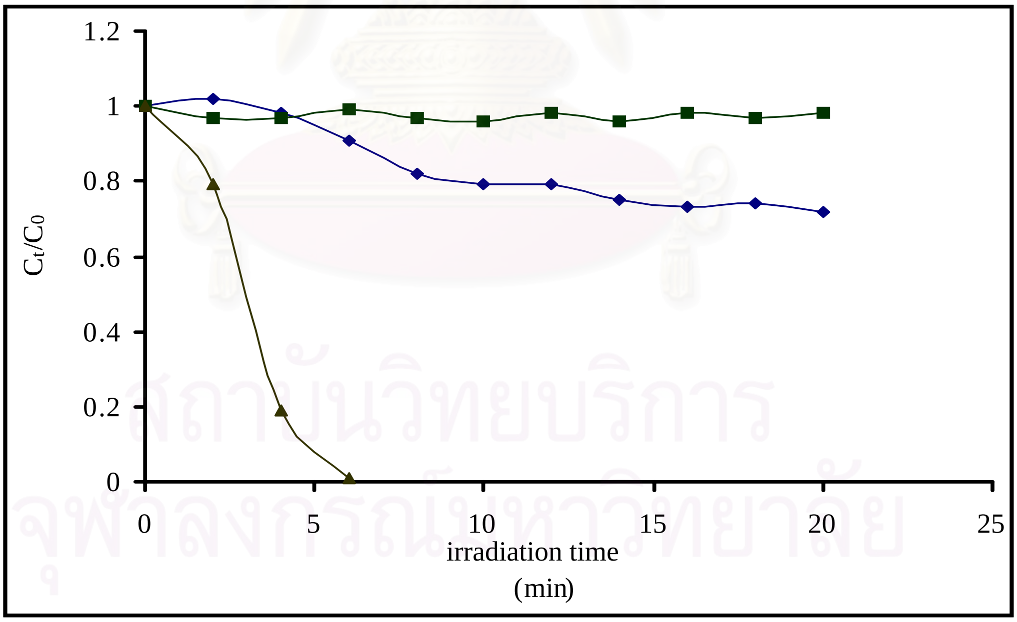


Figure 3.2 The change of Pb-EDTA concentration with irradiation time; initial concentration of Pb-EDTA 2 mM. (♦) Pb-EDTA with UV radiation (direct photolysis), (■) Pb-EDTA with hydrogen peroxide and (▲) Pb-EDTA with hydrogen peroxide/UV radiation (photooxidation)

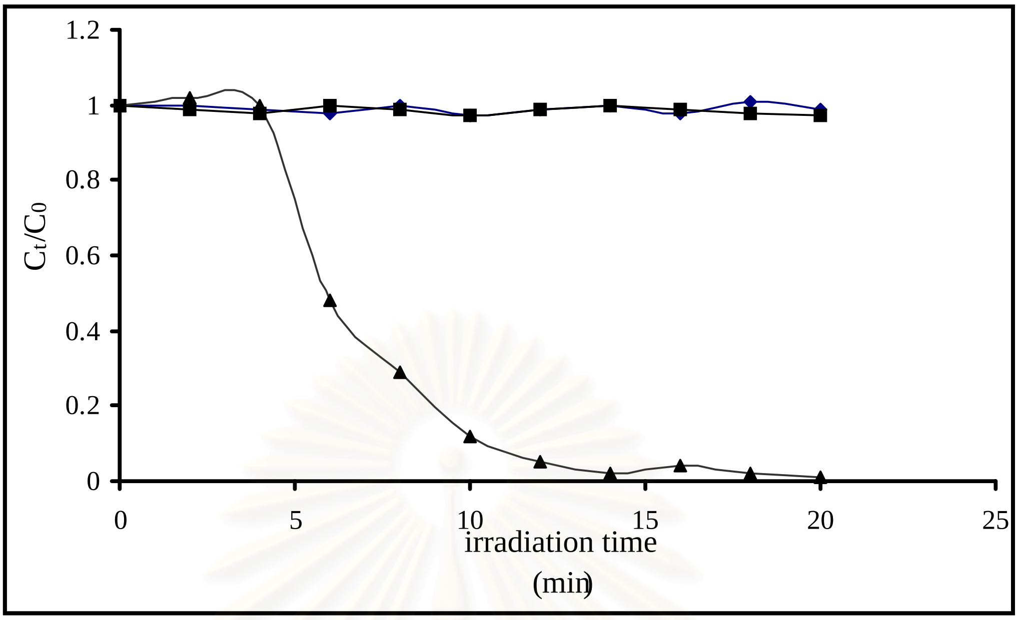
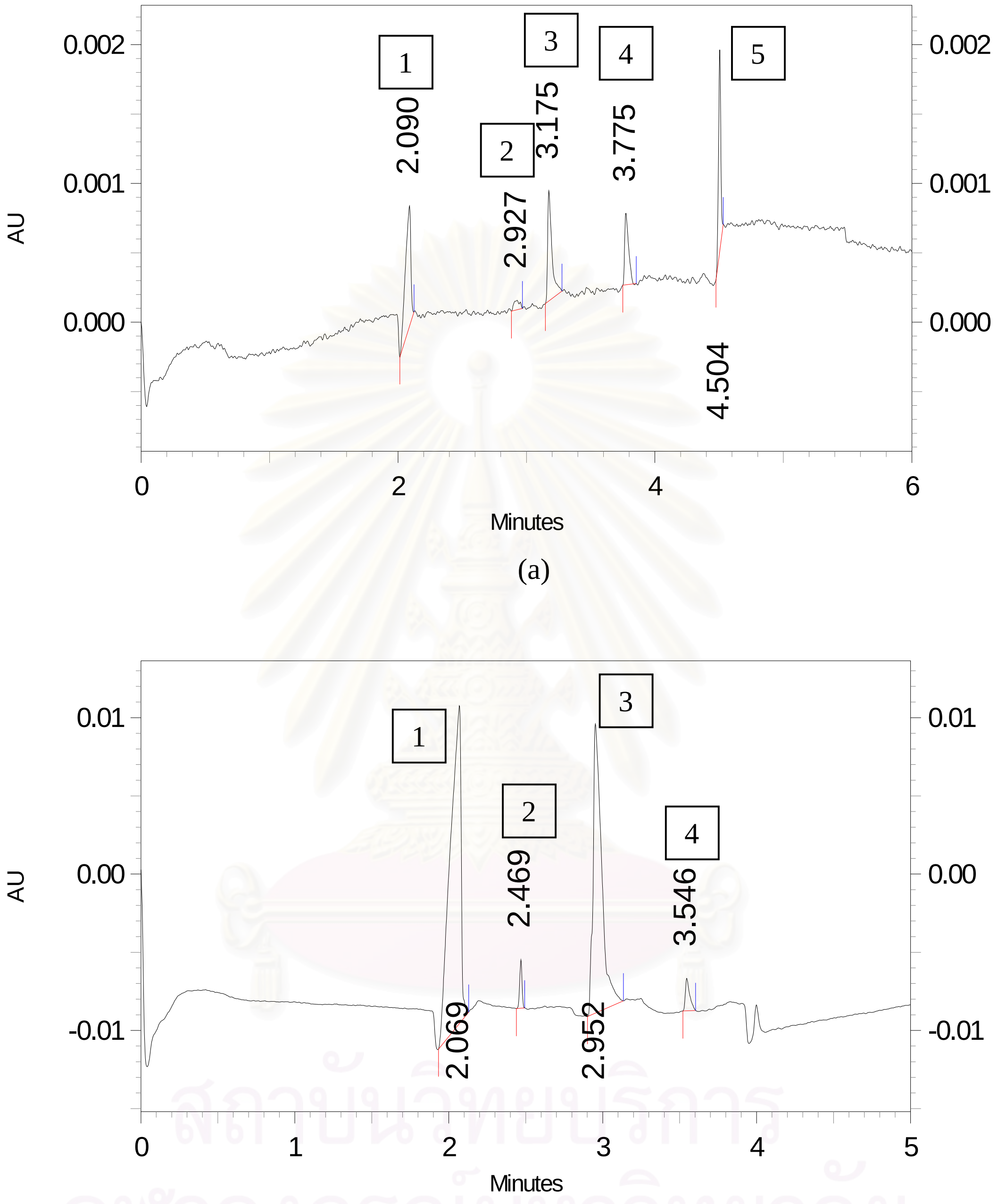


Figure 3.3 The change of lead concentration with irradiation time; initial concentration of Pb-EDTA 2 mM. (♦) Pb-EDTA with UV radiation, (■) Pb-EDTA with hydrogen peroxide and (▲) Pb-EDTA with hydrogen peroxide/UV radiation

3.2 By-products of the degradation of Pb-EDTA

In this work, by-products of the degradation of Pb-EDTA by H_2O_2/UV process have been identified. Based on the information of previously reported by-products of EDTA degradation, NTA, IDA, and EDDA were used as by-products standards. The separation and quantification of the by-products were performed with CE. The by-products observed in the samples were compared with the standards using the retention time obtained from CE experiments. The electropherogram of the mix standards of by-products and an irradiated sample are shown in figure 3.4.



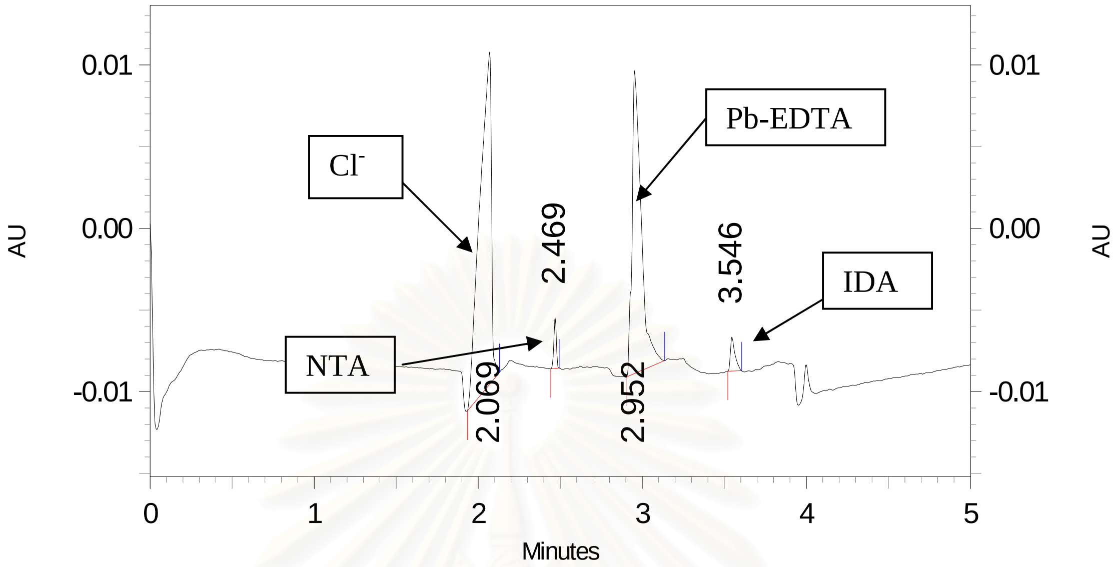
(a)

(b)

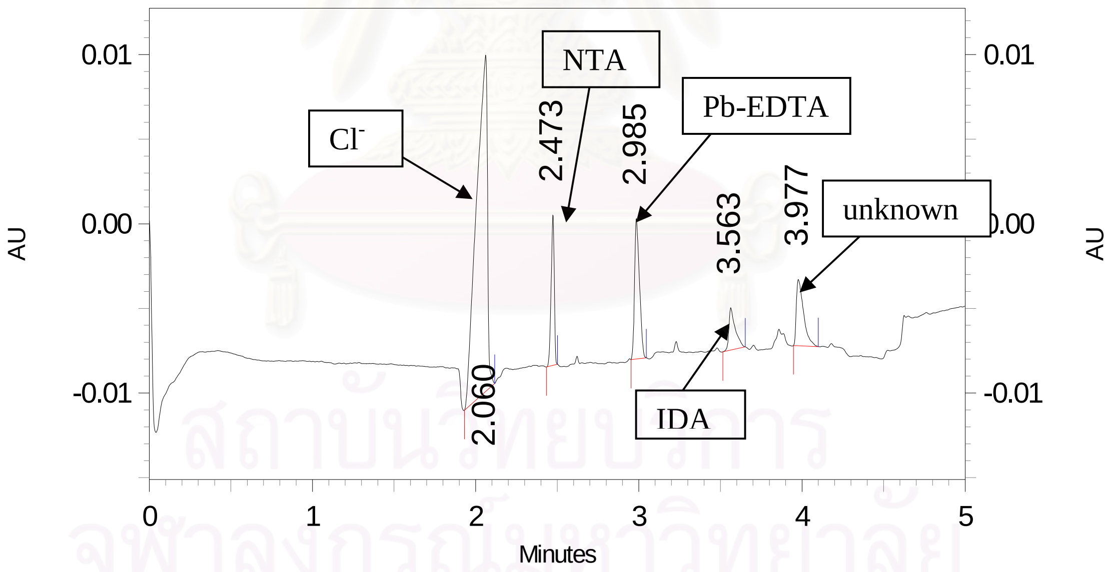
Figure 3.4 The electropherogram of standard (a) and irradiated sample of Pb-EDTA (b). (a) mix standards (1 mM) of Pb-EDTA (3), NTA (2), IDA (4), EDDA (5) and Cl^- (1) and (b) sample of degradation of Pb-EDTA (2 mM) by H_2O_2/UV process, irradiated 2 min

It is example of electropherograms of standard and irradiated sample, that was a different day. Therefore, the migration time may be little difference between standard and sample. From the electropherograms, Pb-EDTA and by-products could be nicely separated and analysed by the method used. The migration time of Pb-EDTA, NTA, IDA, and EDDA were 3.175, 2.927, 3.775, and 4.504 min, respectively. The peak at 2.090 min was chloride. The analysis of samples was carried out with the analytical method used in the analysis of the standards. As the analytical conditions of CE could change from day to day due to the solution preparation, a little change in retention time was observed. Thus, it is necessary to analyse the standards and samples in the same analytical conditions. From figure 3.4 (b), Pb-EDTA was present at about 2.952 min. The by-products in the irradiated sample were detected at 2.469 and 3.546 min. By comparing the retention times to those of standards analysed in the same day, we assume that it was NTA and IDA, respectively.

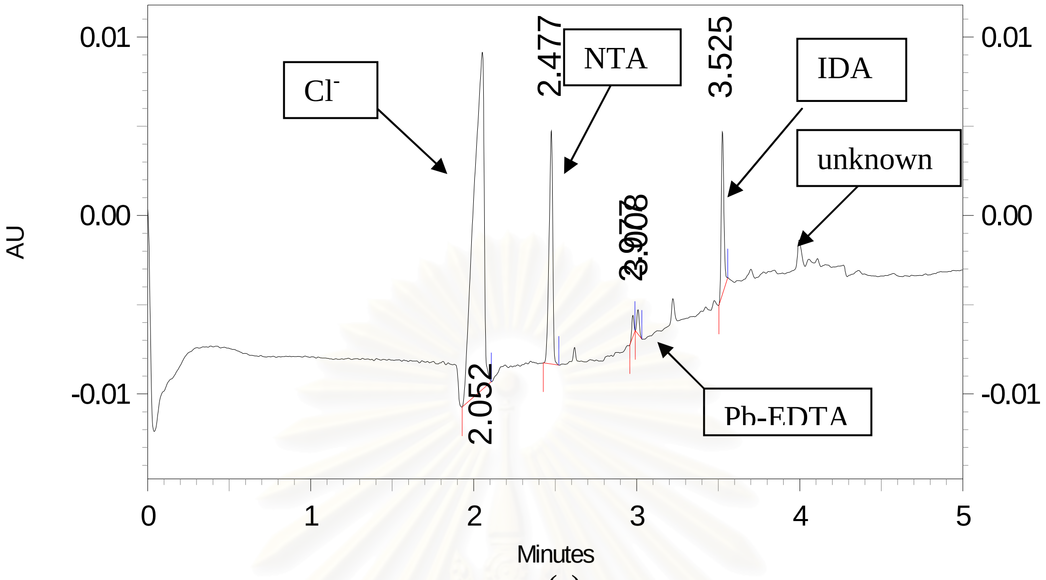
After 12 min of irradiation, unknown peaks coeluted with NTA and IDA. By comparing the retention times with those of standards available, unknown peaks at about 2.6-2.8 and 3.4-3.5 min seem to be nitrate and oxalate ions, respectively. These ions may occur in the last step of EDTA degradation [Ku *et al.* 1998]. Nitrate and oxalate coelute with NTA and IDA, respectively, and cannot be quantified. NTA and IDA cannot be quantified either because of the coelution. A change in electropherogram of Pb-EDTA sample during irradiation is shown in figure 3.5.


0.01
0.00
-0.01
AU
0.01
0.00
-0.01
AU
Cl$^-$
Pb-EDTA
NTA
IDA
2.069
2.469
2.952
3.546
0
1
2
3
4
5
Minutes

(a)


0.01
0.00
-0.01
AU
0.01
0.00
-0.01
AU
Cl$^-$
NTA
Pb-EDTA
unknown
IDA
2.060
2.473
2.985
3.563
3.977
0
1
2
3
4
5
Minutes

(b)



(c)

Figure 3.5 The electropherogram of Pb-EDTA degradation samples; initial concentration of Pb-EDTA 2 mM and hydrogen peroxide 0.04 M at initial pH of solution 3.0. (a) 2 min irradiation time, (b) 4 min irradiation time and (c) 6 min irradiation time.

Figure 3.5 shows a change in electropherogram of Pb-EDTA solution at 2 to 6 min of irradiation time. It was found that the amount of Pb-EDTA detected at about 2.9 min was remarkably reduced. NTA and IDA were detected at about 2.5 and 3.5 min, respectively. In some electropherograms, we found that nitrate and oxalate formed coeluted with NTA and IDA peaks.

When EDTA undergoes the photooxidation (H_2O_2/UV process), the by-products such as nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), ethylenediaminediacetic acid (EDDA), oxalic acid and formic acid were produced. [Ku *et al.* 1998; Nörtemann 1999]. The proposed steps in EDTA degradation are illustrated in scheme 1.1 (chapter I). These compounds have also been found in our irradiated samples. This indicates that there is a degradation of EDTA of the complex. And NTA seems to be the primary by-product obtained that will be further degraded to yield IDA. The change of by-products concentration during photooxidation is shown in figure 3.6.

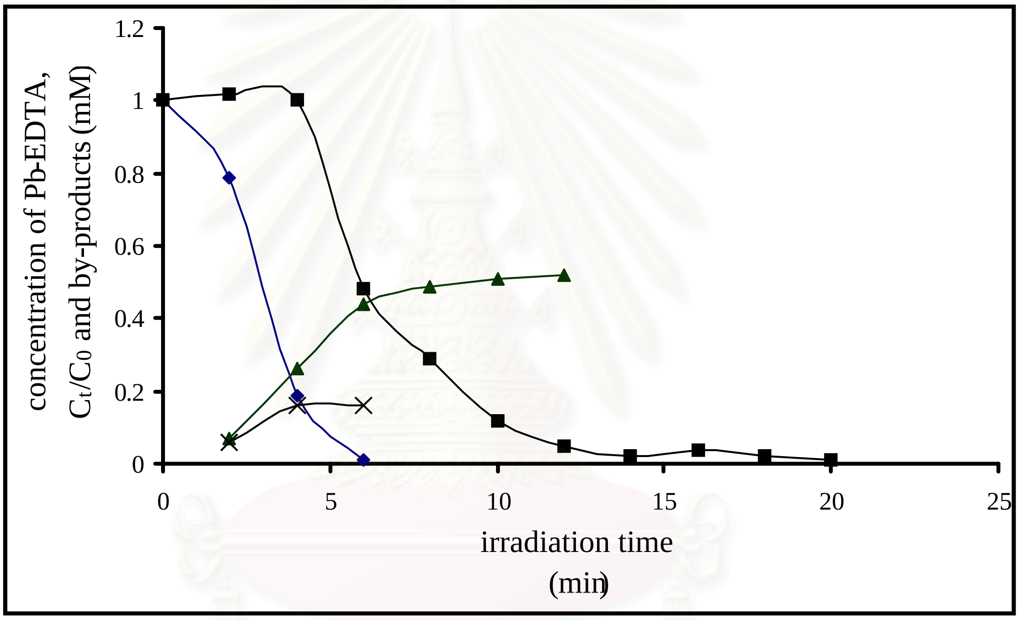


Figure 3.6 The photooxidation of Pb-EDTA and by-products; initial Pb-EDTA concentration 2 mM, initial hydrogen peroxide concentration 0.04 M and pH of solution 3.0. (♦) Pb-EDTA, (■) total lead concentration, (▲) NTA concentration and (x) IDA concentration

From figure 3.6, it was found that Pb-EDTA complex and total lead concentration were rapidly reduced by H_2O_2/UV process. NTA and IDA were found after the radiation. After 12 min of irradiation, NTA could be detected but it coeluted with nitrate and could not be quantified. In the same way, after 6 min of irradiation, IDA coeluted with oxalate, and therefore, cannot be quantified either.

3.3 Influence of hydrogen peroxide concentration

In this study, the initial concentration of Pb-EDTA was kept constant at around 2 mM. The initial concentration of hydrogen peroxide was varied from 0 to 0.08 M and the initial pH of solutions studied were around 3.0. The results of photooxidation of Pb-EDTA at various hydrogen peroxide concentrations are shown in figures 3.7 - 3.10.

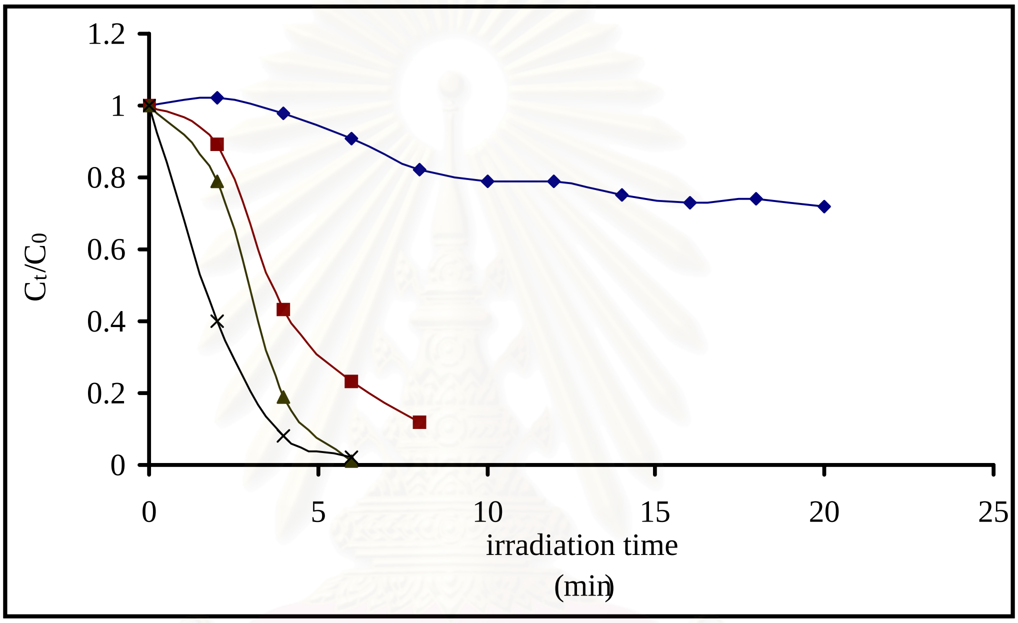


Figure 3.7 The change of Pb-EDTA concentration at different hydrogen peroxide concentrations; initial Pb-EDTA 2 mM and initial pH 3.0. (♦) H_2O_2 = 0 M, (■) H_2O_2 = 0.02 M, (▲) H_2O_2 = 0.04 M and (x) H_2O_2 = 0.08 M

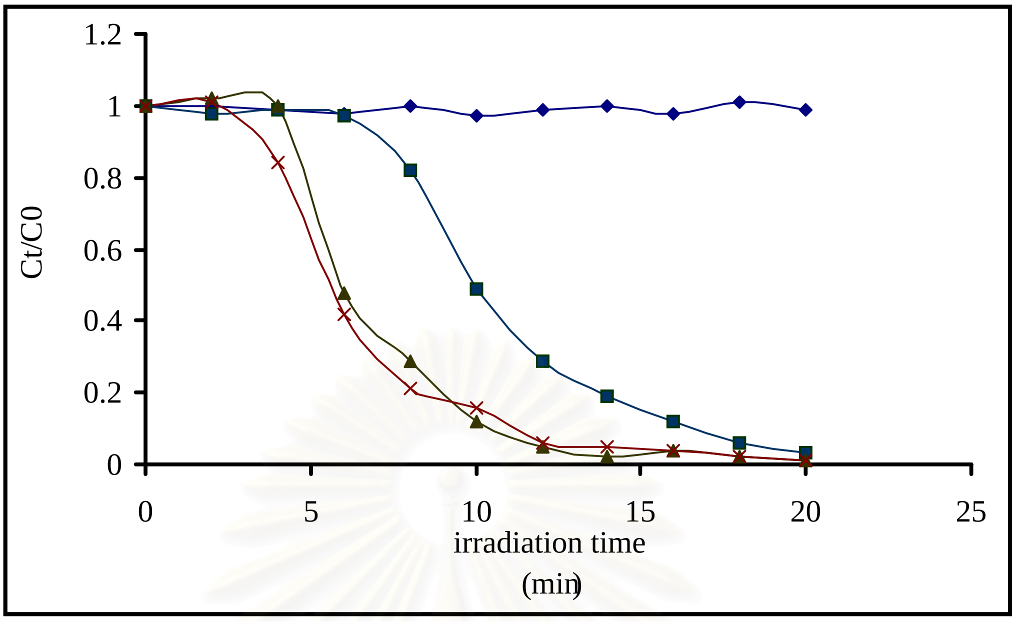


Figure 3.8 Total lead concentration at different hydrogen peroxide concentration; initial Pb-EDTA 2 mM and initial pH 3.0. (♦) H_2O_2 = 0 M, (■) H_2O_2 = 0.02 M, (▲) H_2O_2 = 0.04 M and (x) H_2O_2 = 0.08 M.

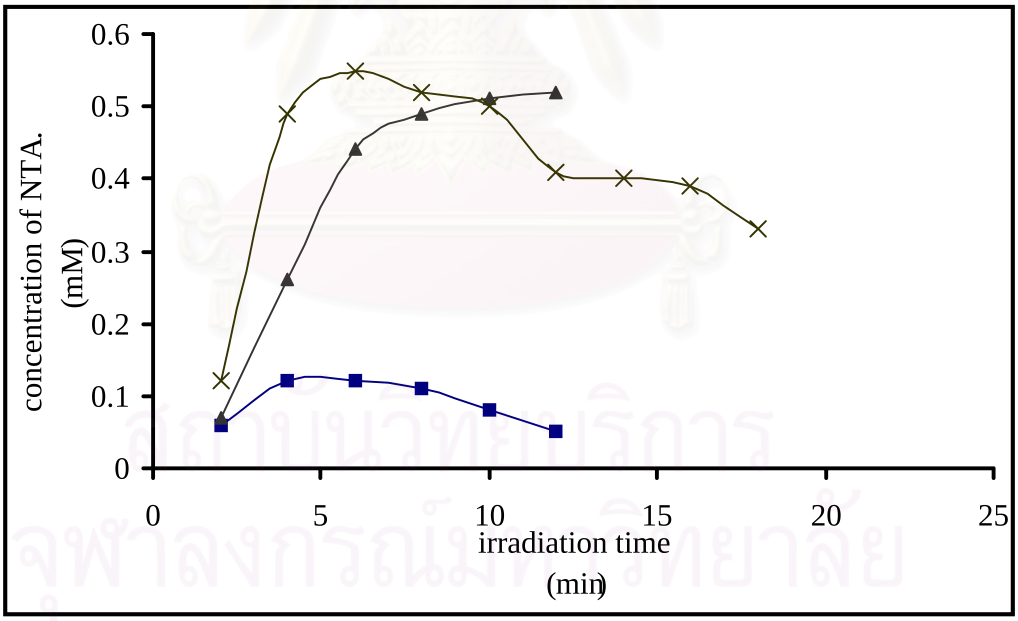


Figure 3.9 NTA concentration at different initial hydrogen peroxide concentration; initial Pb-EDTA 2 mM and initial pH 3.0. (■) H_2O_2 = 0.02 M, (▲) H_2O_2 = 0.04 M and (x) H_2O_2 = 0.08 M

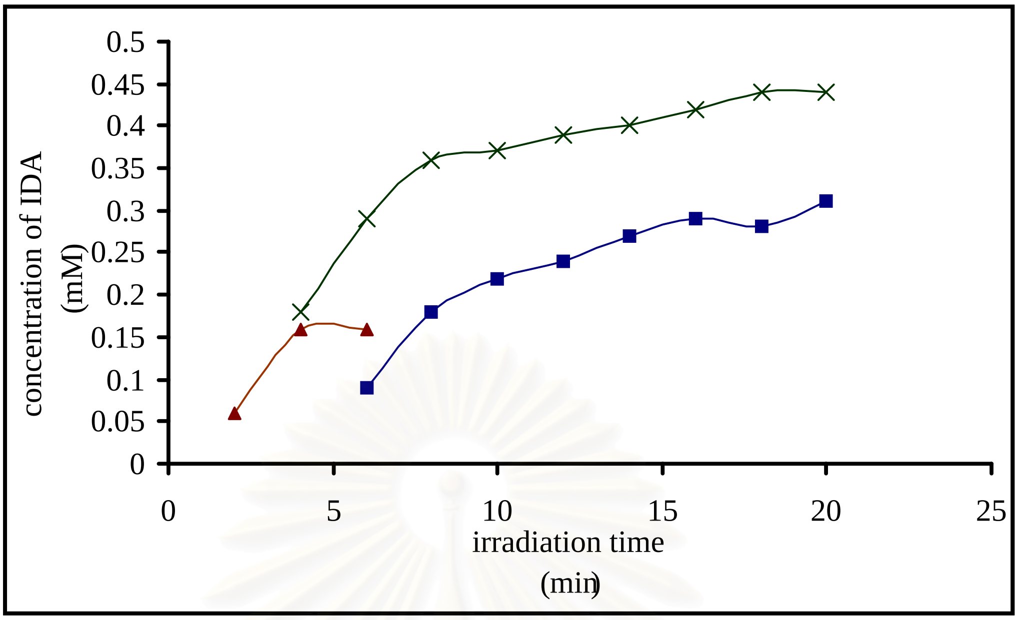


Figure 3.10 IDA concentration at different initial hydrogen peroxide concentration; initial Pb-EDTA 2 mM and initial pH 3.0. (■) H_2O_2 = 0.02 M, (▲) H_2O_2 = 0.04 M and (x) H_2O_2 = 0.08 M

In the absence of hydrogen peroxide, Pb-EDTA concentration slowly decreased. This is because, without any oxidizing agents, Pb-EDTA is very stable. Datye *et al.* [1997] found that 22% of Pb-EDTA were reduced by only UV radiation in 50 min. Our results are in agreement with what was previously reported. In addition, the total lead concentration is not decreased and the by-products such as NTA and IDA were not detected.

The presence of hydrogen peroxide enhanced the degradation of Pb-EDTA greatly comparing to the direct photolysis. During the irradiation, a white precipitate was observed. The precipitate seems to be consisted of lead as lead concentration also decreased with longer radiation time. Unfortunately, we can not identify the precipitate yet. At 0.02 M hydrogen peroxide, Pb-EDTA concentration was reduced by about 88.46% in 8 min and total lead concentration by about 96.57% within 20 min. When the concentration of hydrogen peroxide increased from 0.02 to 0.08 M, the more rapid degradation of Pb-EDTA and precipitation of lead were observed. And at 0.08 M hydrogen peroxide, the concentration of Pb-EDTA and total lead decreased by 98.17% in 6 min and 98.58% within 20 min, respectively.

From figure 3.9 and 3.10, NTA concentration was increased and then slowly decreased when the irradiation is continued. At 0.04 M hydrogen peroxide, it was found that peak of NTA coeluted with nitrate peak after 12 min of irradiation and thus could not be quantified. IDA concentration increased after the appearance of NTA and at hydrgen peroxide 0.04 M, oxalate peak coeluted with IDA. So we could detect and quantify IDA at only 2 to 6 min. The more Pb-EDTA was degraded, the more NTA and IDA were observed. We have found that within the concentration range of hydrogen peroxide and the irradiation time used, only NTA, IDA, nitrate and oxalate could be identified as by-products.

At our operating wavelength and light intensity, we deduced that the optimum concentration of hydrogen peroxide is 0.04 M or equivalent to the Pb-EDTA:H_2O_2 molar ratio of 1:20. The molar ratio higher than 1:20 does not make a lot of change in the degradation of Pb-EDTA. Moreover, at very high hydrogen peroxide concentration, hydrogen peroxide can act as a free-radical scavenger itself resulting in a decrease of the hydroxyl radical concentration. The mechanism are shown in the equations (3.1) and (3.2) [Akgerman and Alnaizy 2000; Galindo and Kalt 1998].

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \qquad \text{……(3.1)}$$

$$H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O \qquad \text{……(3.2)}$$

3.4 Influence of initial pH of solution

To investigate the influence of the initial pH, solutions of Pb-EDTA (2 mM) having initial pH at 3.0, 6.0 and 8.0 were irradiated. Hydrogen peroxide was added to obtain the Pb-EDTA:H_2O_2 molar ratio of 1:20. The results are shown in figures 3.11 -3.15. When the initial pH of the solution was about 3.0, the pH value increased continuously from 2.78 to 6.30 during the irradiation. Pb-EDTA and total lead concentration decreased by 98.60% in 6 min and 99.07% in 20 min, respectively. The precipitation was obtained after 6 min of irradiation at pH higher than 4. We also observed a rapid reduction in total lead concentration at this time.

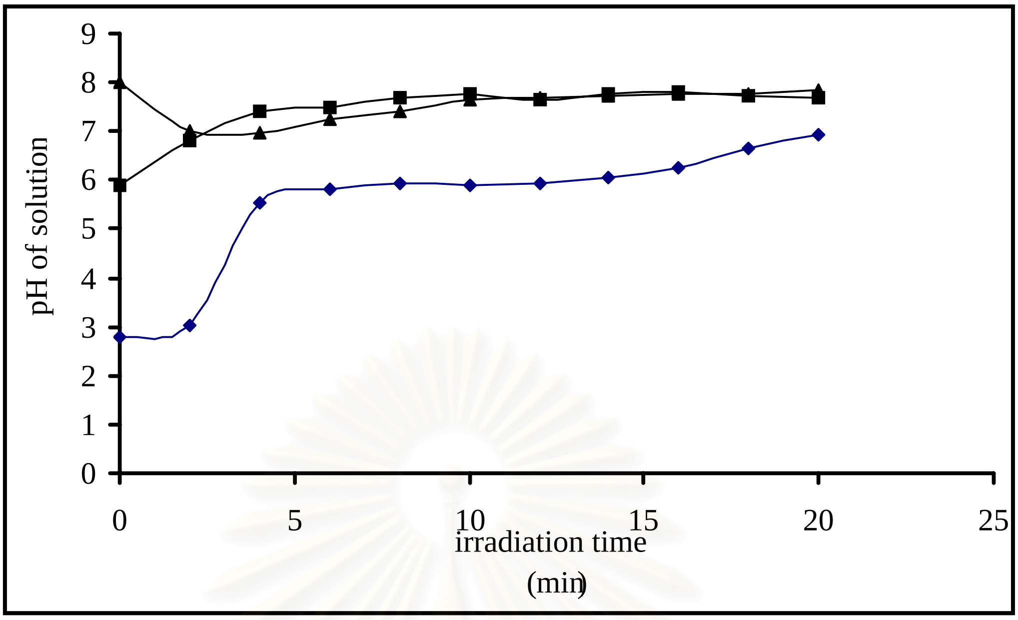


Figure 3.11 The pH of solution during irradiation; initial Pb-EDTA 2 mM and initial hydrogen peroxide 0.04 M. (♦) pH 3.0, (■) pH 6.0 and (▲) pH 8.0

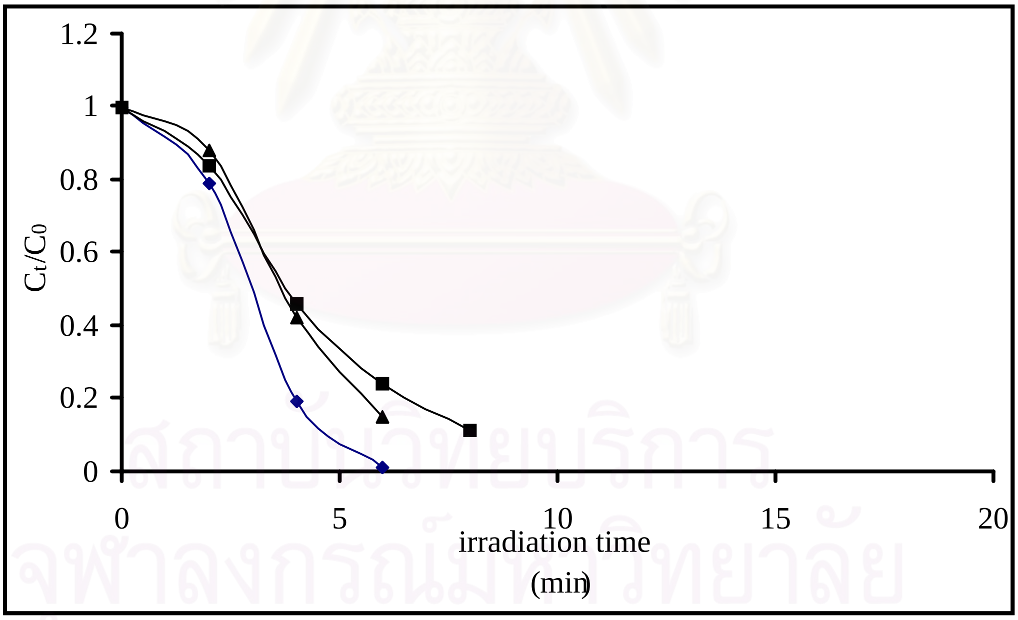


Figure 3.12 Effect of initial pH of solution on Pb-EDTA degradation; initial Pb-EDTA 2 mM and initial hydrogen peroxide 0.04 M. (♦) pH 3.0, (■) pH 6.0 and (▲) pH 8.0

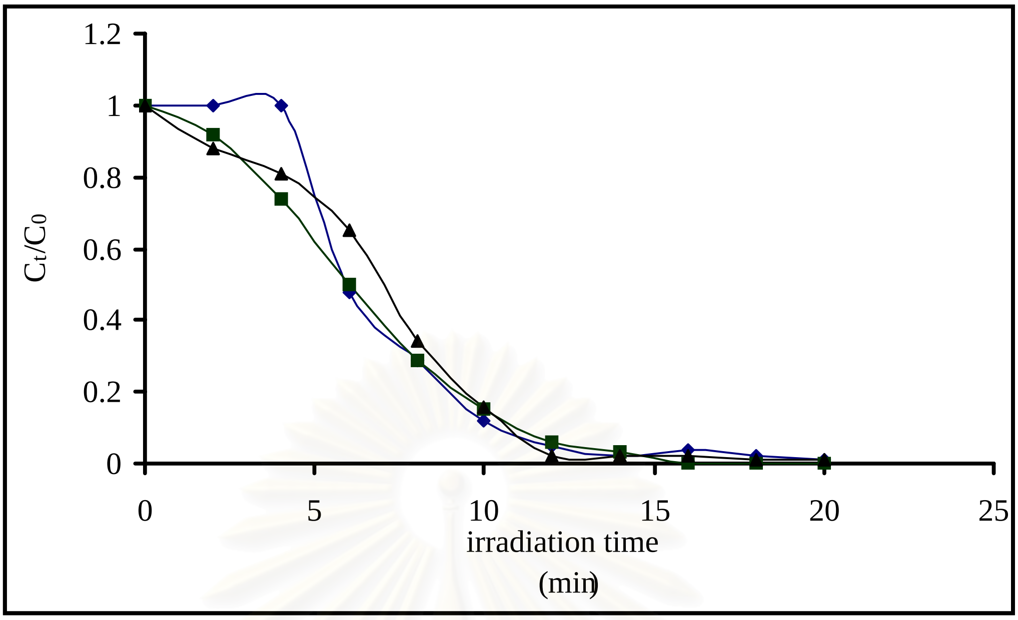


Figure 3.13 Effect of initial pH of solution on total lead concentration; initial Pb-EDTA 2 mM and initial hydrogen peroxide 0.04 M. (♦) pH 3.0, (■) pH 6.0 and (▲) pH 8.0

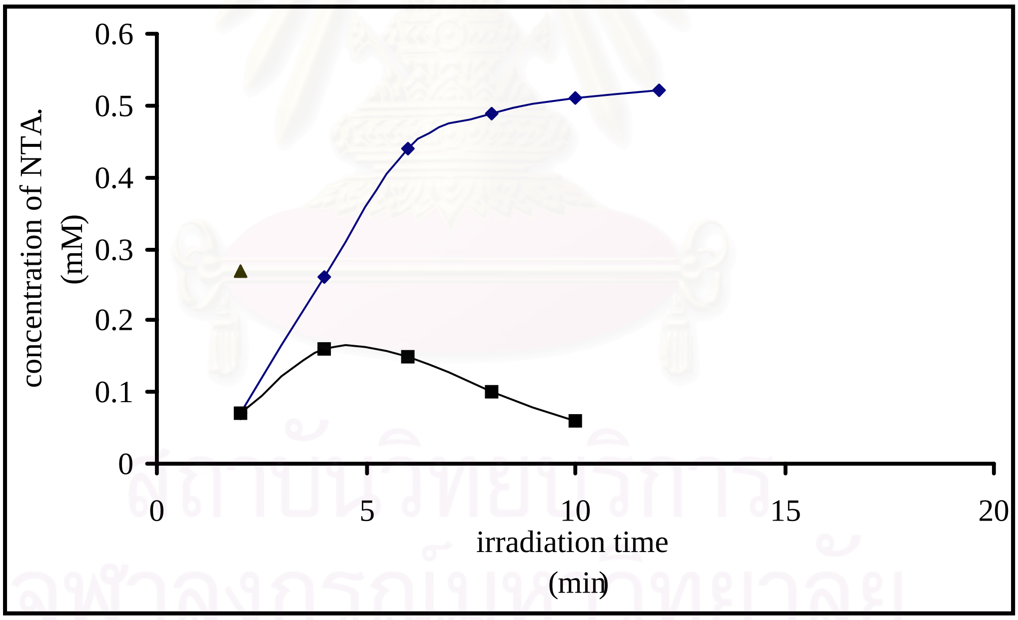


Figure 3.14 NTA concentration at different initial pH of photooxidation; initial Pb-EDTA 2 mM and initial hydrogen peroxide 0.04 M. (♦) pH 3.0, (■) pH 6.0 and (▲) pH 8.0

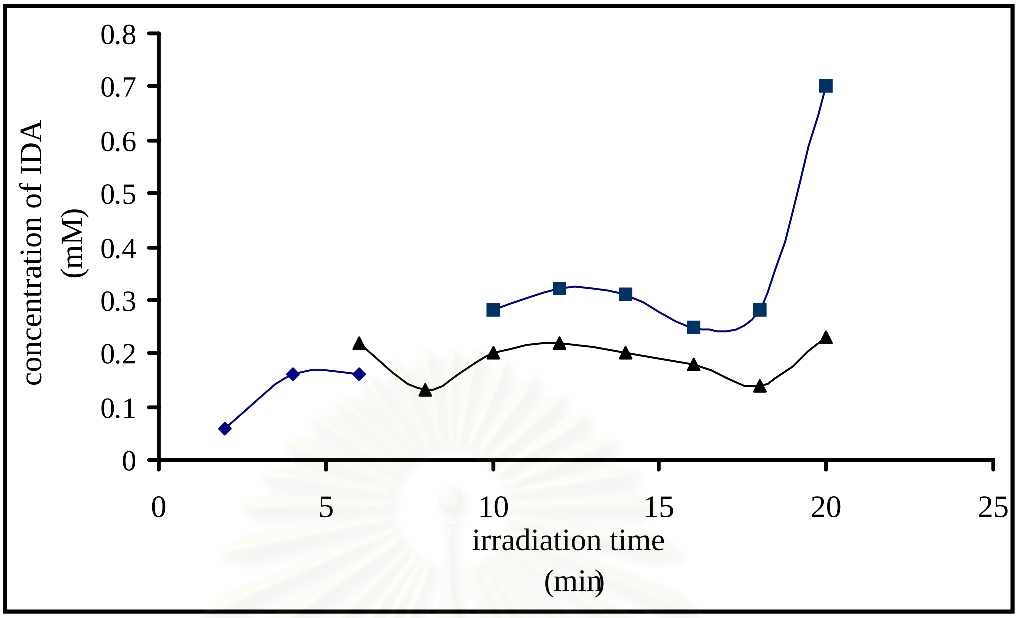


Figure 3.15 IDA concentration at different initial pH of photooxidation; initial Pb-EDTA 2 mM and initial hydrogen peroxide 0.04 M. (♦) pH 3.0, (■) pH 6.0 and (▲) pH 8.0

When the initial pH of solution was about 6.0, the pH value increased continuously from about 5.9 to 7.7 during the radiation. There was a little change in pH when the initial pH of solution was adjusted to about 8.0. From figures 3.12 and 3.13, there was a small difference in the degradation of Pb-EDTA and lead removal when the initial pH of solution were 6.0 and 8.0. It was found that the complex degraded more rapidly at pH 3.0 than at pH 6.0 and 8.0.

From figure 3.13, when the initial pH was 6.0 and 8.0, the reduction of lead concentration was observed at the beginning of the irradiation. This was not found when the initial pH of the solution is 3.0. In the last case, only when the pH of the solution was higher than 4.0, the reduction of lead concentration and the precipitation were observed. It seems that the precipitation of lead is a function of pH. Unfortunately, we cannot identify the precipitate yet.

In alkaline condition, a portion of hydrogen peroxide will be deprotonated to yield HO_2^- anion. The reaction of hydroxyl radical with HO_2^- anion can occur 100 times faster than the reaction of hydroxyl radical with hydrogen peroxide [Galindo and Kalt 1998]. The reactions and rate constants are shown in equations (3.3) and (3.5).

$$H_2O_2 \longleftrightarrow HO_2^- + H^+ \quad ; pK_a = 11.6 \quad \ldots\ldots(3.3)$$

$$OH^{\bullet} + HO_2^- \longrightarrow H_2O + O_2^{\bullet -} \quad ; k_1 = 7.5 \times 10^9 \ l \ mol^{-1} \ s^{-1} \quad \ldots\ldots(3.4)$$

$$H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O \ ; \ k_1 = 2.7 \times 10^7 \ l \ mol^{-1} \ s^{-1} \quad \ldots\ldots(3.5)$$

Therefore, at the high pH, the concentration of hydroxyl radical may be lower than expected. This explains the slower degradation of Pb-EDTA observed at high pH.

Figures 3.14 and 3.15 show the change of NTA and IDA concentration during the irradiation. At the initial pH value of 3.0, it was found that NTA appeared since 2 min of irradiation and increased in concentration within 12 min. At pH value of 6.0, NTA also appeared at 2 min and the concentration increased and slowly decreased afterward. And after12 min, NTA could not be quantified because of a coelution with unknown peaks. At initial pH value of about 8.0, NTA was quantified only at 2 min of irradiation. At longer irradiation time, there was an unknown compound that occurred and coeluted with NTA in CE. By comparing the retention time with standard, the compound that was coeluted with NTA may be nitrate. Concerning IDA, it was found during 2 and 6 min of irradiation when the initial pH was 3.0. After 6 min, peak of IDA coeluted with an unknown peak and it could not be quantified. At both pH values of 6.0 and 8.0, it was found that the IDA concentration increased within 20 min. The formation and degradation of by-products seem to depend on pH of solution. In alkaline solution, Pb-EDTA was degraded to NTA that was further decomposed rapidly to yield IDA. When the initial pH was 6.0, NTA could be observed during the first period of irradiation and IDA was found after the disapparance of NTA. On the other hand, in acidic solution (pH=3.0), the majority of by-products was NTA and small amount of IDA could be found during irradiation period.

In general, wastewater from industries such as electroplating, batteries production often has an average pH of 1.5 or less [Atwood *et al.* 2002]. So we have also studied an initial pH of solution about 1.5. The results are shown in figures 3.16 and 3.17.

When initial pH of solution was 1.5, it was found that the pH value of solution did not change during the irradiation. The Pb-EDTA concentration was rapidly decreased by 91.31% in 8 min. But total lead concentration was not reduced and the precipitate was not found during irradiation. From previous experiments, lead precipitation was observed at pH higher than 4. Therefore, lead did not precipitate when the pH of the solution was 1.5. NTA concentration was increased continuously within 20 min and no IDA was found. This observation confirms the hypothesis that the formation and degradation of NTA and IDA and also the precipitation of lead are a function of pH.

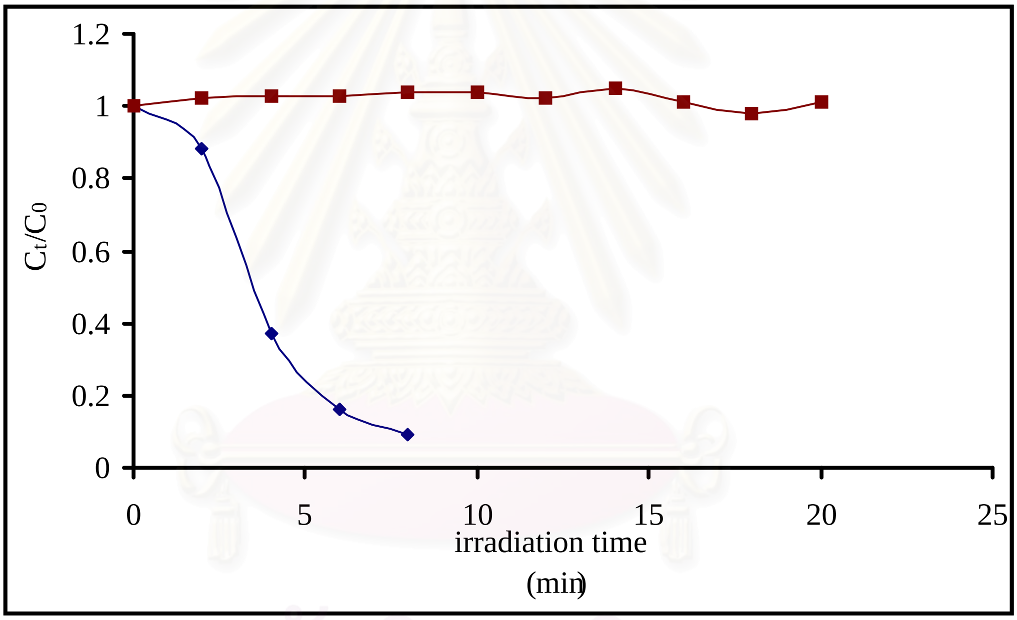


Figure 3.16 Photooxidation of Pb-EDTA at initial pH of 1.5; initial Pb-EDTA 2 mM, initial hydrogen peroxide 0.04 M and initial pH of solution 1.5. (♦) Pb-EDTA and (■) total lead concentration.

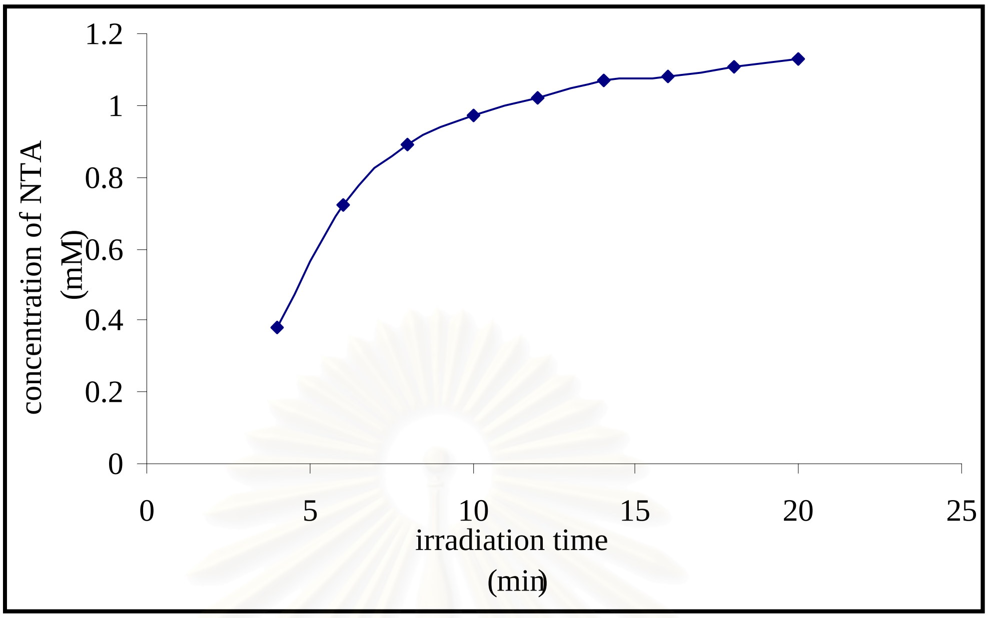


Figure 3.17 NTA concentration at initial pH of solution 1.5; initial Pb-EDTA 2 mM and initial hydrogen peroxide 0.04 M.

From this experiment, we deduced that the optimum initial pH is 3.0. At this pH the degradation of Pb-EDTA was better than other pH and total lead concentration has decreased to less than 0.044 mg L^{-1}. Furthermore, we want to apply the process in treatment of wastewater, that often has initial pH of solution about 1.5 or less. But at pH value 1.5, the total lead concentration can not be reduced simultaneously. So we choose the initial pH of solution as 3.0 that is the closest pH to the real wastewater.

3.5 Optimization of conditions used

To study the feasibility of using the technique in wastewater treatment, we first reduced the amount of hydrogen peroxide to reduce the operating cost. The molar ratio of Pb-EDTA:H_2O_2 was reduced from 1:20 to 1:15 and 1:10. In this study, the initial concentration of hydrogen peroxide was kept constant at 0.02 M and concentration of Pb-EDTA was varied from 1.3 to 2 mM. The initial pH of solution was 3.0. The results are shown in figure 3.18 and 3.19.

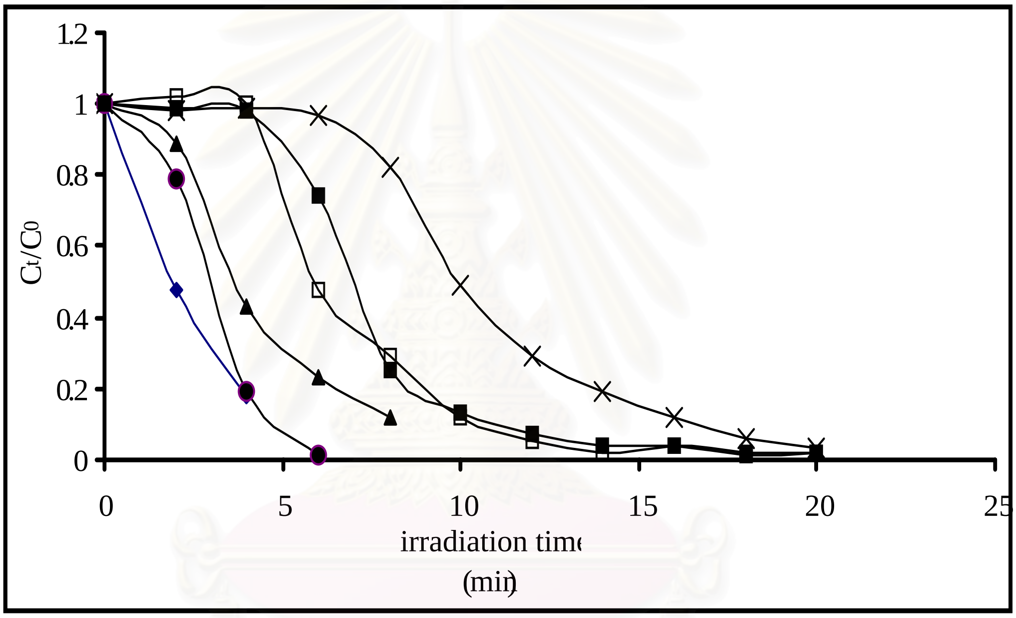


Figure 3.18 The photooxidation of Pb-EDTA at different Pb-EDTA:H_2O_2 molar ratio; initial hydrogen peroxide 0.02 M and initial pH of solution 3.0. (♦) Pb-EDTA at molar ratio was 1:15 and (■) total lead concentration at molar ratio was 1:15, (▲) Pb-EDTA at molar ratio was 1:10, (x) total lead concentration at molar ratio was 1:10, (●) Pb-EDTA at molar ratio was 1:20 and (□) total lead concentration at molar ratio was 1:20

When the molar ratio of Pb-EDTA:H_2O_2 was 1:15, 82% of Pb-EDTA concentration has been reduced in 4 min. The total lead concentration has reduced by 97.76% within 20 min. From figure 3.19, NTA concentration increased in 10 min and then slowly decreased within 20 min. IDA was not detected.

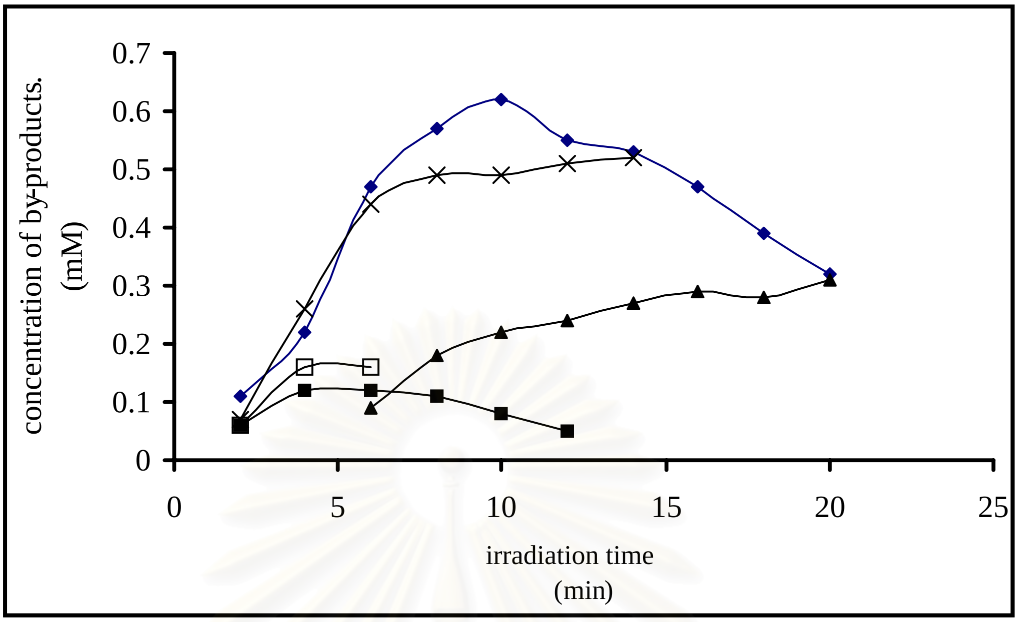


Figure 3.19 NTA and IDA concentration at initial hydrogen peroxide 0.02 M and initial pH of solution 3.0. (♦) NTA at molar ratio was 1:15, (■) NTA at molar ratio was 1:10, (▲) IDA at molar ratio was 1:10, (x) NTA at molar ratio was 1:20 and (□) IDA at molar ratio was 1:20

Comparing Pb-EDTA:H_2O_2 molar ratio between 1:15 and 1:10, it was found that, Pb-EDTA:H_2O_2 of 1:15, both Pb-EDTA and total lead concentration were reduced better than 1:10 molar ratio. At molar ratio of 1:15 and 1:20, there is a small difference in the reduction of Pb-EDTA and total lead concentration. When compare the by-products found, molar ratio of 1:15, only NTA was detected and quantified. On the other hand, when Pb-EDTA:H_2O_2 was 1:20, NTA and IDA were observed after irradiation. More over, after 6 min of irradiation, oxalate was found and coeluted with IDA. Nitrate was also detected coeluted with NTA after 12 min of irradiation. NTA and IDA could not be quantified at this irradiation time because of the coelution. The appearance of nitrate and oxalate indicated that EDTA could be completely degraded. So we deduced that the optimum Pb-EDTA:H_2O_2 molar ratio was 1:20.

3.6 Influence of nitrate concentration

In H_2O_2/UV process, hydroxyl radicals are produced and used as oxidizing agent. It is very reactive and will react non-selectively with the substrates present in the solution. In our experiments, the desired reactions are the degradation of Pb-EDTA and its by-products by hydroxyl radicals. When the substrates like bicarbonate, carbonate, and nitrate are simultaneously present in the solution, they will also react with hydroxyl radicals. The substrates are called “scavenger” that can violently reduce the efficiency of the oxidation of the desired substrates [Braun *et al*. 1993; Zappi *et al*. 2002]. So we have studied the effect of nitrate, one of the scavengers found in wastewater, on complex degradation.

To investigate the effect of nitrate, the concentration of Pb-EDTA and hydrogen peroxide were kept constant at around 2 mM and 0.04 M, respectively. The initial pH of solution was 3.0. The concentration of nitrate was varied from 0.004 to 0.04 M. The molar ratio of nitrate:H_2O_2 was 1:10 and 1:1, respectively. The results are shown in figures 3.20 - 3.22.

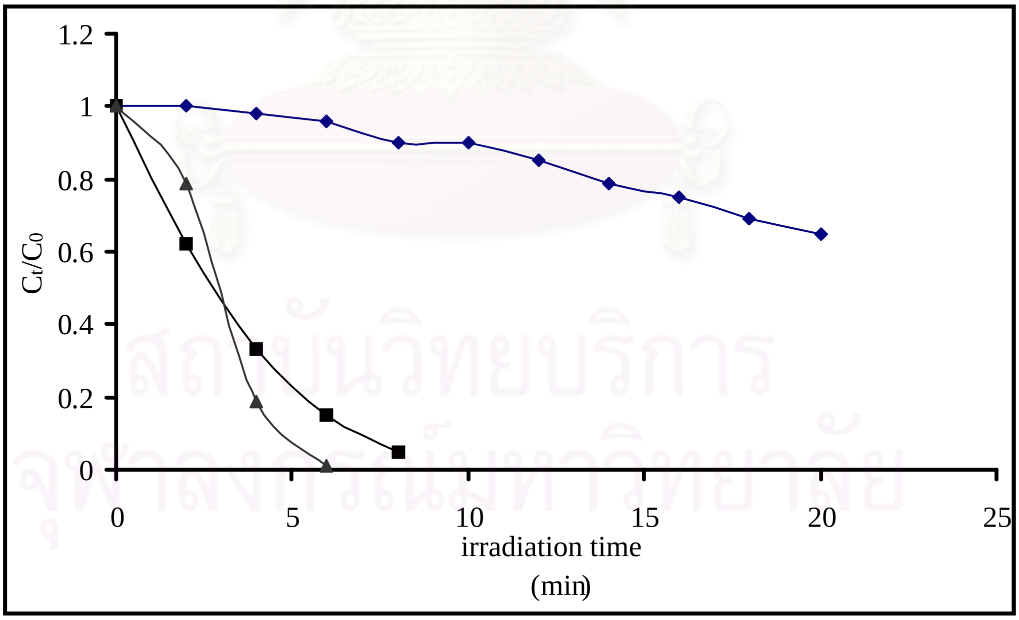


Figure 3.20 Effect of nitrate concentration on Pb-EDTA degradation; initial Pb-EDTA 2 mM, initial hydrogen peroxide 0.04 M and initial pH of solution 3.0. (♦) nitrate 0.04 M, (■) nitrate 0.004 M and (▲) no nitrate

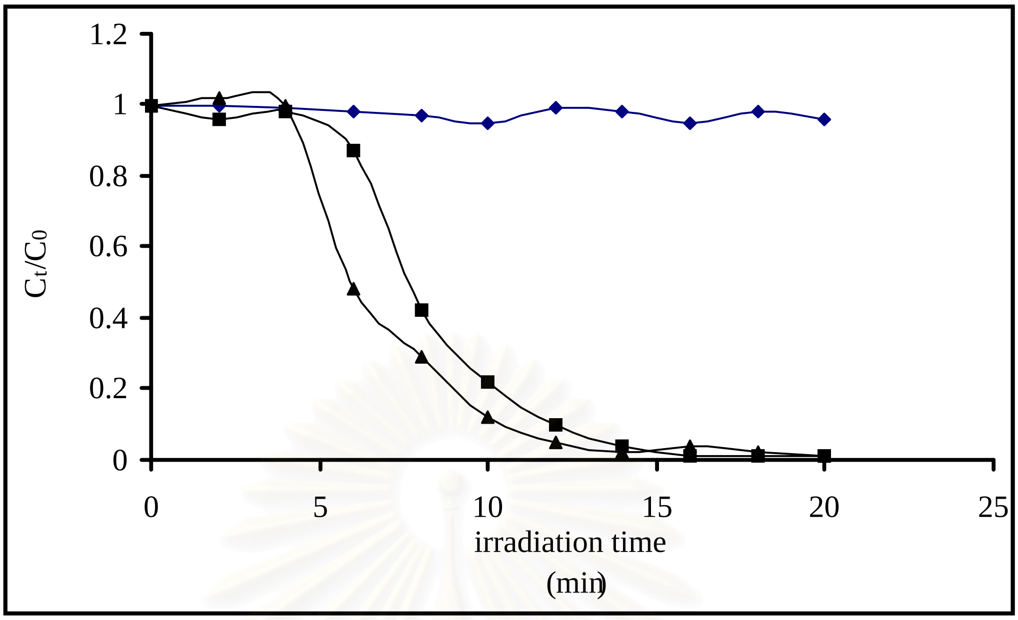


Figure 3.21 Effect of nitrate concentration on total lead concentration; initial Pb-EDTA 2 mM, initial hydrogen peroxide 0.04 M and initial pH of solution 3.0. (♦) nitrate 0.04 M, (■) nitrate 0.004 M and (▲) no nitrate

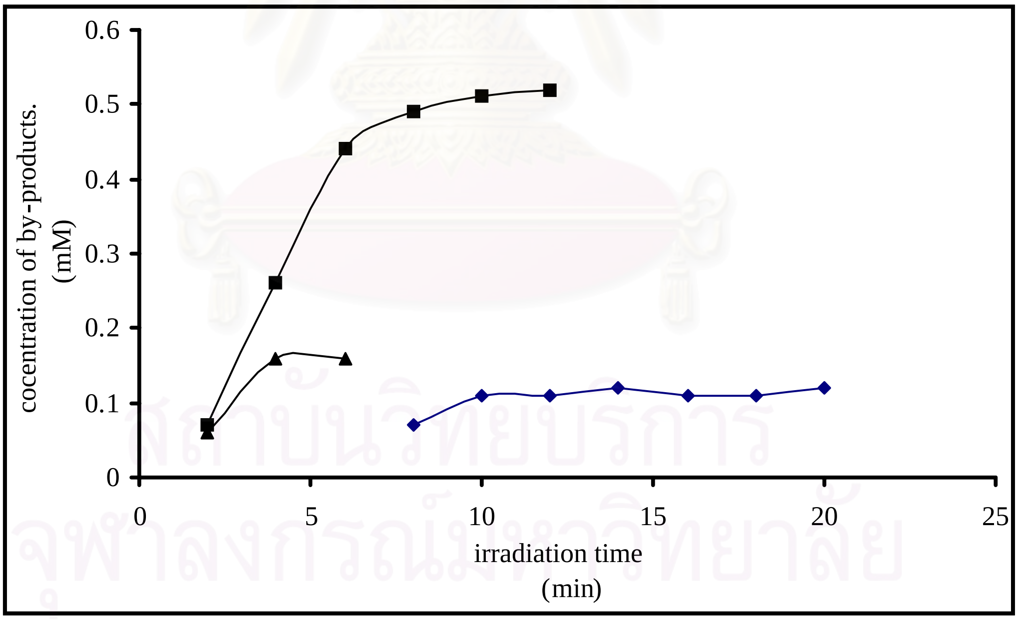


Figure 3.22 Effect of nitrate concentration on NTA and IDAformation at initial Pb-EDTA concentration 2 mM, initial hydrogen peroxide 0.04 M and initial pH of solution 3.0. (♦) IDA nitrate 0.004 M, (■) NTA no nitrate and (▲) IDA no nitrate

From figures 3.20 and 3.21, at nitrate concentration 0.004 M, Pb-EDTA and total lead concentration were reduced in the same way as found in the oxidation of Pb-EDTA without nitrate. When the nitrate concentration increased to 0.04 M, Pb-EDTA was slowly decomposed. The reduction of total lead concentration was not observed. The results indicated that nitrate could affect the oxidation of Pb-EDTA especially at very high concentration. Nitrate at high concentration probably acts as radical scavenger and reduces the efficiency of the desired reaction. Ku *et al.* [1998] also indicated that nitrate can reduce the rate of decomposition of EDTA by H_2O_2/UV process. Laat *et al.* [2004] have investigated the effect of chloride, sulfate and nitrate ions on the rates of decomposition of H_2O_2 and organic compounds by Fenton's process. It was found that the rate of decomposition of H_2O_2 and organic compounds were reduced by the inorganic ions, such as chloride, sulfate and nitrate. Nitrate can violently reduce the efficiency of oxidation via the reactions (3.6) - (3.8) [Bolton and Mack 1999].

$$NO_3^- + h\nu \longrightarrow NO_2^- + O \quad \text{……(3.6)}$$

$$NO_3^- + h\nu \longrightarrow NO_2^{\bullet} + O^{\bullet -} \quad \text{……(3.7)}$$

$$NO_2^- + OH^{\bullet} \longrightarrow NO_2 + OH^- \quad \text{……(3.8)}$$

Unfortunately, NTA could not be quantified by CE because it coeluted with nitrate. Only IDA has been analysed. At nitrate concentration 0.004 M, IDA occurred after 8 min of irradiation. When nitrate concentration was 0.04 M, IDA was not detected. It is probably because only small amount Pb-EDTA was degraded.

3.7 Effect of irradiation time on Pb-EDTA and by-products degradation

From the previous experiments, we have obtained the optimum condition for Pb-EDTA degradation by H_2O_2/UV process. Afterwards, we are interested in the formation and degradation of by-products when increase the irradiation time. In this study, we used 2 mM Pb-EDTA, 0.04 M hydrogen peroxide and solution initial pH of 3.0. The irradiation time was increased from 20 to 30 min. The results are shown in figures 3.23 and 3.24.

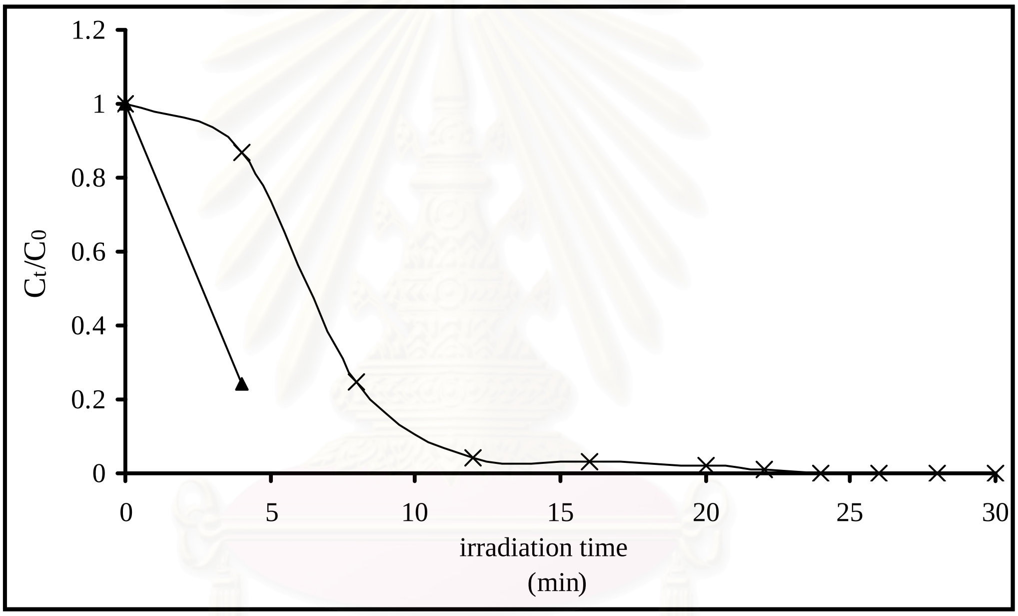


Figure 3.23 Change in Pb-EDTA and total lead concentration; initial Pb-EDTA 2 mM, initial hydrogen peroxide 0.04 M, initial pH of solution 3.0 and 30 min of irradiation time. (▲) Pb-EDTA and (x) total lead concentration

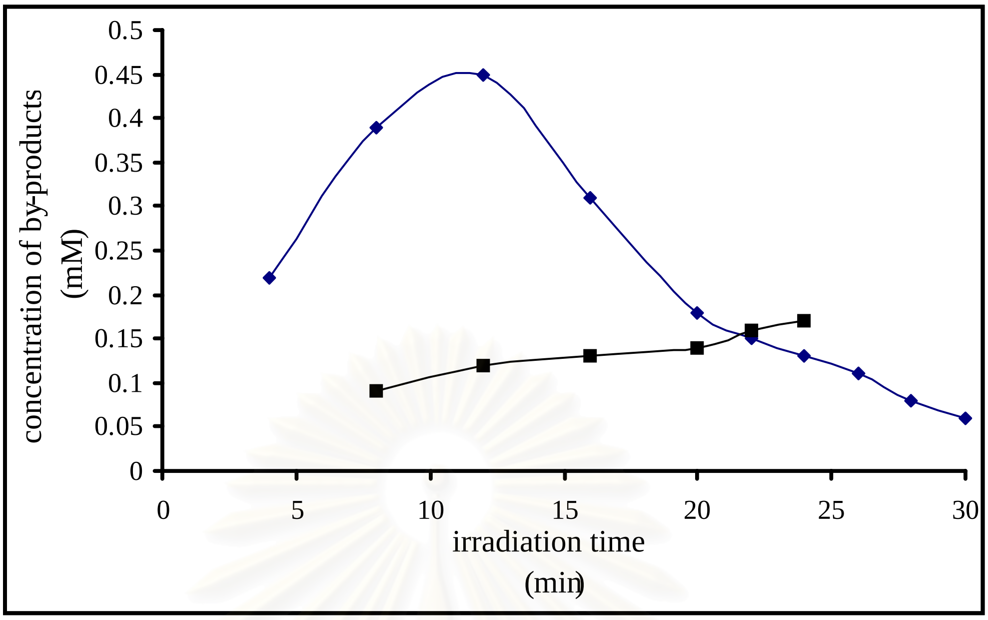


Figure 3.24 Change in NTA and IDA concentration; initial Pb-EDTA 2 mM, 0.04 M hydrogen peroxide, initial pH 3.0 and 30 min irradiation time. (♦) NTA and (■) IDA

Pb-EDTA and total lead concentration changed in the same way as what observed earlier when the irradiation time was 20 min. NTA and IDA were again identified as by-products of photooxidation. NTA amount increased within 12 min and afterwards it was continuously decreased in 30 min of irradiation time. IDA appeared in the same time and its concentration slowly increased. After 25 min of irradiation, IDA was coeluted with oxalate peak so it could not be quantified. During irradiation, we observed NTA, IDA, oxalate, nitrate, and unknown peaks by CE. Nitrate occurred at about 8 min of irradiation and its concentration slowly increased until 16 min. After 16 min nitrate concentration did not change until 30 min. The appearance of nitrate indicated that EDTA could be completely degraded, as shown in scheme 1.1 (chapter I).

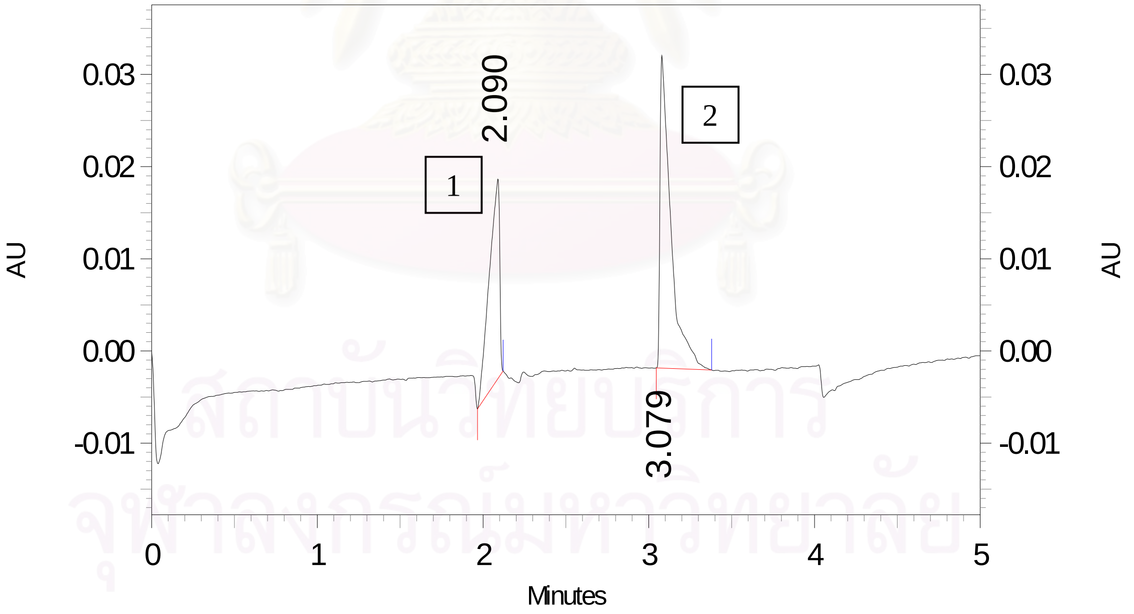
The results show that the longer irradiation time leads to a decomposition of the by-products of Pb-EDTA. The final by-products seems to be nitrate and oxalic acid or even carbon dioxide.

3.8 The degradation of other metal-EDTA

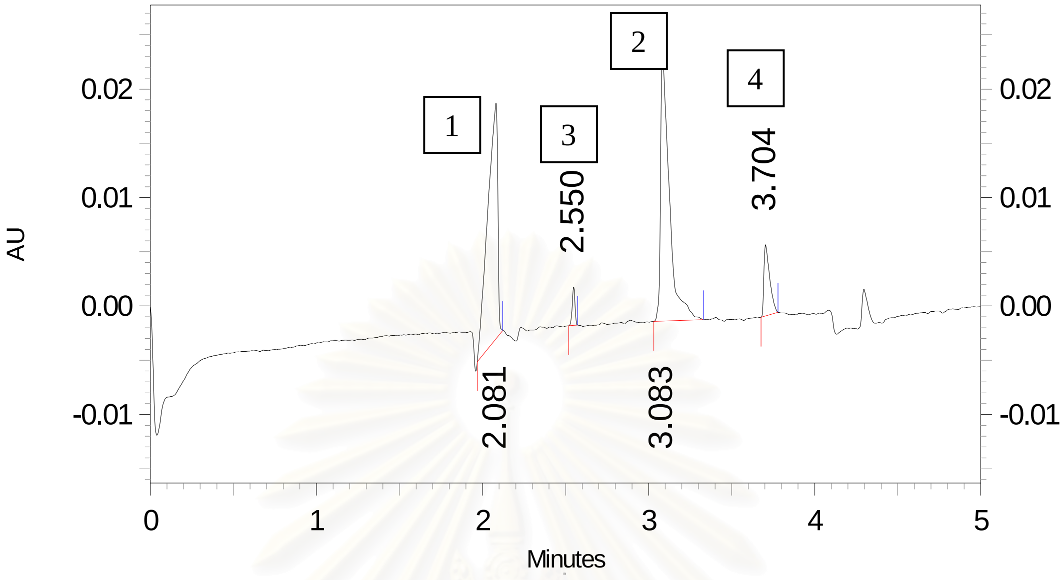
In this investigation, the conditions used for the degradation of Pb-EDTA were applied to the photooxidation of Zn-EDTA and Cd-EDTA complex. We further compare the degradation of these complexes to that of Pb-EDTA.

3.8.1 Zn-EDTA degradation

In this study, the initial concentration of Zn-EDTA was around 2 mM. The hydrogen peroxide concentration was 0.04 M and the initial pH of solution was 3.0. The Zn-EDTA:H_2O_2 molar ratio was 1:20. Zn-EDTA and by-products in solution were analysed by CE. Figure 3.25 shows electropherograms of the complex and by-products occurred in solution before and after irradiation.



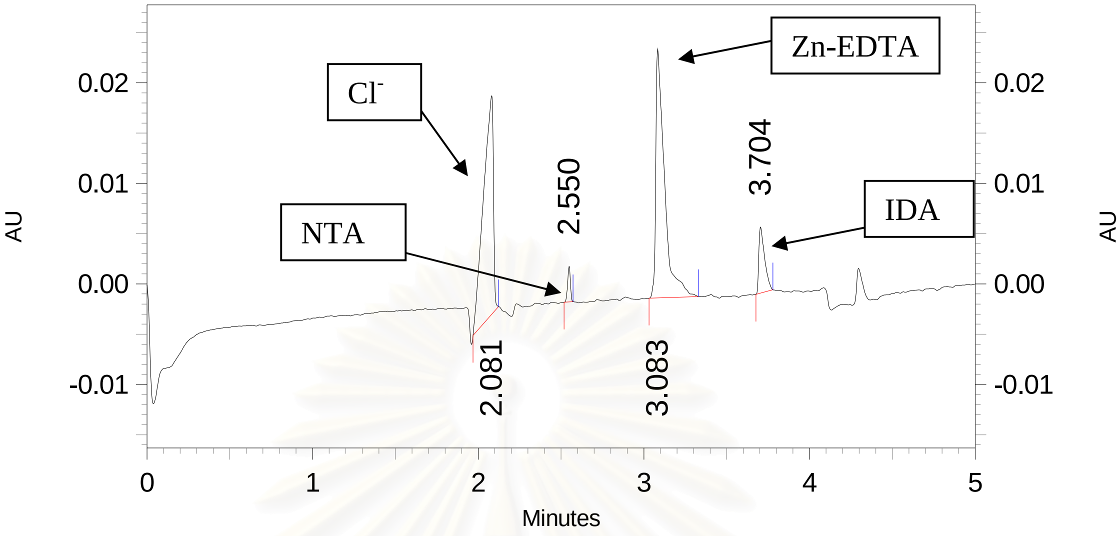
(a)



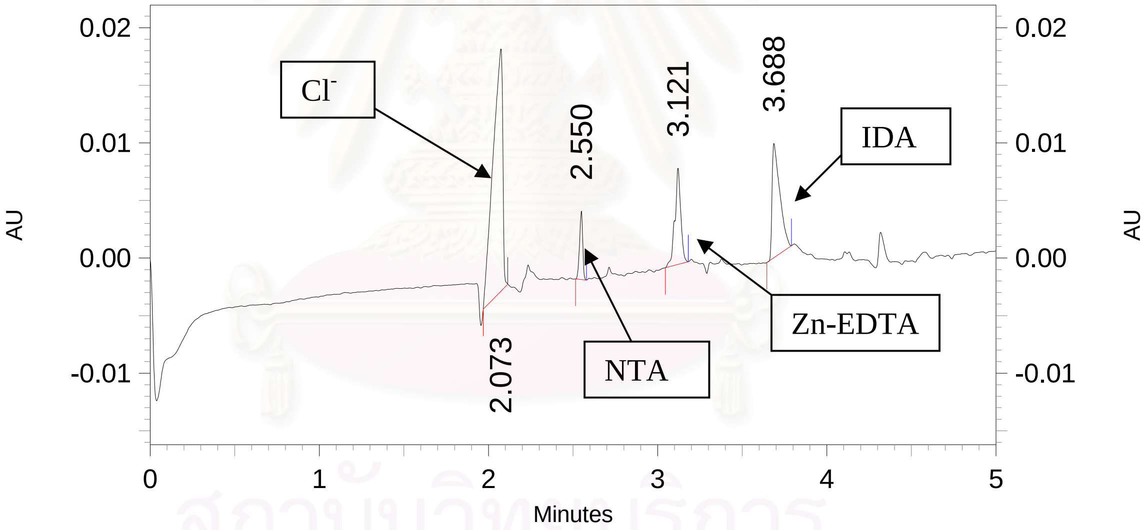
(b)

Figure 3.25 The electropherogram of standard (a) and irradiated sample of Zn-EDTA (b). (a) standards (2 mM) of Zn-EDTA (2), (b) irradiated sample of Zn-EDTA at 4 min; Zn-EDTA (2), NTA (3), IDA (4) and chloride (1).

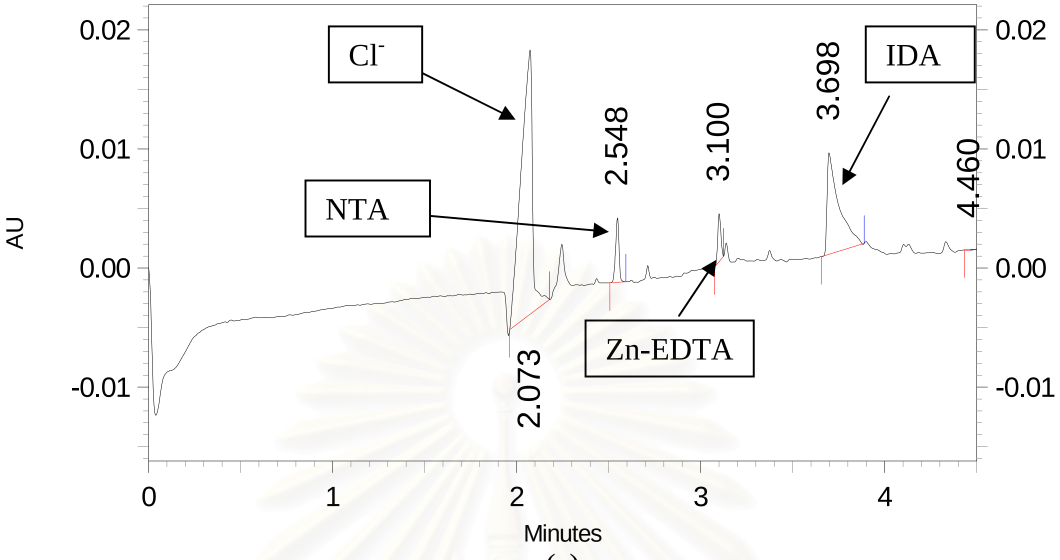
Zn-EDTA was detected and quantified at about 3.079 min. The retention time at 2.090 min was chloride ions. When irradiated, Zn-EDTA can be degraded to the by-products of NTA and IDA, eluting at about 2.5 and 3.7 min of retention time respectively. Figure 3.26 shows a change in electropherogram of Zn-EDTA solution during irradiation.


AU
0.02
0.01
0.00
-0.01
Cl-
NTA
Zn-EDTA
IDA
2.081
2.550
3.083
3.704
0
1
2
3
4
5
Minutes

(a)


AU
0.02
0.01
0.00
-0.01
Cl-
NTA
Zn-EDTA
IDA
2.073
2.550
3.121
3.688
0
1
2
3
4
5
Minutes

(b)



(c)

Figure 3.26 The electropherogram of Zn-EDTA degradation samples; initial concentration of Zn-EDTA 2 mM and hydrogen peroxide 0.04 M at initial pH of solution 3.0. (a) 4 min irradiation time, (b) 6 min irradiation time and (c) 8 min irradiation time

During the irradiation, pH of the solution increased slowly from 2.8 to 6.3. The conditions used were 2 mM Zn-EDTA and 0.04 M hydrogen peroxide at initial pH 3.0. From electropherograms, by-products of Zn-EDTA degradation such as NTA and IDA were identified. The change in concentration of Zn-EDTA and by-products as a function of irradiation time are shown in figures 3.27 and 3.28, respectively.

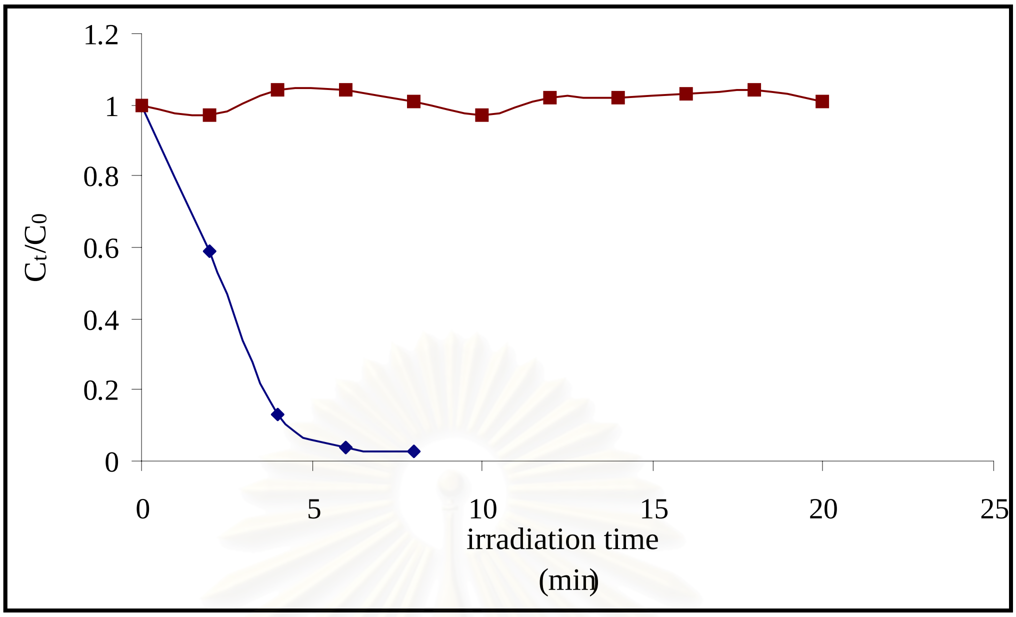


Figure 3.27 The degradation of Zn-EDTA by photooxidation; initial Zn-EDTA 2 mM, 0.04 M hydrogen peroxide, initial pH 3.0. (♦) Zn-EDTA and (■) total zinc concentration

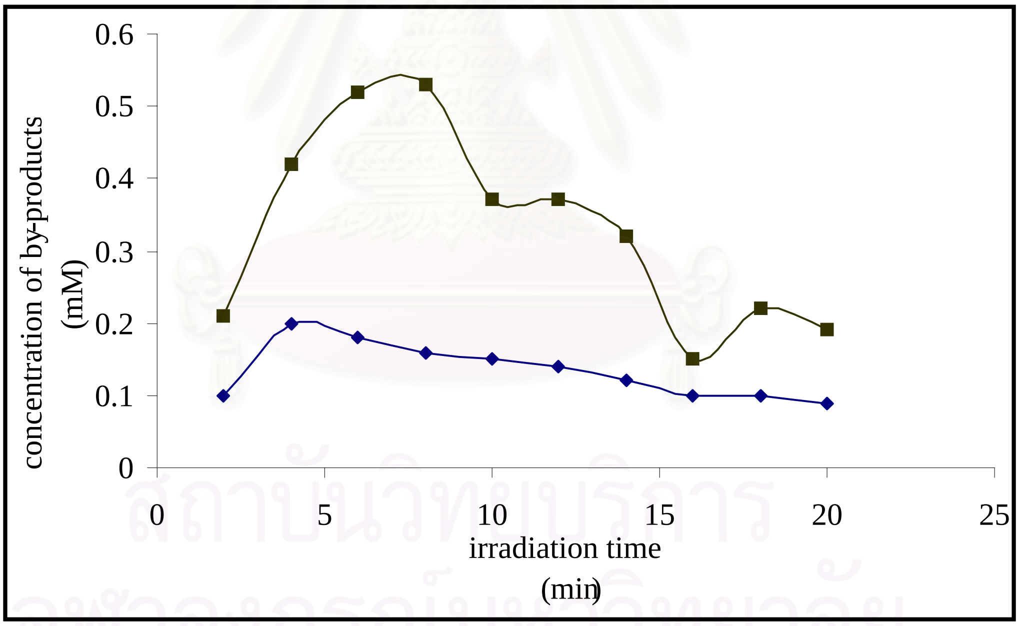


Figure 3.28 NTA and IDA concentration after Zn-EDTA degradation; initial Zn-EDTA 2 mM, 0.04 M hydrogen peroxide, initial pH 3.0. (♦) NTA and (■) IDA concentration

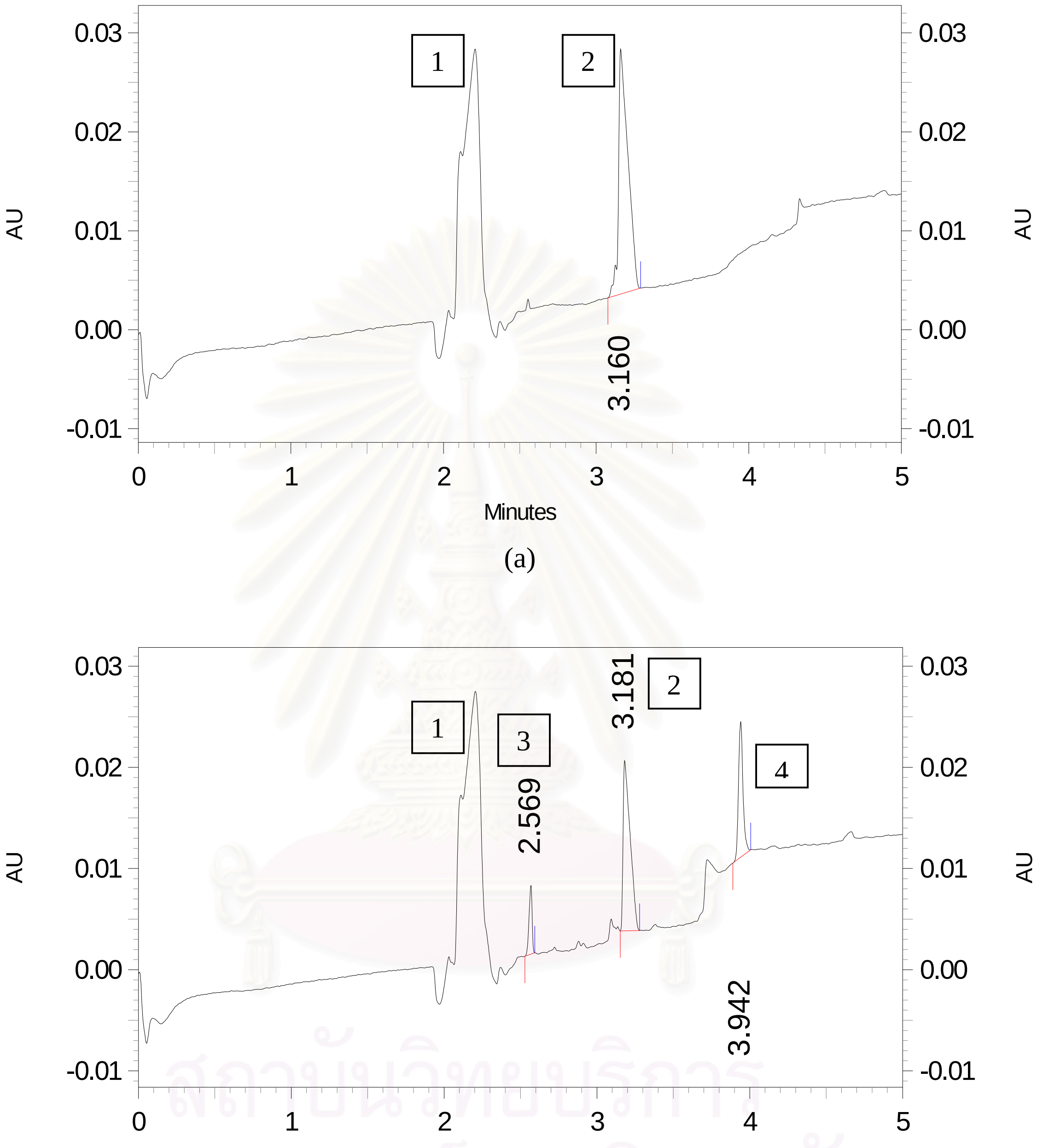
The results show that Zn-EDTA can be degraded by photooxidation process. Almost total consumption of Zn-EDTA was observed within 8 min. On the other hand, the total zinc concentration did not change during irradiation. Unlike Pb-EDTA, no precipitate was observed. Zinc will precipitate as hydroxide at pH value about 10.6 [Akgerman and Alnaizy 2000] but the solution after the photooxidation has a pH value only about 6.0. Unfortunately, we cannot identify the form of soluble zinc yet.

NTA and IDA could be observed at the beginning of the irradiation. The by-products concentration increased during the first period of irradiation (2-8 min) as the Zn-EDTA was degraded. After 10 min of irradiation, NTA and IDA themselves were also degraded. We found that NTA occurred in lower concentration than what was found in the degradation of Pb-EDTA. As for IDA, both the degradation of Zn-EDTA and Pb-EDTA have yielded the same IDA concentration. From the experiment, we deduced that this condition can be used for the degradation of Zn-EDTA but it can not remove zinc from water.

Datye *et al.* [1997] also investigated the oxidation of metal-EDTA complexes by TiO_2 photocatalysis. It was found that Zn-EDTA concentration was slowly reduced and completely degraded within 120 min. The amount of zinc and total organic carbon were also decreased. In our study, Zn-EDTA could be degraded more rapidly by H_2O_2/UV process than what was observed using TiO_2/UV process. Nevertheless, H_2O_2/UV process could not be used for zinc removal.

3.8.2 Cd-EDTA degradation

In this study, the initial concentration of Cd-EDTA was around 2 mM. The hydrogen peroxide concentration was 0.04 M with initial pH of solution of 3.0. The Cd-EDTA:H_2O_2 molar ratio is 1:20. Cd-EDTA and by-products in solution were analysed in CE. Figure 3.29 shows electropherograms of the complex and by-products present in solution before and after irradiation.

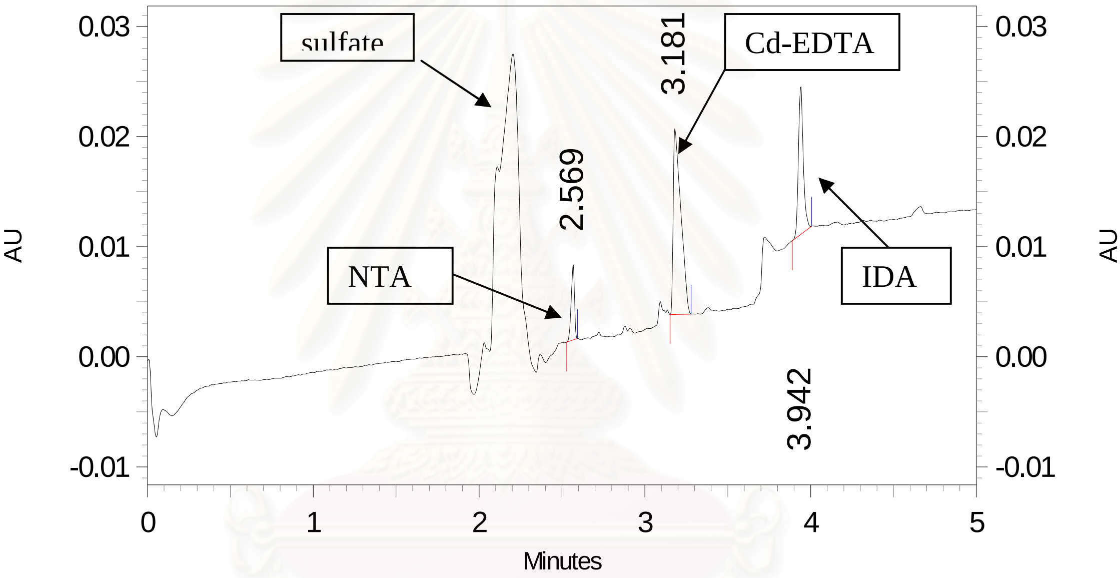


(a)

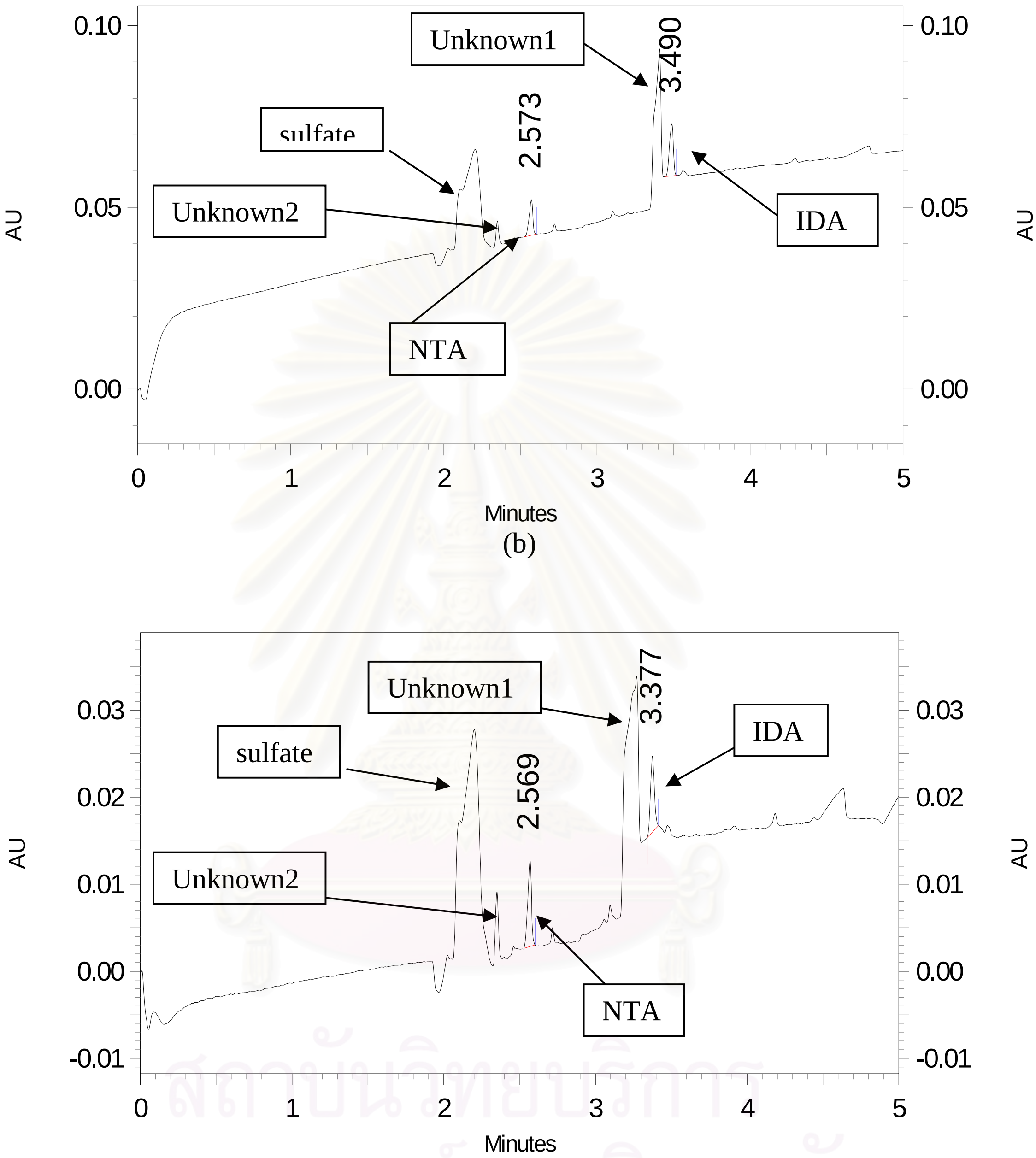
(b)

Figure 3.29 The electropherogram of standard (a) and irradiated sample of Cd-EDTA (b); (a) standards (2 mM) of Cd-EDTA (2), (b) sample of degradation of Cd-EDTA (2 mM) by H_2O_2/UV process; Cd-EDTA (2), NTA (3), IDA (4) and sulfate (1)

Cd-EDTA standard was detected and quantified at about 3.160 min. Sulfate ions from $CdSO_4$ was detected at about 2 min. When irradiated, Cd-EDTA can be degraded to the by-products NTA and IDA which were eluted at about 2.5 and 3.9 min of retention time respectively. Figure 3.30 shows a change in electropherogram of Cd-EDTA solution during irradiation.



(a)



(b)

(c)

Figure 3.30 The electropherogram of Cd-EDTA degradation samples; initial concentration of Cd-EDTA 2 mM and hydrogen peroxide 0.04 M at initial pH of solution 3.0. (a) 4 min irradiation time, (b) 8 min irradiation time and (c) 10 min irradiation time

From figure 3.30, it was found that Cd-EDTA was reduced during irradiation and the by-products as NTA and IDA were observed. From experiments, unknown peaks were also detected during irradiation and unknown 1 was coeluted with IDA when its concentration increased. The change in Cd-EDTA and total cadmium concentration are shown in figure 3.31.

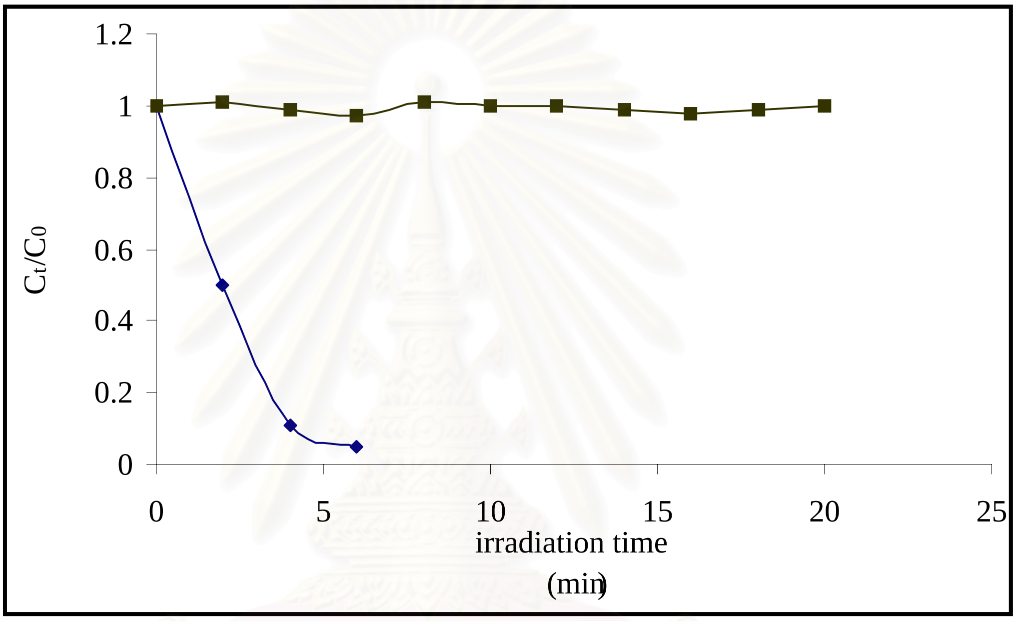


Figure 3.31 The degradation of Cd-EDTA by photooxidation; initial Cd-EDTA 2 mM, 0.04 M hydrogen peroxide, initial pH 3.0. (♦) Cd-EDTA and (■) total cadmium concentration

During irradiation, pH of the solution increased slowly from 2.8 to 6.4. From figure 3.31, Cd-EDTA concentration was reduced by more than 90% within 6 min.The total cadmium concentration did not decrease in 20 min and it indicated that, unlike lead, cadmium cannot precipitate by photooxidation. Cadmium will precipitate as hydroxide at pH value about 11[Akgerman and Alnaizy 2000] but the solution, after the photooxidation, has a pH value only about 6.0. Unfortunately, in this study, we were unable to identify the form of soluble cadmium yet. The change in by-products concentration is present in figure 3.32.

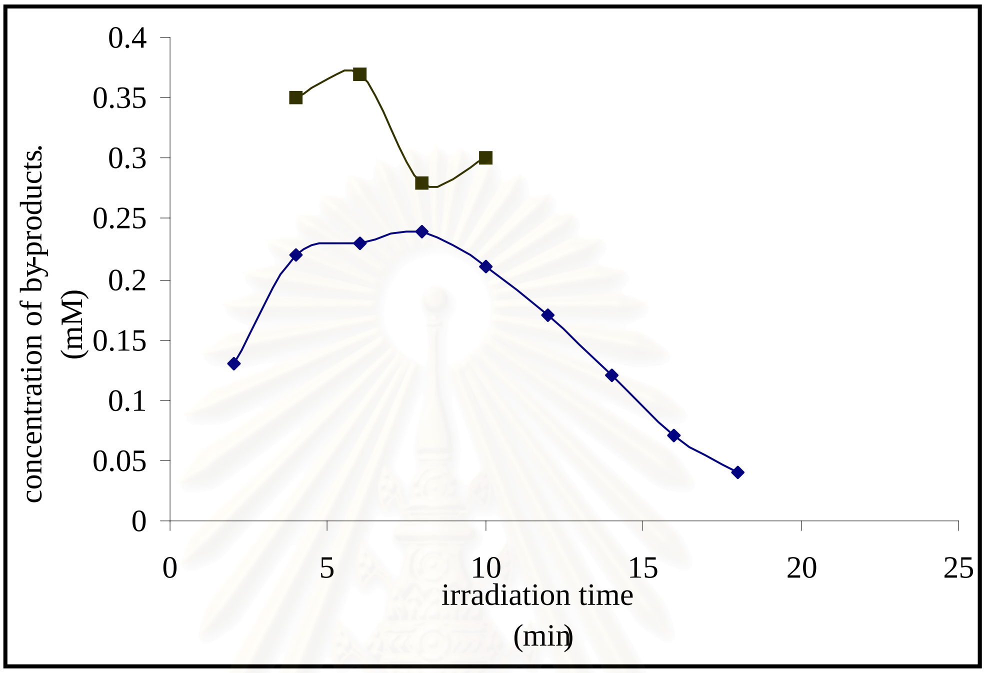


Figure 3.32 NTA and IDA concentration after Cd-EDTA degradation; initial Cd-EDTA 2 mM, 0.04 M hydrogen peroxide, initial pH 3.0. (♦) NTA and (■) IDA concentration

From figure 3.32, after photooxidation of Cd-EDTA, NTA and IDA have appeared. In the case of NTA, the concentration increased within 8 min and further decreased continuously until 18 min. IDA could be detected and quantified only at 4 and 10 min of irradiation. After 10 min of irradiation time, an unknown peak coeluted with peak of IDA. IDA could be detected until 8 min despite coelution with unknown.The results show that the conditions used in photooxidation is suitable for Cd-EDTA degradation but not for cadmium removal.

Datye *et al.* [1997] also investigated the oxidation of metal-EDTA complexes by TiO_2 photocatalysis. It was found that Cd-EDTA concentration was slowly reduced and completely degraded within 120 min. The amount of cadmium and total organic carbon were also decreased. In our study, Cd-EDTA could be degraded more rapidly by

H_2O_2/UV process than what was observed using TiO_2/UV process. Nevertheless, H_2O_2/UV process could not be used for cadmium removal.

3.9 The photonic flux and quantum yield

In this work, the light intensity was measured via photonic flux. Potassium ferrioxalate actinometer has been used for the determination of photonic flux. The photonic flux was calculated by equation (1.23).

$$R_{0,\lambda} = \frac{n_B}{\Phi_B t(1-10^{-A_\lambda^{Ac}})} \text{..........................(1.23)}$$

For equation; $R_{0,\lambda}$ = the incident photonic flux of the irradiation source

n_B = the number of moles of Fe^{2+} produced from ferrioxalate actinometer

Φ_B = the quantum yield of moles of ferrioxalate actinometer (Φ_B =1.24 at 254 nm)

t = time of irradiation (min)

A_λ^{Ac} = the absorbance of ferrioxalate actinometer at wavelength λ

When concentration of actinometer solution is high enough to keep $A_\lambda^{Ac} \geq 2$ during the entire irradiation period, so $R_{0,\lambda}$ is given by:

$$R_{0,\lambda} = \frac{n_{Fe^{2+}}}{\Phi_{Fe^{2+}} t}$$

For example, at t = 20 min, n_{Fe2+} = 3.05 x 10^4 moles and Φ_{Fe2+} = 1.24, so the photonic flux is 1.22 x 10^3 Einstein/min.

From the experiments, the average of photonic flux was 1.29 x 10^3 Einstein/min (%RSD = 1.27). And the quantum yield was determined by the equation (1.19).

$$\Phi_{\mathrm{Pb-EDTA}} = \frac{\text{number of PbEDTA complex degraded}}{\text{number of photon absorbed}} \text{..............(1.19)}$$

In this study, the quantum yield of decomposition of Pb-EDTA, Zn-EDTA and Cd-EDTA complex are shown in table 3.2.

Table 3.2 The quantum yield of decomposition of metal-EDTA complex at different conditions

Complex	Condition of the decomposition				Quantum yield[a] ($\Phi_{complex}$)
	[complex] (mM)	[H_2O_2] (M)	Molar ratio	Initial pH of solution	
Pb-EDTA	2	0	0	3	0.02
Pb-EDTA	2	0.02	1:10	3	0.20
Pb-EDTA	2	0.02	1:10	1.5	0.18
Pb-EDTA	2	0.04	1:20	3	0.30
Pb-EDTA	2	0.08	1:40	3	0.30
Pb-EDTA	2	0.04	1:20	6	0.22
Pb-EDTA	2	0.04	1:20	8	0.22
Pb-EDTA	1.3	0.02	1:15	3	0.22
Zn-EDTA	2	0.04	1:20	3	0.21
Cd-EDTA	2	0.04	1:20	3	0.22

a; average value, n = 2

The quantum yield of a reaction indicates the efficiency of the reaction. In the absence of hydrogen peroxide, the quantum yield obtained was 0.02. When higher hydrogen peroxide concentration was used, the quantum yield increased up to 0.30. In addition, at different Pb-EDTA: H_2O_2 molar ratios, it was found that the quantum yield increased when the molar ratio was higher but not more than 0.30. At 0.04 and 0.08 M hydrogen peroxide, there was no difference in quantum yield. So we choose 0.04 M hydrogen peroxide and the molar ratio Pb-EDTA: H_2O_2 of 1:20 for the decomposition condition.

At different initial pHs of the solution, the quantum yield of the degradation at initial pH 3.0 is higher than the other pH when Pb-EDTA: H_2O_2 was kept constant. Furthermore, when the pH of solution is lower than 3.0, there is no change in quantum yield of Pb-EDTA degradation. The initial pH of 3.0 seems to be a suitable pH for degradation of the complex Pb-EDTA.

When the photooxidation of Zn-EDTA and Cd-EDTA was studied using the same conditions as Pb-EDTA, the quantum yields obtained of Zn-EDTA and Cd-EDTA are 0.21 and 0.22 respectively. It seems that the nature of metal is also the important factor affecting the photooxidation. Pb-EDTA can be degraded by photooxidation better than Zn-EDTA and Cd-EDTA. Moreover, unlike zinc and cadmium, lead can be simultaneously removed during photooxidation process.

CHAPTER IV

CONCLUSION AND FUTURE WORKS

In the present study, we have found that lead-EDTA complex (Pb-EDTA) can be destroyed by H_2O_2/UV process. Pb-EDTA and total lead concentration have been reduced within 20 min of irradiation time. The Pb-EDTA degradation depends on the hydrogen peroxide concentration, Pb-EDTA to H_2O_2 molar ratio and initial pH of solution. The optimum condition for the degradation was Pb-EDTA to H_2O_2 molar ratio as 1:20 and initial pH of solution 3.0. After the degradation of complex, ethylenediamintetraacetic acid (EDTA) can be degraded to nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), nitrate and oxalate.

Furthermore, the effect of nitrate was investigated as a scavenger. It was found that the low concentration of nitrate (0.004 M) has not effected to Pb-EDTA degradation. At high concentration (0.04 M), it has a remarkable effect on the degradation. We found that Pb-EDTA concentration was small reduced and total lead concentration did not disappear within 20 min of irradiation time in the presence of 0.04 M nitrate. The quantum yield of Pb-EDTA ($\Phi_{Pb\text{-}EDTA}$) was about 0.30.

In addition, we have studied the degradation of other metal complex as zinc-EDTA (Zn-EDTA) and cadmium-EDTA (Cd-EDTA). The condition used was the same as the optimum condition for Pb-EDTA degradation. The results show that Zn-EDTA and Cd-EDTA complex can be degraded within 20 min. But total zinc and cadmium concentration in solution did not change. The by-products such as NTA and IDA were also observed.

Potential applications and suggestion for future work

The photooxidation in the presence of hydrogen peroxide seems to be an effective alternative way for simultaneous Pb-EDTA degradation and lead removal. Nevertheless, more studies will need to be done. The limit of application was the characteristic of wastewater. If wastewater is muddy or contaminated with organic substrates, the efficiency of process will be decreased. The radiation could be scattered by the colloid in water and little reacted with desired substrates. The organic substrates can also absorb UV radiation as well as hydrogen peroxide so the efficiency of the photooxidation of desired substrate will be decreased. So we should study the characteristic of water before apply to real wastewater treatment.

Furthermore, the by-products in the form of free metal ions in the solution should be identified after irradiation. CE or ion selective electrode can be used for this purpose. The by-products have to be investigated in order to know the toxicity of the treated water, the form of metal in solution and the method of further treatment.

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