การย่อยสลาย 2,-6 ไดเมทิลเอนิลิน และ เอนิลิน โดยเทคโนโลยีเฟนตัน

นางสาวนลินรัตน์ มาสมบูรณ์

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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ปีการศึกษา 2551

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

DEGRADATION OF 2,6-DIMETHYLANILINE AND ANILINE BY FENTON TECHNOLOGIES

Miss Nalinrut Masomboon

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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นลินรัตน์ มาสมบูรณ์ : การย่อยสลาย 2,6 -ไดเมทิลเอนิลิน และ เอนิลิน โดยเทคโนโลยีเฟนตัน.
(DEGRADATION OF 2,6-DIMETHYLANILINE AND ANILINE BY FENTON TECHNOLOGIES)
อ. ที่ปรึกษา : รศ.ดร.ชวลิต รัตนธรรมสกุล, อ.ที่ปรึกษาร่วม: PROF. MING-CHUN LU, Ph.D. 257 หน้า.

สารประกอบในกลุ่มอะโรมาติกเอมีน เช่น 2,6-ไดเมทิลเอนิลิน และเอนิลิน เป็นสารที่ใช้อย่างแพร่หลายในอุตสาหกรรมสี ยาง ยาฆ่าแมลง และยา ซึ่งสารทั้งสองชนิดมี ความเป็นพิษและเป็นสารก่อมะเร็งอีกด้วย ดังนั้นน้ำเสียจากโรงงานอุตสาหกรรมที่มีการปนเปื้อนสารเหล่านี้จึงมีความจำเป็นที่จะต้องถูกบำบัดก่อนปล่อยทิ้งสู่แหล่งธรรมชาติ งานวิจัยนี้จึงมุ่งเน้นเพื่อศึกษาการย่อยสลาย 2,6-ไดเมทิลเอนิลิน และเอนิลิน โดยใช้กระบวนเฟนตัน ซึ่งเป็นกระบวนการที่สามารถย่อยสลายสารมีพิษและสารอินทรีย์ได้ดีและรวดเร็ว ซึ่งกระบวนการเฟนตันที่ใช้ในการศึกษาครั้งนี้มี 3 กระบวนการ ได้แก่ กระบวนการเฟนตัน กระบวนการอิเลคโตรเฟนตัน ซึ่งใช้ ไทเทเนียมฉาบด้วย IrO_2/RuO_2 เป็นแอโนด และเหล็กกล้าไร้สนิมเป็น แคโทด และกระบวนการโฟโตอิเลคโตรเฟนตัน ซึ่งใช้หลอดรังสียูวีเอเป็นแหล่งให้กำเนิดพลังงานแสง นอกจากนี้ยังศึกษาถึงตัวแปรที่มีผลต่อการย่อยสลายสาร2,6-ไดเมทิลเอนิลิน และเอนิลิน คือ ค่าพีเอชเริ่มต้น ความเข้มข้นเฟอรัสเริ่มต้น ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์เริ่มต้น ปริมาณกระแสไฟฟ้า และการให้แสงของหลอดยูวีเอ ผลการศึกษาพบว่ากระบวนการโฟโตอิเลคโตรเฟนตันมีประสิทธิภาพในการย่อยสลายสูงสุดเมื่อเปรียบเทียบกับกระบวนการเฟนตันและอิเลคโตรเฟนตัน โดยสามารถลด2,6-ไดเมทิลเอนิลินได้ 100% และลดซีโอดีได้ 48% ที่สภาวะค่าพีเอชเริ่มต้นที่ 3 ความเข้มข้นของเฟอรัสเริ่มต้น 1 มิลิโมลาร์ ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์เริ่มต้น 20 มิลิโมลาร์ กระแสไฟฟ้าที่ใช้ 2 แอมแปร์ และ การให้แสงของหลอดยูวีเอ 4 หลอด ในเวลา 1 ชั่วโมง และสามารถลดเอนิลินได้ 100%และซีโอดี 84%ที่สภาวะค่าพีเอชเริ่มต้นที่ 2 ความเข้มข้นของเฟอรัสเริ่มต้น 0.25 มิลิโมลาร์ ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์เริ่มต้น 10 มิลิโมลาร์ กระแสไฟฟ้าที่ใช้ 2 แอมแปร์ และ การให้แสงของหลอดยูวีเอ 4 หลอด ในเวลา 40 นาที เมื่อศึกษาจลนพลศาสตร์ของกระบวนการเฟนตันในการย่อยสลาย 2,6-ไดเมทิลเอนิลิน และเอนิลิน พบว่าสารทั้งสองชนิดเกิดปฏิกิริยาออกซิเดชันอันดับที่สองในทุกกระบวนการ ซึ่งกระบวนการโฟโตอิเลคโตรเฟนตันให้ค่าอัตราการย่อยสลายเริ่มต้นในการย่อยสลาย 2,6-ไดเมทิลเอนิลิน และเอนิลิน สูงสุดคือ 0.0584 และ0.0739 มิลิโมลาร์/นาที ตามลำดับ โดยค่าคงที่ของปฏิกิริยาการย่อยสลายสารเอนิลิน ทั้งจากกระบวนการเฟนตัน อิเลคโตรเฟนตัน และโฟโตอิเลคโตรเฟนตัน สูงกว่าค่าคงที่ของปฏิกิริยาการย่อยสลายของ2,6-ไดเมทิลเอนิลิน นอกจากนี้เส้นทางการย่อยสลายของ2,6-ไดเมทิลเอนิลิน และ เอนิลิน ได้มีการเสนอขึ้นในการศึกษานี้ด้วย

สาขาวิชา วิทยาศาสตร์สิ่งแวดล้อม
ปีการศึกษา 2551

ลายมือชื่อนิสิต......Nalinrat Masomboon......
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สถาบันวิทยบริการ
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NALINRUT MASOMBOON: DEGRADATION OF 2,6-DIMETHYLANILINE AND ANILINE BY FENTON TECHNOLOGIES. THESIS ADVISOR: ASSOC. PROF. CHAVALIT RATANATAMSKUL, Ph.D. THESIS COADVISOR: PROF. MING-CHUN LU, Ph.D. 257 pp.

Chemical compounds with aromatic amine group such as 2,6-dimethylaniline and aniline are widely used in dyestuff, rubber, pesticide and pharmaceutical industries. Both are considered toxic and carcinogenic, and therefore, the industry wastewater that are contaminated with these chemicals need to be treated prior to discharge into the environment. This research aimed to study the degradation of 2,6-dimethylaniline and aniline by Fenton technologies which are the processes that have the potential to rapidly degrade toxic and organic compounds. The Fenton processes applied were: (1) Fenton process; (2) electro-Fenton process using IrO_2/RuO_2 coated titanium metal as anode and stainless steel cathode; and (3) photoelectro-Fenton process using UVA as light source. The effects of parameters such as initial pH, initial ferrous ion concentration, initial hydrogen peroxide concentration, electricity application and UVA lamps irradiation were also determined in this study. Results showed that the photoelectro-Fenton process had the highest degradation efficiency compared to Fenton and electro-Fenton processes. In the photoelectro-Fenton process, 100% removal of 2,6-dimethylaniline and 48% COD removal were achieved in 1 hour (initial pH = 3, initial Fe^{2+} concentration = 1 mM, initial H_2O_2 concentration = 1 mM, electric current = 2 A and UVA, 4 lamps), and 100% removal of aniline and 84% COD removal were achieved in 40 minutes (initial pH = 2, initial Fe^{2+} concentration = 0.25 mM, initial H_2O_2 concentration = 10 mM, electric current 2 A and UVA, 4 lamps). The kinetics of 2,6-dimethylaniline and aniline degradation by Fenton processes were also determined. The oxidation reactions of both chemicals were found to follow the second-order reaction rate. The photoelectro-Fenton process provided highest value of initial degradation rate of 2,6-dimethylaniline and aniline which were determined to be 0.0584 mM/min and 0.0739 mM/min, respectively. The rate constants of aniline degradation by Fenton, electro-Fenton and photoelectro-Fenton processes were higher than the rate constants of 2,6-dimethylaniline degradation. The degradation pathways for 2,6-dimethylaniline and aniline were also proposed in this study.

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CHAPTER I

INTRODUCTION

1.1 Rational

Nowadays, the pollution of environment by toxic and non-biodegradable organic material of industrial or agriculture has brought about very serious health hazards for all living species in the world. The different kinds of chemical composition led to the development of special treatment methods for each of them. Some of the pollutants that need to be treated are aromatic compounds.

Aromatic compounds are widely used in many industries including explosives, pesticides and dyes production. 2,6-Dimethylaniline is used as a chemical intermediate in the manufacture of pesticides, dyestuffs, antioxidants, pharmaceuticals and other products. It is a metabolite of the xylidine group of anesthetics, including, for example, lidocaine, and is produced by the reduction of certain azo dyes by intestinal microflora. It may also enter the environment through degradation of certain pesticides. Aniline is a compound used as synthetic products, dyes and as a chemical intermediate for rubber processing, corrosion inhibitors, accelerators, resins, pesticides. For the industrial process, the mixture of 2,6-dimethylaniline and aniline would be discharged in the same water. Major industries releasing those two substances are chemical industries such as pesticide manufacture. The concentrations of both substances are varied in the wide range depending on type of industry. They are toxic to microorganisms; hence, resistant to oxidation by biological process. Therefore, the chemical oxidation process is needed (Bell et al., 2003)

Recently, the development in chemical water treatment has led to the progress and development of Advanced Oxidation Processes (AOPs). Advanced oxidation processes (AOPs) provide an effective mean of rapidly treating biorefractory compounds with efficient process control. Common processes involved in AOPs are Fenton's reagent, Ozone, Ozone/H_2O_2, and UV/H_2O_2 of which the primary intermediate is the hydroxyl radicals ($OH^{\bullet}$). Fenton's technology has been studied for the treatment of biorefractory organic contaminants in aqueous waste streams, soils, and groundwater. Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions, is an effective and simple oxidant for organic oxidation. It has been proven to be effective in treating various

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organic contaminants such as nitrophenol, dye, aromatic amines, polycyclic aromatic, ethers, and photographic wastewater (Korenaga et al., 1998, Ewa et al., 1991). The Fenton’s reagent as an oxidant for wastewater treatment is attractive due to the facts that iron is a highly abundant and non- toxic element and H_2O_2 is easy to handle and environmental benign making (Munter, 2001; Pinatello, 1992). In Fenton’s reaction, hydroxyl radical ($OH^{\bullet}$) is easily produced by iron (II) catalyst and hydrogen peroxide. The reaction is performed under acidic condition to keep the iron soluble and to enhance the oxidative character of the hydroxyl radicals. The process includes a neutralization step to allow the elimination of ferric ions by precipitation as hydroxide. Moreover, this process is easy to operate with low cost (Lu et al., 2003).

A modification of Fenton’s reagent by using goethite as the source of iron catalyst was found to effectively degrade organic pollutants under acidic condition (Teel et al., 2001; Lu, 2000; Kong et al., 1998; Lin and Gurol, 1996). Although the kinetics of mineral catalyzed hydrogen peroxide decomposition have been investigated(Lin and Gurol, 1996) , the mineral catalyzed modified Fenton’s reaction have not been clearly understood as compared to other modified or standard Fenton’s reactions for contaminant degradation. Such data may be important in selecting the most effective treatment configuration for a given system. However, the application of Fenton’s reagent in the destruction of organic has been limited by the slurry because ferric hydroxide sludge requires addition separation process and disposal or the production of substantial amount of sludge that requires further disposal. There are several new Fenton modifications, which can solve this problem. One of such alternatives is the development of new advanced electrochemical oxidation process (AEOP) which is so-call Electro-Fenton for the detoxification of organic wastewater without the slurry disadvantage (Brillas et al.,2001). This method is based on electrocatalytic generation of Fenton’s reagent to produce hydroxyl radical.

2,6-Dimethylaniline and aniline were chosen as target compounds. They are the organic compounds with benzene ring but having different functional groups and also been categorized as hazardous wastes. This research intended to investigate the efficiency of 2,6-dimethylaniline and aniline removal by Fenton processes including Fenton process, electro-Fenton process, photo-Fenton process and photoelectro-Fenton. The designed of novel reactor for photoassisted-Fenton was studied in this experiment. The proposed degradation partway and kinetic study of Fenton processes were also examined.

1.2 Objectives of Investigation

The main objectives of this study are:

1. To study the feasibility of using Fenton, electro-Fenton and photoelectro-Fenton processes on the removal of 2,6-dimethylaniline, aniline, COD and TOC in wastewater.
2. To determine the effects of initial concentration of 2,6-dimethylaniline, aniline, Fe^{2+} (ferrous) concentration, H_2O_2 (hydrogen peroxide) dosage, pH, electrical current and UV lights on the removal efficiency of Fenton, electro-Fenton and photoelectro-Fenton processes.
3. To determine the kinetic information of synthetic wastewater by varying the conditions including Fe^{2+} concentration, initial H_2O_2 dosage, initial 2,6-dimethylaniline and aniline concentration.
4. To determine the optimum condition of 2,6-dimethylaniline and aniline, COD and TOC removal for wastewater by varying the conditions including initial pH, Fe^{2+} concentration, H_2O_2 dosage, electric current and UV lights.
5. To compare the removal efficiency of 2,6-dimethylaniline and aniline by various Fenton processes.
6. To determine the mechanism degradation pathway of 2,6-dimethylaniline and aniline.

1.3 Hypotheses

1. 2,6-dimethylaniline and aniline could be removed by Fenton, electro-Fenton and photoelectro-Fenton processes.
2. Efficiency of Fenton process, electro-Fenton and photoelectro-Fenton processes on 2,6-dimethylaniline and aniline oxidation depends on initial pH, amount of H_2O_2 and Fe^{2+}, initial concentration of 2,6-dimethylaniline, electric current application and UV lights.

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1.4 Scope of Investigation

1. Using lab scale reactor of 5 liters.
2. Using synthetic wastewater with 2,6-dimethylaniline and aniline
3. Working at room temperature.
4. Operating in batch mode.
5. Working at laboratory of Chia Nan University of Pharmacy and Science, Tainan, Taiwan

CHAPTER II
THEORIES AND LITERATURE REVIEWS

2.1 2,6-Dimethylaniline and Aniline

2.1.1 Properties of 2,6-Dimethylaniline (2,6-Xylidine)

2.1.1.1 General Information

2,6-Dimethylaniline (2,6-Xylidine) is used as a chemical intermediate in the manufacture of pesticides, dyestuffs, antioxidants, pharmaceuticals and other products. 2,6-Dimethylaniline has many synonym such as 2,6-xylidine, 2,6-dimethylbenzeneamine, 2,6-xylyamine, 2-amino-1,3-xylene and 2-amino-1,3-dimethylbenzene. Xylidine is the trivial name of dimethylaniline, $(CH_3)_2C_6H_3NH_2$. There are six structural isomers (Table 2.1). The names of six compounds indicate methyl group positions relative to the amino on the benzene ring. They can be obtained from coal tar as by-products in the fractional distillation or can be prepared by heating aniline hydrochloride with methanol at 220 °C. Xylidine is an aniline homologue and has similar properties to aromatic amines. Xylidines are brown liquids at room temperature except 3,4-Xylidine. They are sparingly soluble in water but miscible with ethanol and diethyl ether. They are sensitive to air and light and tend to darken on storage. They are toxic if inhaled, ingested, or absorbed through the skin. Xylidines and derivatives are widely used as raw materials to produce imaging chemicals like pigments and dyestuffs. All of these compounds are also used in the production of antioxidants, agricultural, pharmaceutical, rubber chemicals and other target organic molecules.

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Table 2.1 Dimethylaniline isomers and their properties (Schuchardt, 2000)

Dimethylaniline	Melting point (°C)	Boiling point (°C)
2,3-Dimethylaniline	2.5	222
2,4-Dimethylaniline	16	218
2,5-Dimethylaniline	11.5	218
2,6-Dimethylaniline	8.4	214
3,4-Dimethylaniline	51	226
3,5-Dimethylaniline	9.8	220-221

2.1.1.2 Physical and Chemical Properties

Aromatic amines are much weaker bases than the aliphatics. One of the most important aromatic amines is aniline, a primary aromatic amine replacing one hydrogen atom of a benzene molecule with an amino group.

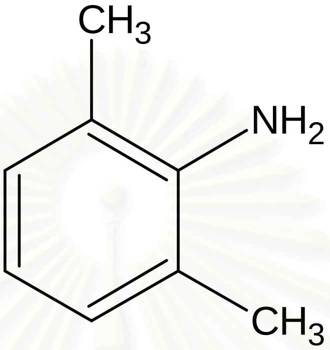

Figure 2.1. Structure of 2,6-dimethylaniline

The physical state and appearance of 2,6-dimethylaniline is in liquid form. It is a pale brown liquid at room temperature; boiling at 216 °C, melting at 11.2 °C; slightly soluble in water and freely soluble in ether and alcohol. 2,6-Dimethylaniline is easily soluble in diethyl ether and it is very slightly soluble in cold water. It causes serious industrial poisoning. The substance may have effects on the blood, resulting in formation of methaemoglobin. Repeated or prolonged exposures may be carcinogenic. Commercial aniline is obtained from nitrobenzene which is prepared from benzene with nitric acid by electrophilic substitution reaction or from chlorobenzene by heating with ammonia in the presence of copper catalyst. It is also obtained as a by-product of coal tar. In commerce the term of aniline oil blue refers to the pure one while aniline oil red indicates a mixture of aniline and toluidines with equimolecular weights. Its physical and chemical properties are shown in Table 2.2.

Table 2.2 Physical and chemical properties of 2,6-dimethylaniline (Schuchardt, 2000)

Properties	
Molecular formula	$(CH_3)_2C_6H_3NH_2$ / $C_8H_{11}N$
Structural formula	As shown in Figure 2.1
Molecular weight	121.18 g/mol
Appearance	Yellow liquid, with characteristic odor and turn brown on exposure to air
Vapor pressure, kPa at 20°C	< 0.1 kPa
Boling point	216 °C
Melting point	11.2 °C
Water Solubility	34 g/L @ 20°C ; 35 g/L @ 25°C
Specific Gravity	0.9842 @ 20°C
Ignition Temperature	520 °C
Flash point(closed cup)	96 °C

2.1.1.3 Toxicology

2,6-Dimethylaniline is a metabolite of the xylidine group of anaesthetics, including, for example, lidocaine, and is produced by the reduction of certain azo dyes by intestinal microflora. It may also enter the environment through degradation of certain pesticides. **Short et al. (1989)** studies the in vivo oxidative metabolism of 2,4- and 2,6-DMA in dogs and rats. From this study, it showed that 2,6-DMA produces hepatic cholangiofibrosis, bile duct proliferation and foci of cellular hyperplasia in rats. The same compound is relatively innocuous in dogs. However, 2,6-Dimethylaniline does not produce hepatic lesions in rat, except at high doses but it is a potent inducer of fatty degeneration in dogs. The result from this study also found that the major urinary metabolite of 2,6-DMA in rats was N-acetyl-4-amino-3-methylbenzoic acid (AAMBA), while in dogs was 6-hydroxy-2,4-dimethylaniline (6HDMA). 2,6-Dimethylaniline was tested for carcinogenicity in one study in rats by pre- and postnatal administration in the diet. It induced adenomas and carcinomas as well as several sarcomas in the nasal cavity.

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It also produced subcutaneous fibromas and fibrosarcomas in both males and females and increased the incidence of neoplastic nodules in the livers of female rats. Methaemoglobinaemia has been observed in humans and animals exposed to 2,6-dimethylaniline. The metabolism of 2,6-dimethylaniline in humans and rats appears to be similar and gives rise to a characteristic haemoglobin adduct in both species.

Kornreich and Montgomery, Jr. (1990) also reported the toxicology and carcinogenic of 2,6-DMA in Charles River CD rats. Under the conditions of 2-year feed studies, it was clearly shown in their study that 2,6-dimethylaniline is a carcinogen for both male and female Charles River CD rats and causes a significant increase in the incidences of adenomas and carcinomas of the nasal cavity. A rare tumor of the nasal cavity or rhabdamyosarcoma was observed in dosed rats of each sex and the increased incidences of subcutaneous fibromas and fibrosarcomas in male and female rats have been related to the administration of 2,6-dimethylaniline.

2,6-Dimethylaniline gave conflicting results for gene mutation in bacteria. Sister chromatid exchange and chromosomal aberrations were induced in cultured mammalian cells. The compound bound covalently to DNA in rat tissues but did not induce micronuclei in the bone marrow of mice treated in vivo. Oral Animal Toxicology LD_{50} is 707 mg/kg (mouse). There is inadequate evidence in humans for the carcinogenicity of 2,6-dimethylaniline. There is sufficient evidence in experimental animals for the carcinogenicity of 2,6-dimethylaniline. So, 2,6-Dimethylaniline is a possible carcinogen to humans.

The vapor of 2,6-dimethylaniline is heavier than air. It decomposes on burning producing toxic and corrosive fumes, reacts violently with strong oxidants, reacts with hypochlorites forming explosive chloroamines and attacks plastic and rubber. This substance can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion. A harmful contamination of the air can be reached rather quickly on evaporation of this substance at 20°C. Effects of short-term exposure are irritation to the eyes, the skin and the respiratory tract. Exposure at high levels may result in the formation of methaemoglobin. The effects may be delayed. Medical observation is indicated that effects of long-term or repeated exposure may possibly induce cancer to humans. The substance may have effects on the blood, resulting in anaemia. The carcinogenic effect to human of this kind of chemical was classified as 2B (possible for human) by IARC.

2.1.1.4 **First Aid Measures** (Environmental Health & Safety)

The first aid measures are shown in Table 2.3.

Table 2.3 Symptom, Prevention and First aid measures of 2,6-dimethylaniline (Schuchardt, 2000)

Contact by	Symptoms	Prevention	How to first aid
Inhalation	Blue lips or finger nails. Dizziness. Headache. Nausea. Confusion.	Ventilation, local exhaust, or breathing protection	Fresh air, rest. Artificial respiration may be needed. Refer for medical attention.
Skin	May be absorbed. Redness. Pain. Blue lips or finger nails. Dizziness. Headache. Nausea. Confusion.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse and then wash skin with water and soap. Refer for medical attention.
Eye	Redness. Pain.	Safety goggles, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
Swallowing	Blue lips or finger nails. Dizziness. Headache. Nausea. Confusion.	Do not eat, drink, or smoke during work. Wash hands before eating.	Rinse mouth. Give a slurry of activated charcoal in water to drink. Rest. Refer for medical attention.

Since, 2,6-dimethylaniline is used as a chemical intermediate in the manufacture of pesticides, dyestuffs, antioxidants, pharmaceuticals and other products. It is also a metabolite of the xylidine group of anaesthetics, including, for example, lidocaine, and is produced by the reduction of certain azo dyes by intestinal microflora. It may also enter the environment through degradation of certain pesticides.

2.1.2 Properties of Aniline

2.1.2.1 General Information

Aniline, phenylamine or aminobenzene is an organic chemical compound which is a primary aromatic amine consisting of a benzene ring and an amino group. Aniline is a colorless to brown oily liquid which an aromatic. It is miscible with all conventional organic solvents and is sparingly soluble in water. The formula of aniline is C_6H_7N and the molecular structure is shown in figure 2.2. It used to make a wide variety of products such as polyurethane foam, specialty resin, agricultural chemicals, synthetic dyes, antioxidants, stabilizers for the rubber industry, paper chemistry, varnishes, and explosives.

Aniline in water can adsorb onto sediment and particle matter. Aniline will partially sorb to the soil, most of it will be broken down by bacteria and other microorganisms. Small amounts may evaporate into the air or pass through the soil into groundwater. Aniline does not typically accumulate in the food chain.

2.1.2.2 Physical and Chemical Properties

Aniline is prepared commercially by the reduction of nitrobenzene, a product of coal tar, or by heating chlorobenzene with ammonia in the presence of a copper catalyst. Sulfonation of aniline yields sulfanilic acid, the parent compound of the sulfa drugs. Aniline is also important in the manufacture of rubber-processing chemicals and antioxidants. Its physical and chemical properties are shown in Table 2.4.

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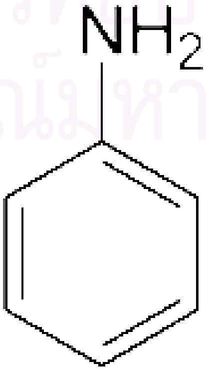

Figure 2.2 Structure of aniline

2.1.2.3 Toxicology

Aniline can be toxic with organism because aniline damages hemoglobin, a protein that normally transports oxygen in the blood. The damaged hemoglobin can not carry oxygen. This condition is known as methemoglobinemia and its severity depends on exposure level and time. Methemoglobinemia is the most prominent symptom of acute aniline poisoning in humans, results in cyanosis (a purplish blue skin color). Dizziness, headaches, irregular heart beat, convulsions, coma, and death may also occur. Direct contact with aniline can also produce skin and eye irritation. Long-term exposure to lower levels of aniline may cause symptom similar to those experienced in acute high-level exposure. There is no reliable information on whether aniline has adverse reproductive effects in humans. Studies in animals have not demonstrated reproductive toxicity for aniline.

Table 2.4 Physical and chemical properties of aniline (Schuchardt, 2000)

Properties	
Molecular formula	C_6H_7N
Molecular weight	93.13 g/mol
Appearance	a colorless to brown oily liquid
Vapor Density(Air=1)	3.22
Boling point	184.4 @ 20°C
Melting point	6.25°C
Water Solubility	34 g/L @ 20°C ; 35 g/L @ 25°C
Specific Gravity	1.02173 @ 20°C / 4°C
Vapor pressure	0.3 mm Hg @ 20 °C
K_{oc}	3870@ pH 6.5 (measured)
Log K_{ow}	0.90
Viscosity	2.17×10^{-2} mPa.s @ 15°C
Density @ 20°C	1.022 g/cm^3
Ignition Temperature	615 °C
Flash point(closed cup)	76°C
Thermal Decomposition 20°C	190

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2.1.2.4 First Aid Measures (Environmental Health & Safety)

Aniline is a chemical substance that is toxic when ingested or in contact with an organism. The first aid measures are shown in Table 2.5. Aniline has an almost unlimited shelf life when properly stored in a protected storage area. Upon prolonged storage, aniline assumes a yellow to reddish brown coloration.

Table 2.5 First aid measures of aniline (Schuchardt, 2000)

Contact by	How to first aid
Inhalation	Ventilate. Apply mouth-to-mouth resuscitation or mechanical ventilation if necessary. Summon doctor.
Skin	Wash off with plenty of water. Dab with polyethylene glycol 400. Immediately remove contaminated clothing.
Eye	Rinse out with plenty of water for at least 10 minutes with the eyelid held wide open. Immediately summon eye specialist.
Ingestion	Make victim drink plenty of water, induce vomiting. Immediately summon doctor.

2.1.2.5 Aniline removal process

There are many methods to remove this chemical. Such as TiO_2 photocatalysis, ozonation, Fenton’s processes. **Piccinini et al. (1997)** investigated on the TiO_2 photocatalytic mineralization of nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline and 4-nitrosophenol in aerated condition. Under slightly acidic condition, all these compounds was converted to carbon dioxide, whereas the nitrogen was converted to nitrate and ammonium ions. The temporal evolution of the NO^-_3/NH^+_4 concentration ratio, besides other experimental conditions (pH, photon flux, reactant concentrations), depends largely on both the initial oxidation state of the nitrobenzene and the nature of the starting organic substrate.

The aniline degradation in acidic medium at pH 3 under photocatalytic and electrochemical conditions were studied by **Brillas et al. (1998).** Benzoquinone, nitrobenzene, phenol, hydroquinone and also 1,2,4- benenetriol were detected as an intermediates by HPLC in electrochemical and photocatalytic experiments. **Sanchez et al. (1998)** attempted to decompose aniline by combined photocatalysis and ozonation. The experimental results showed that the ozonation pretreatment followed by photocatalysis strongly increased the yield of TOC removal in comparison to either ozonation or photocatalysis conducted separatedly. A mechanism involving the formation of an ozonation anion radical before to the generation of hydroxyl radicals implied the synergic effect between ozone and TiO_2 under illumination.

Another study from **Utset et al. (2000)** conducted a research on the consumption of oxygen during the degradation of aniline by Fenton and photo-Fenton reaction. This study examined the effects of aniline, Fe^{2+} and H_2O_2 initial concentration, pH, temperature, and O_2 flow rate on the ratio O_2 consumed H_2O_2. The experiment results indicated that this replacement took place in a variable extent, but the presence of H_2O_2 was necessary along the reaction. **Sarasa et al. (2002)** treated aqueous solution of aniline and p-chloroaniline with ozone in order to investigate the reaction and oxidation by-product. The main examined aromatic by-products were nitrobenzene and azobenzene when the experiment was performed at acidic pH. All the aromatic by-products found were less toxic than the raw materials.

Moreover, **Widera et al. (2002)** determined electrochemical oxidation of aniline in a silica sol-gel matrix. An acid catalyzed process that used tetramethyl orthosilicate as the precursor. When the aging time is limited to one day so that a mesoporous solid was obtained, the potentiodynamic oxidation of aniline at carbon fiber electrode results in the formation of polyaniline. The results supported the hypothesis that the pore structure of sol-gel electrolytes can influence the pathways of electrode reactions.

Aniline can also be degraded by Ultrasonic/Ozone (US/O_3). The aniline removal was 82% and TOC reduction was 20% when using the energy density of ultrasound at 0.1 W/ml and the flow rate of ozone at 2 mg/min after 5 minutes of reaction **(Song et al., 2007).**

2.1.3 Thailand’s Effluent Standard

Thailand effluent standard for industrial and industrial estate is shown in Table 2.6 and Table 2.7. The information is from INDUSTRIAL ESTATE AUTHORITY OF THAILAND STRATEGY FOR ENVIRONMENTAL COMPLIANCE, Environmental and Safety Control Division, Industrial Estate Authority of Thailand.

Table 2.6 Effluent Standard for Industrial and Industrial Estate Sources (Notification of Ministry of Science, Technology and Environment No. 3 (B.E. 2539))

Parameter	**Acceptable value**
pH	5.5 - 9.0
TDS	3,000 - 5,000 mg/l
SS	50 - 150 mg/l *
Temperature	40 °C
Color or Odor	unobjectionable
Sulfide (H_2S)	1.0 mg/l
Cyanide (HCN)	0.2 mg/l
Heavy Metal	
1. Zn	5.0 mg/l
2. Cr^{6+}	0.25 mg/l
3. Cr^{3+}	0.75 mg/l
4. As	0.25 mg/l
5. Cu	2.0 mg/l
6. Hg	0.005 mg/l
7. Cd	0.03 mg/l
8. Ba	1.0 mg/l
9. Se	0.02 mg/l
10. Pb	0.2 mg/l
11. Ni	1.0 mg/l
12. Mn	5.0 mg/l
9. Fat, Oil & Grease	5 – 15 mg/l *
10. Formaldehyde	1.0 mg/l
11. Phenols	1.0 mg/l
12. Free Chlorine	1.0 mg/l
14. BOD	20 – 60 mg/l *
15. TKN	100 - 200 mg/l *
16. COD	120 – 400 mg/l *

Table 2.7 Industrial Effluent Standards (Notification of Ministry of Industry NO. 2 (1996)

Parameter	**Acceptable concentration**
pH	5.5 - 9.0
TDS	1. Discharged into fresh waters 3,000 - 5,000 mg/l, depend on effluent volume, receiving waters or types of industries 2. Discharged into receiving waters Less than TDS of receiving waters with salinity > 2,000 mg/l 5,000 mg/l
SS	50 - 150 mg/l *
Temperature	40 °C
Color or Odor	unobjectionable
Sulfide (H_2S)	1.0 mg/l
Cyanide (HCN)	0.2 mg/l
Heavy Metal	
1. Zn	5.0 mg/l
2. Cr $^{6+}$	0.25 mg/l
3. Cr $^{3+}$	0.75 mg/l
4. As	0.25 mg/l
5. Cu	2.0 mg/l
6. Hg	0.005 mg/l
7. Cd	0.03 mg/l
8. Ba	1.0 mg/l
9. Se	0.02 mg/l
10. Pb	0.2 mg/l
11. Ni	1.0 mg/l
12. Mn	5.0 mg/l
9. Fat, Oil & Grease	5 – 15 mg/l *
10. Formaldehyde	1.0 mg/l
11. Phenols	1.0 mg/l
12. Free Chlorine	1.0 mg/l
14. BOD	20 – 60 mg/l *
15. TKN	100 - 200 mg/l *
16. COD	120 – 400 mg/l *

Remarks * The standard depends on the condition of receiving waters and type of industries, under consideration of the Pollution Control Committee

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2.2 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) have been viewed with great interest as a promising method for the removal of organic contaminants from water. AOPs rely on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radical ($OH^{\bullet}$). The hydroxyl radical is a powerful oxidant and a short-lived, highly reactive, and non-selective reagent that is easy to produce. The generation of $OH^{\bullet}$ in sufficient quantities can carry out the destruction of toxic pollutants(Glaze et al.,1987). AOPs, with the generation of a powerful hydroxyl radical, provide an effective mean of rapidly treating biorefractory compounds with efficient process control. The reaction rate constants of $OH^{\bullet}$ are shown in Table 2.8. The hydroxyl radical can be produced in a homogeneous system by two ways (Munter, 2001).

Table 2.8 Reaction rate constants (k, $M^{-1}s^{-1}$) of hydroxyl radical (Richard, 1998)

Compound	**Reaction rate constant of $OH^{\bullet}$**
Monocyclic Aromatic Hydrocarbon	
- Benzene	7.8×10^{9}
- Ethylbenzene	7.5×10^{9}
- Toluene	3.0×10^{9}
Chloronated Solvents	
- Trichloroethylene (TCE)	4.0×10^{8}
- Vinyl Chloride	1.2×10^{10}
Insecticides	
- Aldicarb	8.1×10^{9}
- Carbofuran	6.0×10^{8}
- Endrin	7.8×10^{8}
Herbicides	
- Atrazine	2.6×10^{9}
- Dalapon	7.3×10^{9}
Industrial Intermediates	
- Nitrobenzene	3.9×10^{9}
- Aniline	1.4×10^{10}
- Phenol	6.6×10^{9}
- Bromoform	1.3×10^{8}

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Several methods are available for generating $OH^{\bullet}$. These include both non-photochemical and photochemical methods.

Non-photochemical

The first is “non-photochemical”; this method is the well known method for generating hydroxyl radicals without using light energy. This method includes ozonation at elevated values of pH up to 8.5, combining ozone with hydrogen peroxide, combining ozone and catalyst, and Fenton system.

Photochemical

Conventional ozone or hydrogen peroxide oxidation of organic compounds does not completely oxidize organics to carbon dioxide (CO_2) and water (H_2O). In some reactions, certain oxidation products still remain in the solution. Completing the oxidation reaction, as well as oxidative destruction, can be achieved by supplementing the reaction with UV radiation, which is the “photochemical” path that can also generate the hydroxyl radical.

AOPs are being widely applied to treat contaminated groundwater, to purify and disinfect drinking waters and process waters, and to destroy refractory of organics in industrial wastewater.

2.3 Fenton Process

In 1894, Henry J. Fenton reported that hydrogen peroxide could be activated by ferrous salts to oxidize tartaric acid (Fenton, 1894). The Fenton process was invented in 1894 by its inventor Henry.J. Fenton, but its utility was not recognized until the 1960s once the mechanisms were identified. Hydrogen peroxide (H_2O_2) is typically used together with ferrous ion (Fe^{2+}) to form Fenton’s reaction. The rate constant for the reaction of ferrous ion (Fe^{2+}) with hydrogen peroxide (H_2O_2) is high and Fe^{2+} is oxidized to ferric ion (Fe^{3+}) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide.

For this reason, it is believed that most waste destruction catalyzed by Fenton’s reagent is simply a Fe(III)- H_2O_2 (Fenton-like reagent) system catalyzed destruction process. In 1934 Haber and Weiss (1934) proposed that the active oxidant generated by

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the Fenton reaction is the hydroxyl radical which is one of the most powerful oxidants known (E^0 = 2.73 V). Reaction rates with Fenton's reagent are generally limited by the rate of $OH^{\bullet}$ generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. Typical Fe: H_2O_2 ratios are 1:5-10 wt/wt, though iron levels less than 25-50 mg/l can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle. Fenton's reagent is most effective as a pretreatment tool where COD is greater than 500 mg/l. This is due to the loss in selectivity as pollutant concentrations decrease. The main advantage is the complete destruction of contaminants to harmless compounds, e.g.CO_2, water, and inorganic salts, under atmospheric pressure and room temperature. However, the limited range of pH (3-5) in which the reaction takes place and the recovery of iron species are the major drawbacks of this homogeneous process.

2.3.1 Hydrogen Peroxide

2.3.1.1 General Information

Hydrogen peroxide was discovered by Thenard, L.J. in 1818. Hydrogen peroxide is an ubiquitous compound present in natural water. Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about 60°C. One benefit of decomposition of hydrogen peroxide is that the released oxygen can stimulate aerobic biological activity. Hydrogen peroxide also decomposes in the presence of numerous catalysts, e.g., most metals, acids, bases, salts of metals, reducing agents, oxidizable organic materials, or flammable substances. Hydrogen peroxide is prepared commercially by oxidation of alkylhydro-anthraquinones or by electrolysis of ammonium bisulfate. It can also be prepared by reaction of barium peroxide with sulfuric acid or is prepared (with acetone) by oxidation of isopropanol.

Aqueous solution of hydrogen peroxide is mainly used of oxidation reactions, including bleaching process, chemical syntheses, and for water and wastewater treatment. In drinking water purification, hydrogen peroxide is used to pre-oxidize organic constituents and to eliminate iron and manganese ions.

Table 2.9 Physical and chemical properties of hydrogen peroxide **(Bishop, 1968)**

General	
Systematic name	Dihydrogen dioxide
Other names	Hydrogen dioxide , Dioxidane
Molecular formula	H_2O_2
Molar mass	34.0147 g·mol·$^{-1}$.
Appearance	Very pale blue color; colorless in solution
Properties	
Density and phase	1.4 g·cm^{-3}, liquid
Melting point	-11 °C (262.15 K)
Boiling point	150.2 °C (423.35 K)
Acidity (pK_a)	11.65
Viscosity	1.245 cP at 20 °C
Hazards	
Main hazards	Oxidant, corrosive
Flash point	Non-flammable

2.3.1.2 Physical and Chemical Properties

An aqueous solution of hydrogen peroxide is clear, colorless, water-like in appearance and nonflammable. It is miscible with cold water and is soluble in alcohol and ether. At high concentration, it has a slightly pungent or acidic odor. The chemical formula for hydrogen peroxide is H_2O_2 and its molecular weight is 34.015 g/mol. It is a weak acid. It has strong oxidizing properties and is therefore a powerful bleaching agent that is mostly used for bleaching paper, but has also found use as a disinfectant, as an oxidizer, and in rocketry (particularly in high concentrations as high-test peroxide (HTP) as a monopropellant), and in bipropellant systems. Hydrogen peroxide can decompose spontaneously into water and oxygen. It usually acts as an oxidizing agent, but there are many reactions where it acts as a reducing agent, releasing oxygen as a by-product. Hydrogen peroxide always decomposes exothermically into water and oxygen gas spontaneously: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

The rate of decomposition is dependent on the temperature and concentration of the peroxide, as well as the pH and the presence of impurities and stabilizers. Hydrogen peroxide is incompatible with many substances that catalyse its decomposition, including most of the transition metals and their compounds. Common catalysts include manganese dioxide, and silver. The same reaction is catalysed by the enzyme catalase, found in the liver, whose main function in the body is the removal of toxic byproducts of metabolism and the reduction of oxidative stress. The decomposition occurs more rapidly in alkali, so acid is often added as a stabilizer.

2.3.1.3 Toxicology

According to the US regulation, no concentration of H_2O_2 is listed as the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) regulated substances (i.e., a persistent environmental hazard) nor is the standard industrial strength hydrogen peroxide (those < 52% wt.%) covered under the Federal Risk Management guidelines. However, a hazardous material permit – termed a Hazardous Materials Inventory Statement (HMIS)–may be required by local response aqencies, depending on the concentration, volume, and location of hydrogen peroxide stored. If released to the environment, hydrogen peroxide will decompose to oxygen and water with concurrent generation of heat.

Spilling high concentration peroxide on a flammable substance can cause an immediate fire, which is further fueled by the oxygen released of the decomposing hydrogen peroxide. Hydrogen peroxide, if spilled on clothing (or other flammable materials), will preferentially evaporate water until the concentration reaches sufficient strength, then clothing will spontaneously ignite. Leather generally contains metal ions from the tanning process and will often catch fire almost immediately.

Concentrated hydrogen peroxide (>50%) is corrosive, and even domestic-strength solutions can cause irritation to the eyes, mucous membranes and skin. Swallowing hydrogen peroxide solutions is particularly dangerous, as decomposition in the stomach releases large quantities of gas (10 times the volume of a 3% solution) leading to internal bleeding. Inhaling over 10% can cause severe pulmonary irritation.

Low concentrations of hydrogen peroxide, on the order of 3% or less, will chemically stain any clothing it comes into contact with a pinkish hue. Extreme care should be exercised when using common products that may contain hydrogen peroxide, such as facial cleaner or contact lens solution, which easily splatter upon other surfaces.

Since it was first commercialized in the 1800's, H_2O_2 production has now grown to over a billion pounds per year (as 100%). In addition to pollution control, H_2O_2 is used to bleach textiles and paper products, and to manufacture or process food, minerals, petrochemicals, and consumer products (detergents). Its use for pollution control parallels those of the movement itself, municipal wastewater applications in the 1970's, industrial waste/wastewater applications in the 1980's, and more recently, air applications in the 1990's. Today, H_2O_2 is readily available throughout the U.S. in drum, tote, mini-bulk, and bulk quantities in concentrations of 35% or 50% by weight.

2.3.1.4 Environmental Applications of H_2O_2 (Bishop,1968)

H_2O_2 applications span the range of possible media including air, water, wastewater, soils, and sludge. Depending on the objective, H_2O_2 may be used either alone or in combination with other chemicals to enhance their performance.

- Odor control: H_2O_2 can be applied directly to aqueous waste containing these odorants, or to wet scrubbers used to remove them from airstreams. If the odors are the result of biological activity, H_2O_2 may instead be added as a preventative to eliminate the anoxic conditions which favor the generation of odors.
- Corrosion control: H_2O_2 destroys residual chlorine and reduces sulfur compounds thiosulfates, sulfites, and sulfides, which form corrosive acids when condensed onto processing equipment and oxidized by air.
- BOD/COD removal: H_2O_2 oxidizes both organic and inorganic pollutants which contribute to BOD and COD. H_2O_2 can also affect BOD/COD removal by enhancing the performance of the other process that can see enhancement (combination) applications.
- Toxicity reduction / Biodegradability improvement: H_2O_2 can react with catalysts, chemically digests complex organics into smaller, less toxic and more biodegradable fragment.
- Organic oxidation: H_2O_2 can hydrolyzes formaldehyde, carbon disulfide, carbohydrates, organophosphorus and nitrogen compounds and destroys virtually any other organic requiring treatment.

Table 2.10 Value of oxidation power, Relative oxidation power of the reactive species (modified from Carey, 1992 and US peroxide, 2001)

Reactive Species	Oxidation (Oxidant Potential Voltage)	Relative Oxidation Power (Cl_2=1.0)
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen (singlet)	-	1.78
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radical	-	1.25
Potassium permanganese	1.67	1.23
Chlorine dioxide	1.50	1.15
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00
Bromine	1.07	0.80
Iodine	0.54	0.54

2.3.1.5 Enhancement (Combination) Applications

The more difficult-to-oxidize pollutants may require the H_2O_2 to be activated with catalysts such as iron, copper, manganese, or other transition metal compounds. These catalysts may also be used to speed up H_2O_2 reactions that may otherwise take hours or days to complete.

Advanced Oxidation Processes present the newest development in H_2O_2 technology. Typically, this means combining H_2O_2 with ozone or ultraviolet light. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely applied to treat contaminated groundwaters, to purify and disinfect drinking waters and process waters, and to destroy trace organics in industrial effluents.

There are four typical chemical reactions of the hydroxyl radical in water which are:

- Addition: the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product such as a cyclohexadienyl radical as shown below.

$$OH^{\bullet} + C_6H_6 \rightarrow (OH)C_6H_6^{\bullet} \quad (1)$$

- Hydrogen Abstraction: an organic free radical and water are formed as shown below.

$$OH^{\bullet} + CH_3OH \rightarrow CH_2OH^{\bullet} + H_2O \quad (2)$$

- Electron Transfer: ions of a higher valence state, or an atom or free are formed radical if a mononegative ion is oxidized as shown below.

$$OH^{\bullet} + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^{-} \quad (3)$$

- Radical Interaction: the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product as shown below.

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (4)$$

2.3.2 Hydroxyl Radical

The hydroxyl radical is an extremely reactive, short lived, and an unselective transient species. The mean lifetime of $OH^{\bullet}$ radicals depends on their chemical environment and was estimated to be in the order of 10 μs in the presence of dissolved natural organic matters, bicarbonate and carbonate (Hoigne,1998). The half-life of hydroxyl radicals in the presence of linoleate ($C_{18}H_{31}O_2^{-}$), the conjugate base of linoleic acid, at 37ºC is in the order of nano seconds.

The hydroxyl radical is one of the most reactive free radical and one of strongest oxidants. It has a very high oxidizing capacity equal to 2.8 V. (Prengle et al., 1978; Masten and Divies, 1994). It attacks on organic compounds are relatively non-selective with its rate constants ranging from 10^{6} - 10^{10} $M^{-1}.s^{-1}$ (Buxton et al., 1998). The hydroxyl radical is the second strongest oxidant that is only inferior to fluoride as shown in Table 2.11.

Table 2.11 Oxidation-Reduction Potentials of Chemical Reagents for Water and Wastewater Treatment (Lide, 1992)

Reaction	Potential in Volts (E^0) at 25 ^oC
$F_2 + 2e^- = 2F^-$	2.87
$HO^{\bullet} + H^+ + e^- = H_2O$	2.33
$FeO_4^{2-} + 8H^+ + 3e^- = Fe^{3+} + 4H_2O$	2.20
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^- = 2H_2O_2$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e^- = MnO^2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e^- = Cl^- + 2H_2O$	1.57
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.49
$HOCl + H^+ + 2e^- = Cl^- + H_2O$	1.49
$Cl_2 + 2e^- = 2Cl^-$	1.36
$HOBr + H^+ + 2e^- = Cl^- + H_2O$	1.33
$O_3 + H_2O + 2e^- = O_2 + 2OH^-$	1.24
$O_2 + 4H^+ + 4e^- = 2H_2O$	1.23
ClO_2 (gas) $+ e^- = ClO_2^-$	1.15
$Br_2 + 2e^- = 2Br^-$	1.07
$HOI + H^+ + 2e^- = I^- + H_2O$	0.99
ClO_2(aq) $+ e^- = ClO_2^-$	0.95
$ClO^- + 2H_2O + 2e^- = Cl^- + 2OH^-$	0.90
$H_2O_2 + 2H_3O + 2e^- = 4H_2O$ (basic)	0.87
$ClO_2 + 2H_2O + 4e^- = Cl^- + 4OH^-$	0.78
$BrO^- + H_2O + 2e^- = Br + 4OH^-$	0.70
$I_2 + 2e^- = 2I^-$	0.54
$I_3 + 3e^- = 3I^-$	0.53
$IO^- + H_2O + 2e^- = I^- + 2OH^-$	0.49

Hydroxyl radicals can oxidize organic (RH) and inorganic substances through different types of reaction (equation 5 – 7) (Hoigne, 1998):

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Electron Transfer Reaction:

$OH^{\bullet} + M^{n} \rightarrow M^{n+1} + OH^{-}$ (5)

Hydrogen Abstraction:

$OH^{\bullet} + R\text{-}H \rightarrow R^{\bullet} + H_2O$ (6)

Electrophilic addition:

$OH^{\bullet} + R_2C{=}CR_2 \rightarrow {}^{\bullet}CR_2\text{-}C(OH)R_2$ (7)

The hydroxyl radical is capable of oxidizing organic compounds mostly by hydrogen abstraction as illustrated in equation 2.5. Electron transfer to hydroxyl radicals (equation 2.4) is of interest in the case where the hydrogen abstraction or electrophilic addition reaction may be unfavored by multiple halogen substitution or steric hindrance. Finally, electrophillic addition of hydroxyl radicals to organic structure is another possible mechanism of oxidative degradation as presented in equation 2.6.

Table 2.12 Rate constant of Fenton's reactions (Kang et al., 2002)

Reaction	**K (M^{-1} s^{-1})**
$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+}$	63
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$	0.01
$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$	2.7×10^{7}
$HO_2^{\bullet} \rightarrow OH^{\bullet-} + H^{+}$	1.58×10^{-5}
$O_2^{\bullet-} + H^{+} \rightarrow HO_2^{\bullet}$	1.0×10^{10}
$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-}$	3.2×10^{8}
$Fe^{2+} + OH^{\bullet}_2\ (+H^{+}) \rightarrow Fe^{3+} + H_2O_2$	1.2×10^{6}
$Fe^{3+} + OH^{\bullet}_2{}^{-} \rightarrow Fe^{2+} + O_2 + H^{+}$	3.1×10^{5}
$O_2^{\bullet-} + Fe^{2+}\ (+2H^{+}) \rightarrow Fe^{3+} + H_2O_2$	1.0×10^{7}
$O_2^{\bullet-} + Fe^{3+} \rightarrow Fe^{2+} + O_2$	5×10^{7}
$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$	4.2×10^{9}
$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	8.3×10^{5}
$OH^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2$	1×10^{10}
$OH^{\bullet} + O_2^{\bullet} \rightarrow HO^{-} + O_2$	1×10^{10}
$HO_2^{\bullet} + O_2^{\bullet-}\ (+H^{+}) \rightarrow H_2O_2 + O_2$	9.7×10^{7}

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Because the hydroxyl radical is a highly reactive transient that can rapidly oxidize most organic compounds. Many studies have focused on its role as an oxidant in the environment. The hydroxyl radical reacts rapidly with many organic substances in water and is a potential oxidant of refractory synthetic and natural organic compounds that are resistant to degradation by other processes in natural waters.

2.3.3 Fenton's Reaction

The hydroxyl radical, as the non-selective oxidant, can be produced from Fenton's reagent. In the Fenton process, H_2O_2 is decomposed by Fe^{2+} to produce highly reactive hydroxyl radical as expressed by equation 8 (Yin and Allen, 1999)

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^- + Fe^{3+} \qquad (8)$$

The hydroxyl radical can non-selectively attack the C-H bonds of organic molecules and is capable of degrading many solvents, haloalkanes, esters, aromatics, and pesticides (Haag and Yao, 1992). Huang, et al (1993) summarized the major advantages of using Fenton's process over other oxidation processes to treat hazardous wastes:

1) there are no chlorinated organic compounds formed during the oxidation process as in chlorination;
2) both iron and hydrogen peroxide are inexpensive and non-toxic;
3) there are no mass transfer limitations because the reaction is homogeneous;
4) no light is required as a catalyst and, therefore, the design is much simpler than ultraviolet light systems;
5) and hydrogen peroxide can be electrochemically generated in situ, which may further increase the economic feasibility and effectiveness of this process for treating contaminated sites.

Under acidic conditions and with an excess of ferrous ions, the hydroxyl radicals generated can further react with ferrous ion to produce ferric ion:

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \qquad (9)$$

By properly controlling experimental conditions, ferric ions can be regenerated back to ferrous ion a subsequent reaction with another molecule of hydrogen peroxide:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (10)$$

The $HO_2^{\bullet}$ radicals produced have been shown to also participate in oxidation of some organic compounds, although they are much less reactive than hydroxyl radicals. Based on equation 8, a low pH range of 2 to 4 is preferred to facilitate the generation of hydroxyl radicals, although the reaction is feasible up to neutral pH. Almost all organic compounds can be treated in situ by this technology. The contaminants of particular interest which include chlorinated solvents (e.g., BTEX) can be effectively removed by the Fenton process. All of these chemicals are very difficult to biodegrade or may take an exceedingly long time in other processes.

The inhibition of Fenton processes can be done by addition of (iron) chelants such as phosphates, EDTA, formaldehyde, and citric/oxalic acids. Because of the sensitivity of the Fenton system to different wastewaters, it is recommended that the reaction should always be characterized through laboratory treatability tests before proceeding to a plant scale.

2.3.4 Effect of Substances and Conditions in the Fenton Process

2.3.4.1 Effect of H_2O_2

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. For example, in a typical application, the following series of reaction will occur:

$$\text{Substrate} \rightarrow \underset{\text{Intermediate “A”}}{\text{Oxidized}} \rightarrow \underset{\text{Intermediate “B”}}{\text{Oxidized}} \rightarrow \underset{\text{Intermediate “C”}}{\text{Oxidized}} \rightarrow CO_2$$

Each transformation in this series has its own reaction rate and is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, where upon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

2.3.4.2 Effect of Iron Concentration

In the absence of iron, there is no evidence of hydroxyl radical formation when, for example, H_2O_2 is added to a phenolic wastewater (i.e., no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature

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(an optimal dose range for the iron catalyst) is a characteristic of Fenton’s reagent, although the definition of the range varies between wastewater.

Three factors typically influence its definition (Walling, 1975):

a. A minimal threshold concentration of 3-15 mg/l Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material.
b. A constant ratio of Fe: substrate above the minimal threshold, typically 1 part Fe per 10-50 parts substrate, which produces the desired end products. (Note that the ratio of Fe: substrate may affect the distribution of reaction products.
c. A supplemental aliquot of Fe which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.

Iron dose may also be expressed as a ratio to H_2O_2 dose. Typical ranges are 1 part Fe per 5-25 parts H_2O_2 (wt/wt)

2.3.4.3 Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction. The catalytic cycle begins quickly if H_2O_2 and organic materials are in abundance. However, if low doses of Fenton’s reagent are being used (e.g., < 10-25 mg/l H_2O_2), Bishop, 1968 suggests ferrous may be preferred (**Bishop et al. 1968).** Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application. It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron flocculate, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

2.3.4.4 Effect of pH

A low pH is important to keep ferric ion in solution. At a pH less than 3, Fe(III) is in solution; at a pH greater than 3 and less than 5, Fe(III) is out of solution in colloidal form; and above pH 5, Fe(III) precipitates as $Fe_2O_3.H_2O$ (Nesheiwat and Swanson, 2000).

The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. There have been some recent developments using non-radical scavenging sequestering agents (e.g., gallic acid) to extend the useful pH range to pH 8-9, but no commercial applications are known. The drop in efficiency on the acid is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates.

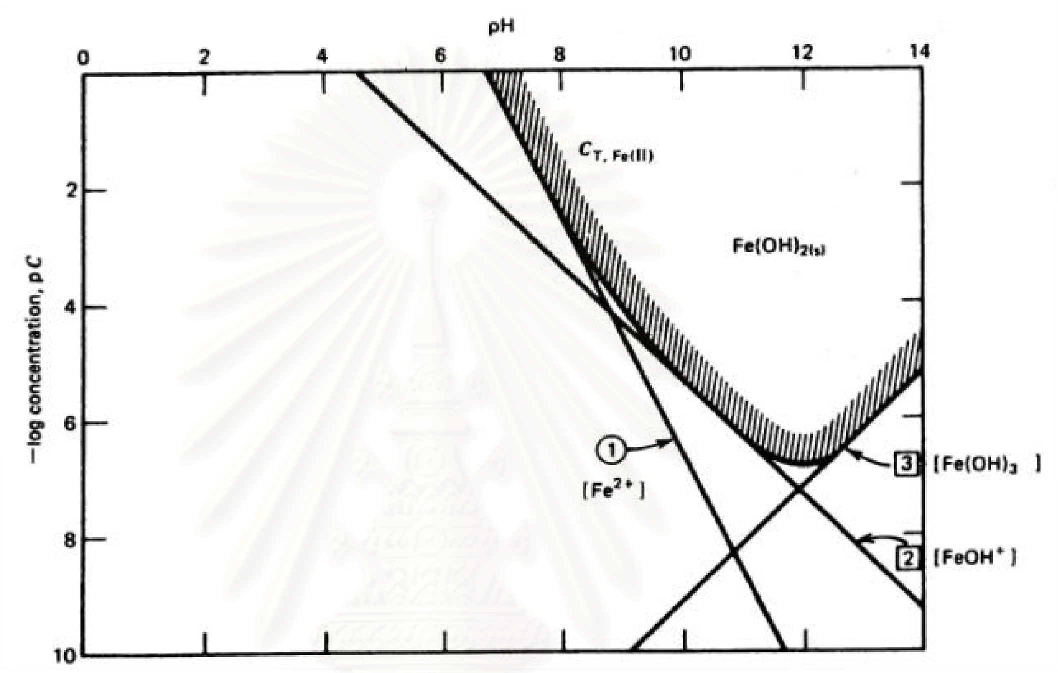

Figure 2.3 Effect of pH on the Fenton process

The first inflection is caused by the addition of $FeSO_4$ catalyst which typically contains residue H_2SO_4. A second, more pronounced drop in pH occurs as the H_2O_2 is added, and continues gradually at a rate which is largely dependent on catalyst concentration. This drop in pH is attributed to the fragmenting of organic material into organic acids. This pH change is often monitored to ensure that the reaction is progressing as planned, the absence of such pH decrease may mean that the reaction is inhibited and that a potentially hazardous build-up of H_2O_2 is occurring within the reaction mixture. In highly concentrated waste streams (>10 g/l COD), it may be necessary to perform the oxidation in steps, readjusting the pH upwards to pH 4-5 after each step or so to prevent low pH from inhibiting the reaction.

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Table 2.13 $k_{p,OH}$ (10^9 s^{-1})

Organic Compounds	**$k_{p,OH}$ (10^9 s^{-1})**
Benzene	7.8
Phenol	7.3
Vinyl chloride	7.1
Toluene	6.8
1-Butanol	4.6
Chlorobenzene	4.5
Trichloroethylene	4.0
Pyridine	3.8
n-Propyl	3.4
Nitrobenzene	3.2
Tetrachloroethylene	2.3
Ethyl	2.1
Methyl	1.2
2-Chloroethylene	0.9
Acetaldehyde	0.5
Hydrogen peroxide	0.43
Formic acids	0.2
Acetone	0.09
Ferric ion	0.027
Acetic acid	0.002

2.3.4.5 Effect of Reaction Time

2.3.4.6

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. Determining the completion of the reaction may prove troublesome. The presence of residual H_2O_2 will interfere with many wastewater analyses. Residual H_2O_2 may be removed by raising the pH to e.g., 7-10, or by neutralizing with bisulphite solution. Often, observation of the color changes can be used to assess the reaction progression. Wastewaters will typically darken upon H_2O_2 addition and clear up as the reaction reaches completion.

Moreover, it was indicated that the hydroxyl radicals are scavenged by inorganic ions, such as CO_3^{2-}, HCO_3^-, PO_4^{3-} and Cl^- as can be seen in equations (11) to (14).

Hydroxyl radical scavengers present in many effluents can drastically reduce the efficiency of pollutant oxidation in direct proportion to their concentration via the reactions (Duguet et al. 1989)

$$OH^{\bullet} + HCO_3^{-} \rightarrow OH^{-} + HCO_3^{\bullet} \tag{11}$$

$$OH^{\bullet} + CO_3^{2-} \rightarrow OH^{-} + CO_3^{-\bullet} \tag{12}$$

$$OH^{\bullet} + PO_4^{3-} \rightarrow OH^{-} + PO_4^{2-\bullet} \tag{13}$$

$$OH^{\bullet} + Cl^{-} \rightarrow OH^{-} + Cl^{\bullet} \tag{14}$$

2.3.4.7 Effect of Temperature

Temperature is one of the important parameters in Fenton’s reaction. The rate of reaction increases with increasing temperature, with the effect more pronounced at temperatures between 5 °C and 20 °C. As the temperature increases above 40-50 °C, the efficiency of H_2O_2 utilization decreases due to the accelerated decomposition of H_2O_2 into oxygen and water. Successive addition of H_2O_2 may be required when treating wastewater with high levels of contaminants in order to moderate the rise in temperature as the reaction proceeds.

The study of **Pérez et al. 2002** showed that temperature has an effect on the Fenton’s reaction. The effect of temperature was carefully tested in a set of experiments where 3 different temperatures (25, 40 and 70 °C) were used. The results showed that temperature markedly influences the degree of removal. The temperature seems to be assisting alternative ways of hydrogen peroxide cleavage and hydroxyl radical formation or ferrous ion recovery. In any case, temperature is a key parameter that has to be taken into account, especially for those applications where TOC removal rate can be increased by using low cost heat (heat exchangers, co-generation, etc.). Wang et al.(2008) studied the temperature effect on the color removal of dyeing wastewater by electro-Fenton process. They found that temperature negatively affected the color removal efficiency. The negative effect of temperature on the production of hydrogen peroxide can be explained by the lower concentration of dissolved oxygen and the self-decomposition of hydrogen peroxide. The concentration of hydrogen peroxide decreased as the temperature was increased because of the decrease in the concentration of dissolved oxygen. Hence, increasing the temperature lowered the color removal efficiency. Additionally, the rate of self-decomposition of the hydrogen peroxide to water and oxygen increased with the temperature. A 10°C rise approximately doubles

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the decomposition rate. In this respect, a lower temperature favored the production and accumulation of hydrogen peroxide, thereby increasing the rate of removal of color.

2.3.4.8 Effect of Anion

Fenton and photo-Fenton oxidations of organic compounds are inhibited in varying degrees by phosphate, sulfate, organosulfonate, fluoride, bromide, and chloride ions, depending on their concentrations. Such anions may be present initially in the wastewater or formed as end products from the compounds undergoing degradation. Inhibition by these species may be due to precipitation of iron, scavenging of $HO^{\cdot}$, or coordination to dissolved Fe(III) to form a less reactive complex. The practitioner and researcher is well advised to be aware of such effects. Nitrate or perchlorate ions do not complex with Fe^{3+} or Fe^{2+} measurably, nor do they react with $HO^{\cdot}$, making them the counter ions of choice for fundamental studies. Iron (III) forms complexes with phosphate that are quite insoluble in neutral or mildly acidic solution. **Lu et al. (1997)** studied oxidation of dichlorvos using Fe^{2+} and an excess of H_2O_2 and observed the typical two-stage (fast-slow) rate profile. In 0.2 *M* phosphate, the fast stage, which is rate-limited by reaction 1, was not affected much. On the other hand, the slow Fe(III)-catalyzed stage, was completely stopped, presumably by precipitation of Fe(III) phosphate complexes. In reactions of sulfonic acid dyes, precipitation of Fe(III) may take place by coordination of Fe(III) with the aryl sulfonate group (Ar-SO−3) **(MacKay and Pignatello, 2001).**

From the study of **Lu et al., (1997),** the results show that anions suppress the decomposition of dichlorovos in the following sequence: $H_2PO_4^- >> Cl^- > NO^{-3} \sim ClO^{-4}$. It can be seen that the Fenton reaction is extremely sensitive to anions. Phosphate ions in particular will seriously suppress the Fenton system’s ability to oxidize dichlorvos. And they also found that the main reason for the suppression of phosphate ions is that phosphate ions will produce a complex reaction together with ferrous ions and ferric ions, which then lowers its ability to catalyze hydrogen peroxide.

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2.3.5 The degradation of various chemical by Fenton process

The destruction of hazardous organic compounds are in urgent demand and an efficient process is needed to get rid of these compounds. The use of hydrogen peroxide with iron salts (so called Fenton process) was then applied in various fields of wastes from water, soil and leachate. In 1991, the degradation of chlorobenzene and its oxidation products by hydroxyl radicals generated with Fenton's reagent was studied. The highest yield of product formed per mole of H_2O_2 consumed was observed in the pH range of 2-3. The pH dependence and product distributions suggest that complexes of aromatic intermediate compounds with iron and oxygen may play a role in regulating reaction pathways. At pH 3.0, approximately 5 mol of H_2O_2/mol of chlorobenzene were required to remove all of the aromatic intermediate compounds from solution **(Sedlak and Andren, 1991).**

In 1992, Joseph J.Pignatello applied Fenton’s reagent both Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2, to degrade 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. He found that pH is one of the important factors for the Fenton process with the optimum pH at 2.7-2.8. Sulfate retards the reaction by its complexation with ferric ions, while chloride inhibits the reaction by interception of hydroxyl radicals. Complete mineralization was achieved after 2 hours and required only 5 mol of H_2O_2/mol of substrate (**Pignatello, 1992).** In 1995, atrazine degradation by Fenton's reagent was determined as a function of reagents' concentration and ratios and pH in batch treatments. The optimal mixture, 2.69 mM **(1:1)** $FeSO_4:H_2O_2$, completely degraded atrazine (140pM) in 530 **s** primarily to 2-chloro-4,6-diamino-striazine (CAAT, 23%) and 2-acetamido-4-amino-6-chloro-s-triazine (CDAT, 28%).

Atrazine degradation decreased from 99% at pH 3 to 37% at pH 9. Thus, Fenton’s reagent can rapidly degrade atrazine, but post-treatments may be necessary to eliminate residual chloro-s-triazines like CDAT and CAAT **(Arnold et al., 1995). Tang and Tassos (1996)** determined the oxidation kinetics and mechanism of trihalomethanes by Fenton’s reagent. All of the experiments were carried out in an air-tight and well-mixed batch reactor. There were no headspace was allowed in order to minimize volatilization of any trihalomethanes during reaction. The optimum conditions of H_2O_2 and Fe^{2+} in the oxidation of bromoform was 3.7 and 1.9 mM for the initial concentration at pH 3.5. The maximum bromoform degradation of 85, 78 and 65 % at 3 minutes were achieved for bromoform concentrations of 295, 98.3 and 49.2 µg/l, respectively. Another study of **Lu et al. (1997, 1999)** on the investigation of the decomposition of dichlorvos insecticide by Fenton process showed that dichlorvos was decomposed through a 2-stage reaction. The first stage is a Fe^{2+} / H_2O_2 reaction in which dichlorvos decomposed swiftly. In the second stage, dichlorvos decomposed less rapidly than the first stage. The detection of ferrous ions also supports the theory of a 2-stage reaction

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for the oxidation of dichlorovos by Fenton’s reagent. The dissolved oxygen of the solution decreased rapidly in the first stage of the reaction, but it slowly increased in the second stage with a zero-order kinetics. The study shows that the higher the amount of ferrous ions added, the higher the elimination rate of dichlorvos. Increasing the concentration of hydrogen peroxide or ferrous ions can enhance the decomposition of dichlorovos. In 2002, Kyung-Duk Zoh and Michael K. Stenstrom studied the oxidation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) by Fenton’s reaction. The optimum H_2O_2 : Fe^{2+} : RDX molar ratio was 5178 : 48 : 1 and complete degradation of RDX and HMX happened in 1-2 hours **(Zoh and Stenstrom, 2002).**

Another three studies of Lu et al. in 2000, 2002 and with Lin et al. in 2002 were also focused on the oxidation of toxic chemicals by the Fenton process. They used goethite as catalyst in the experiment to degrade chlorophenol. The studies revealed that the Fenton method catalyzed by goethite decomposed chlorophenol. The oxidation rate increased with decreasing goethite particle size. They also found that pH, various kind of catalysts such as goethite, ferrous ion and ferric ion had major impacts on the oxidation of this compound. However, it was shown that when applied goethite with ferrous ion giving the best decomposition rate due to the main mechanism from Fenton’s process and from the catalysis of ferrous ions and goethite surface (**Lu, 2000, Lu et al., 2002 and Lin et al ., 2007).**

Gozmen et al. (2003) investigated the electrochemically generated Fenton’s reagent to treat bisphenol A (BPA) in aqueous medium. Hydroxyl radicals that were formed in Fenton’s reagent reacted with the organic substrate producing two different isomers of monohydroxylated product. Upon successive hydroxylation, one dihydroxylated product was left. It was found that the use of cuprous/cupric ion pair resulted a faster conversion of BPA and faster mineralization when compared with the use of ferrous/ferric ions, but this happened at the expense of excess electrical charge utilized for an equivalent conversion or mineralization. A mineralization of 82% was achieved by applying 107.8 mF of charge to a 0.7 mM BPA solution of 0.200 dm3. Another study from **Lu et al. (2005)** on the Fenton process explored the mechanism of chloride ions affecting aniline oxidation by Fenton’s reagent. The results indicated that the inhibition caused by chloride ions can be overcome by increasing the reaction time if the concentration of chloride ion is low.

Phenol oxidation by Fenton's reagent in aqueous solution has been studied. An initial phenol concentration of 100 mg/L was used as a representative for a phenolic industrial wastewater. Under milder operating conditions (H_2O_2 and Fe^{2+} at lower concentrations), a great difference was found between the measured total organic carbon (TOC) and the amount of carbon in all analyzed species in the reaction medium. This difference decreased as the doses of H_2O_2 and Fe^{2+} increased, indicating that the unidentified compounds must correspond to oxidation intermediates between phenol and the organic acids. Oxalic and acetic acid appeared to be fairly refractory to this oxidation treatment. A detailed knowledge of the time evolution of the oxidation intermediates is of environmental interest particularly in the case of hydroquinone and p-benzoquinone because their toxicities are several orders of magnitudes higher than that of phenol itself. The time evolution of the intermediates and TOC was fitted to a simple second-order kinetic equation **(Zazo et al., 2005).**

The color removal by Fenton's reagent was also examined. From the study of **Mijangos et al.(2006),** the phenol oxidation was studied. They found that during phenol oxidation, the oxidized water takes on a dark brown color associated with increased toxicity. The experiments were carried out following the batch-wise procedure at pH 3.0. The color is formed at the beginning of the reaction in less than five minutes. This was due to aromatic intermediates generate higher colored compounds such as ortho- and parabenzoquinone. On the other hand the dihydroxylated rings can react with their own quinones to generate charge transfer complexes (quinhydrone), compounds which take on a dark color at low concentrations. Moreover, when iron reacts with hydrogen peroxide, the ferric ions generated can coordinate with benzene rings to produce colored metal complexes. They concluded that observed color depends on the level of oxidation reached. The maximum color observable during oxidation treatment depends only on initial phenol concentration and not on oxidant or catalyst doses.

In 2007, the degradation of nitroaromatic explosives by Fenton process such as 2,4,6-trinitrophenol (PA), ammonium picrate (AP), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) were studied. The results found that the oxidation rate of the 4 chemicals were in following sequence: DNT>PA>AP>TNT. It means that the decomposition reactions are found to be dependent on the characteristics and numbers of substituents on the phenol rings (**Liou and Lu, 2007).** Moreover, they also studied about the degradation of these explosives by using goethite as the catalyst. The goethite/hydrogen peroxide can be applied to oxidize explosives and the optimum dosage of goethite was 0.4g/50 ml. The kinetic was also determined in their study (**Liou and Lu, 2008).**

2.4 Electro-Fenton Process

In recent years, another wastewater treatment method using electrochemically generated hydroxyl radicals has been investigated. Electrochemical methods have a relevant place among the different techniques for wastewater treatment. Anodic oxidation or indirect electrooxidation can produce the mineralization of toxic and biorefracotry organic pollutants to carbon dioxide, water and inorganic ions. In electrooxidation, hydroxyl radicals are produced from water oxidation and are adsorbed on the anode (Pt, PbO_2, doped SnO_2, bboron-doped diamond, etc.) (Casado et al., 2005). Since, electrochemical techniques are more environmentally friendly than typical chemical methods used in polluted water treatment. Electro-Fenton process is based on the use of an undivided electrolytic cell containing an anode (Pt) and a cathode (Graphite) where H_2O_2 is electro-generated via a two-electron reduction of O_2 at the cathode. When Fe^{2+} is added to the solution, pollutants can be mainly destroyed by $OH^{\bullet}$, which is produced via Fenton reaction. Fe^{3+} can be continuously transformed to Fe^{2+} via a one-electron reduction at the cathode.

The electro-Fenton process can be generally divided into three groups. The first group (EF-H_2O_2 method) uses Fe^{2+} and electrogenerated H_2O_2, that can be produced from the two-electron reduction of sparged oxygen on graphite, reticulated vitreous carbon, or carbon-PTFE cathodes. Its disadvantage is the low current efficiency in acidic condition **(Sudoh et al., 1986; Tzedakis et al., 1989 ; Hsiao and Nobe , 1993; Brillas et al., 1996).** The second group (EF-Feox method) utilizes H_2O_2 and electrogenerated Fe^{2+} which is produced via the oxidation of iron, the sacrificial anode (**Pratap and Lemley, 1994 ; Huang et al., 1997).** The last group called Fenton sludge recycling (FSR) system, involves a Fenton reactor and electrolytic cell for reducing the ferric hydroxide sludge to ferrous ion **(Gnann, 1993).**

In the equations below, the radicals $OH^{\bullet}$, $OH^{\bullet}_2$ and $OH^{\bullet}_2{}^{-}$ are consumed and regenerated in the reaction system, which is influenced by H_2O_2, Fe^{2+} and Fe^{3+} as shown in Figure 2.3 and equation (18) to (21). When electricity is employed in the process, Fe^{3+} can be reduced to Fe^{2+} more efficiency and rapidly which increases the reaction rate. In addition, low pH and anaerobic conditions are employed by many investigators

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to prevent the oxidation of ferrous ion. However, very low pH will decrease the reaction rate. Solution pH should be kept at an optimum value to maintain the high efficiency of hydrogen peroxide decomposition to hydroxyl radicals.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$ (15)
$OH^\bullet + \text{Organic} \rightarrow \text{Products}$ (16)
$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+$ (17)
$FeOOH^{2+} \rightarrow Fe^{2+} + OH^\bullet_2$ (18)
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$ (19)
$Fe^{2+} + OH^\bullet_2 \rightarrow Fe^{3+} + OH^{\bullet -}_2$ (20)
$Fe^{3+} + OH^{\bullet -}_2 \rightarrow Fe^{2+} + O_2 + H^+$ (21)

Iron salt acts as a catalyst for hydrogen peroxide decomposition, further reaction (17) and (18) regenerate Fe^{2+}. In addition to free radical scavengers, the process is inhibited by (iron) chelants such as phosphates, EDTA, formaldehyde, and citric/oxalic acids. It is recommended that reactions should always be characterized through laboratory treatability tests before proceeding to plant scale due to the sensitivity of Fenton’s reagent to different wastewater.

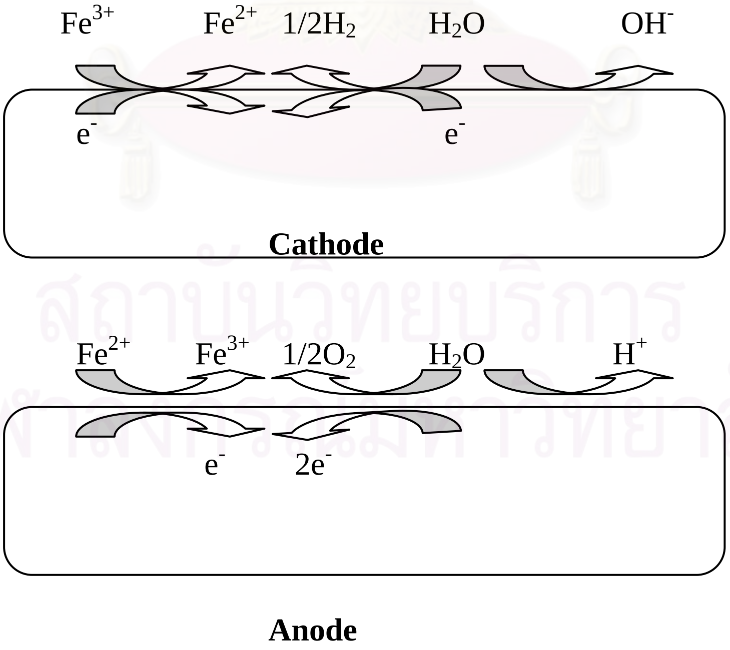

Figure 2.3 Electro-Fenton reaction

On Cathode Side :
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (22)
$H_2O + e^- \rightarrow ½ H_2 + OH^-$ (23)

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On Anode Side :

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (24)$$

$$H_20 \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^- \quad (25)$$

The capabilities of the electro-Fenton process have been confirmed by more than 90% COD removal of solutions containing phenol, aniline, acetic acid, formaldehyde, three azo dyes, and other organics. The current efficiencies are higher than 50% and energy consumptions are acceptable.

2.4.1 The degradation of various chemical by Electro-Fenton process

The electrochemically assisted Fenton’s reagent or the so called Electro-Fenton (EF) process has been examined by many researchers. Here we will provide some interesting and useful research focused on the electro-Fenton process which is useful for this experiment. Firstly, **Chou et al. (1999)** studied about the treatment of high strength hexamine contaminating wastewater by electro-Fenton method. The performance of Fe^{2+} generation in the electrolytic system was evaluated, including the factor of cathode material, initial pH, initial ferric concentration and current density. When the pH exceeded 2.5, the current efficiency decrease was due to the formation of $Fe(OH)_3$. The initial current efficiency of Fe^{2+} generation was almost constant (85-87%) when ferrous ion was between 3,000-10,000 mg/l. This dropped sharply to 39% at 1,000 mg/l. The COD removal efficiency was above 94% after 5 hrs of reaction. The changes in hexamine and its oxidation intermediates (methanol, formaldehyde, formate, ammonium and nitrate) during the reaction were also investigated.

Later on year 2000**, Lin et al. (2000)** treated old-aged landfill leachate by a combination chemical and biological methods. The electro-Fenton method assisted by chemical coagulation was employed and was found to be highly efficient in the removal of refractory organic and inorganic compounds in the leachate. The electro-Fenton oxidation employed was able to enhance the removal of COD of the leachate effluent from chemical coagulation. At optimum pH of 4, the oxidation process made leachate colorless. An optimum H_2O_2 dosage of 750 mg/l yield a very good COD, color, NH_3-N and phosphorus removal in less than 30 minutes. Final treatment of the leachate effluent by sequencing batch reactor was able to comply with the standard for direct discharge or for reuse as non-potable water.

Oturan et al. (2000) used electro-Fenton process for the degradation of p-Nitrophenol in aqueous medium. The electro-Fenton is based on electrocatalytical

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generation of Fenton’s reagent to produce hydroxyl radical. The intermediate products of degradation were hydroquinone, benzoquinone, 1,2,4-trihydroxybenzene, 3,4,5-trihydroxynitrobenzene and 4-nitrocatechol. The mineralization of the initial pollutant and the intermediates that were formed during electro-Fenton treatment was studied using TOC analysis. Mineralization rate was higher at the beginning of the electrolysis but diminished with the decrease in compound concentration in the reaction mixture and with changes in their structure, such as from aromatics to aliphatics, which are more resistant to mineralization by ring disrupting reactions. Under the optimum condition, the mineralization process reached 95% efficiency. In 2001, **Brillas et al. (2001)** investigated on aniline degradation by electro-Fenton and peroxi-coagulation processes using a flow reactor for wastewater treatment. The electro-Fenton process with 1 mM Fe $^{2+}$ and Ti/Pt or DSA anode yields an insoluble violet polymer while the soluble TOC is gradually removed. The degradation reaches 61% after 2 hrs at 20 Ampere. In this experiment, aniline was oxidized by hydroxyl radicals formed in solution from reaction of Fe^{2+} with H_2O_2. The peroxi-coagulation process with a Fe anode has higher degradation power, allowing to remove more than 95% of pollutants at 20 A.

Huang et al.(2001) compared a novel electro-Fenton method with the traditional Fenton process in treating a highly contaminated wastewater. By combining electrochemical reduction and chemical oxidation, the process can successfully remove organic compounds and heavy metals in a batch reactor. A PVC-stabilizer processing wastewater was treated in this investigation owing to its high heavy-metal concentration (Pb=7,500 mg/l) and high organic concentration (COD=11,000 mg/l). The major organic component was acetate. Direct anodic oxidation showed no effect on COD removal. Fenton’s method only removed 36% of COD with 4,000 mg-Fe^{2+}/l and 28,000 mg-H_2O_2/l. In the Fered-Fenton method, about 89% of COD was removed with 2,000 mg-Fe^{3+}/l and 28,000 mg-H_2O_2/l. Moreover, the COD removal attained an efficiency of about 98% for 56,000 mg-H_2O_2/l used. Results demonstrate that the Fered-Fenton method is superior to direct anodic oxidation and Fenton’s method in this case. **Panizza et al.(2001)** investigated on the treatment of naphthalene and anthraquinone-sulphonic acids by electrogenerated Fenton’s reagent. The hydrogen peroxide was produced in situ by electrochemical reduction of oxygen on a graphite-felt cathode and the Fe^{2+} ion was also regenerated by cathodic reduction of Fe^{3+}. The influence of cathode potential, Fe^{2+} concentration and electrode surface pre-treatment on the treatment performance was investigated. The reduction of oxygen to H_2O_2 on graphite-felt occurred at -1 volt versus the saturated calomel electrode (SCE). The maximum COD removal of 87% and color fading of 89% were obtained with a Fe^{2+} concentration of 3 mM in electro-Fenton treatment process. The COD removal kinetics followed a pseudo-first-order reaction. Chemical or electrochemical surface pretreatment had no significant impact on organic oxidation.

Arapoglou et al.(2002) used electrochemical method that had a Ti/Pt anode and stainless steel as a cathode to treat methyl-parathion (MeP). Sodium chloride was added as an electrolyte and the mixture was passed through an electrolytic cell for 2 hrs. Reduction of COD was over 80%. The degradation of MeP was more effective when the pH of the solution was in the acidic range than when it was in the alkaline range. **Brillas et al. (2002)** studied the degradation of 10-30 l of a 1000 ppm aniline solution in 0.05 M Na_2SO_4 + H_2SO_4 at pH 3 and 40 degrees C by electro-Fenton and peroxi – coagulation processes at constant current until 20 A has been studied using a pilot flow reactor in recirculation mode with a filter-press cell containing an anode and an oxygen diffusion cathode. Both had an area of 100 cm^2. H_2O_2 was produced by the two-electron reduction of O_2 at the cathode, being accumulated with a current efficiency between 60% and 80% at the first stages of electrolyses performed with a Ti/Pt anode. In the presence of 1 mM Fe^{2+}, less H_2O_2 was accumulated but it was not detected using an Fe anode. The electro-Fenton process with 1 mM Fe^{2+} and a Ti/Pt or DSA anode yields an insoluble violet polymer, while the soluble TOC was gradually removed, reaching 61% degradation after 2 hrs at 20 A. In this treatment, pollutants were oxidized by hydroxyl radicals formed in the solution from the reaction of Fe^{2+} with H_2O_2. The peroxi-coagulation process with an Fe anode has a higher degradation power which can remove more than 95% of pollutants at 20 A. Both advanced electrochemical oxidation processes showed moderate energy costs, which increased with increasing electrolysis time and applied current. **Chun et al. (2002)** designed a three-phase three-dimension electrode reactor or TTER for wastewater treatment. The result showed that TTER can degrade aniline. Its degradation efficiency depended on applied voltage, Fe^{2+} concentration, pH and electrolysis time. The degradation of aniline in the presence of Fe^{2+} was faster than in the absence of Fe^{2+}. **Maurizio De Francesco and Paola Costamagna (2002)** studied on the design of electrochemical reactors for the treatment of polluted water. They found that the fundamental criteria were a high hydrogen potential for the cathodes to avoid electrode combustion and high oxygen overpotential for the anodes. In all the electrochemical processes, the cathodes were based on carbon/PTFE, copper, steel and/or iron. Platinum or titanium coated with IrO_2 or RuO_2 also gave good results. In all the electrochemical processes, except for the direct ones, anodes based on platinum, sacrificial iron and lead oxide were frequently utilized. The choice of the direct processes was more complex since the reaction mechanism was strongly dependent on the electrode properties. Anodes for the complete combustion should not have oxygen vacancies. For these reasons, tin oxide (SnO_2) showed a non-selective behavior and platinum and titanium coated with IrO_2 were selective electrodes. In this case the non-selective activity towards the electro-oxidation of organics in a liquid medium was due to the high oxidation states of iridium (V and VI).

Qiang et al. (2002) studied the optimum condition for the treatment of the iron sludge produced in Fenton oxidation processes by electro-regenerating Fe^{2+} with constant potential (CPM) or constant current modes (CCM). Results showed that the optimal cathodic potential for Fe^{2+} regeneration is -0.1 volt versus the saturated calomel electrode (SCE). The suitable pH for iron sludge dissolution is much lower than the predicted value based on the Fe^{3+} hydrolysis curve. Increasing of cathode surface area and solution temperature notably increases the Fe^{2+} regeneration rate. The maximum current efficiency (η) that is obtained under the optimum condition is 96-98%. The unit energy consumption is 2.0-3.0 kW.h/kg Fe^{2+} regenerated. Another study from **Qiang et al. (2002)** on the removal of hazardous organic compounds from aqueous solution by using electro-Fenton oxidation process was studied. H_2O_2 was electro-generated by the reduction of dissolved oxygen in acidic solution. The optimum conditions are a cathode potential of -0.5 volt versus saturated calomel electrode (SCE), oxygen mass flow rate of 8.2×10^{-2} mol/min and pH 2. The average current density and current efficiency are 6.4 A/m^2 and 81%, respectively. Fe^{2+} was electro-regenerated from ferric salt or Fenton’s iron sludge. The Fenton oxidation process can effectively degrade all selected polycyclic aromatic hydrocarbons (PAHs), such as naphthalene, fluorine and anthracene. Fe^{2+} can also be regenerated from Fenton’s iron sludge. The dosing mode of H_2O_2 and Fe^{2+} significantly affects the reaction efficiency. The electro-Fenton oxidation process is more efficient than the conventional Fenton oxidation process because of the continuous regeneration of Fe^{2+} at the cathode. **Ventura et al. (2002)** investigated on electrochemical generation of Fenton’s reagent by choosing atrazine as a model since its reaction with hydroxyl radical has been extensively studied. The degradation of atrazine was compare between the electro-Fenton process and the conventional Fenton process. The result showed that the electro-Fenton process was more efficient. In the Fenton process, the first 15 minutes of degradation was faster than those after that. The result showed that the Fenton’s reagent can be electrochemically produced in an aqueous solution and it has lead to an efficient and continuous hydroxyl radical production with a limited competitive reaction. This simple system produced ferrous iron in situ by the reduction of ferric iron, with the simultaneous reduction of oxygen into hydrogen peroxide.

Another study by **Brillas et al. (2003)** determined the electrochemical degradation of chlorophenoxy and chlorobenzoic herbicide in acidic aqueous medium by the peroxi-coagualtion method. This electrochemical method yields a very effective depollution of all compounds in an acidic aqueous medium of pH 3.0. Target compounds are oxidized substantially by the corresponding Fe anode and O_2-diffusion cathode. Their products can then be removed by mineralization or coagulation with the $Fe(OH)_3$ precipitate formed. Both degradation paths completed at low current. The decay of all herbicides follows a pseudo-first-order reaction. Formaldehyde-containing organic wastewater was treated by an electro-Fenton reactor which had granular carbon as the filled electrode**, Hu et al. (2003)**. The optimum conditions were 90 min, 25 V, 30-40ºC, insulating carbon content of 40%, Fe^{2+} concentration of 300 mg/l and a $pH < 3.5$. The oxidation products were analyzed with UV absorbance spectrum. The removal rates of formaldehyde and COD were about 90% and 30%, respectively. In addition, the operating cost was 42.3% less than that of the conventional Fenton method. **Chang et al. (2004)** studied a novel electro-Fenton method, called the Fered-Fenton method, by applying H_2O_2 and electrogenerated ferrous ions for treating organic containing wastewater. By combining electrochemical reduction and chemical oxidation, the process can regenerate ferrous ions and remove organic compounds simultaneously in a batch reactor. It showed that increasing the initial ferric ion concentration can achieve high initial current efficiency. The wastewater from nickel plating was treated in this studied. The average pH, COD and Ni concentrations of this wastewater were 5.0, 30,000 and 2,000 mg/l, respectively. The results showed that the conventional Fenton method can removed only 60% of COD when using 5,000 mg/l of ferrous ions. However, the COD removal efficiency was promoted after the electricity was introduced into the system. Ni concentration can be reduced from 2,080 to 0.3 mg/l, indicating that the removal efficiency was higher than 99.9%.

The production of reclaimed water was also studied by using the electro-Fenton process. **Duran et al. (2004)** studied the electro-Fenton process to generate simultaneously both of Fenton's reagent species (Fe^{2+}/ H_2O_2) to produce reclaimed water. An air-saturated combined water (mixture of municipal and laboratory effluents) was treated in discontinuous (2 L reactor with concentric graphite and iron electrodes) and continuous reactors (comprising the aforementioned electrochemical cell, two clarifiers and one sand filter) at pH 3.5. The best operating conditions were 60 min and 1 A without filtration of the effluents. Using these conditions for discontinuous and continuous reactors with filtration, the COD, turbidity and color removal were 65-74.8%, 77-92.3% and 80-100%, respectively. **Mu et al. (2004)** carried out a study on reductive degradation of nitrobenzene by zero-valent iron. The results demonstrated that the nitrobenzene removal was effected by pH (3.0) and nitrobenzene concentration. Following year later, **Wang et al. (2004)** studied the comparison of activated carbon filter (ACF) felt and graphite cathode. They suggested H_2O_2 might effectively be electrogenerated from O_2 reduction on the large surface area ACF felt cathode. This was more adaptive for electro-Fenton process when using dye wastewater containing Acid Red 14(AR14). After 360 min of electrolysis, under the operation conditions of 0.36 A current, 1 mM Fe^{2+}, and pH 3, 70% TOC was removed as well as complete decolorization. **Song-hu Y and Xiao-hua L. (2005)** described a comparative degradation of various chlorophenols by the electro-Fenton method. Using pentachlorophenol as the model compound, it was shownthat the addition of small quantities of Fe^{3+} or Fe^{2+} significantly accelerated the degradation rate. The pseudo first-order degradation rate constants at the first stage were calculated and compared. They gave the following sequence: 2,4-dichlorophenol > 2,4,6- trichlorophenol > pentachlorophenol > 4-chlorophenol.

The study on Aniline degradation by electro-Fenton process was examined again using kinetic description. **Anotai et al. (2006)** studied the degradation of aniline at pH 2 by Fenton and electro-Fenton processes. The electro-Fenton process was found to be superior to the conventional Fenton process with current impacts of 1.2 to 3.1 for the removal efficiency and 1.2 to 5.8 for the degradation rate depending on the initial Fe^{2+} concentration. In addition, for complete removal of 0.01 M aniline, the delay in current supply at the initial stage could save up to one-third of the total energy required by the conventional Fenton process. From results, significant reduction in energy consumption and operating cost could be obtained by the current-delay operating mode. **Diagne et al. (2006)** investigated on the degradation of methyl parathion by electro-Fenton process. This oxidation process allowed the production of hydroxyl radicals which react on the organic compounds, leading to their mineralization. Degradation experiments were performed either in perchloric, sulfuric, hydrochloric and nitric acid media under current controlled electrolysis conditions at different pH values. The mineralization of the initial pollutants was investigated by TOC measurements which showed a complete mineralization at pH 3 in perchloric medium. The absolute rate constant of methyl parathion hydroxylation reaction was determined as (4.2 +/- 0.11) x 10^{9} M^{-1} s^{-1}. Complete degradation of methyl parathion and its metabolites occur in less than 45 minutes. Degradation reaction intermediates were aromatic compounds, carboxylic acids and inorganic ions.

Wastewater is not the only waste that can be removed by the electro-Fenton process. Polluted soil was also examined using this kind of treatment. **Samuele Meinero and Orfeo Zerbinati (2006)** studied the treatment of solutions from washing polluted soil by oxidation in an undivided cell, where H_2O_2 was generated electrochemically by reduction of atmospheric oxygen bubbled at a carbon cloth cathode. Electro-Fenton removed 75% COD of this wastewater with a specific energy consumption of 0.3 kWh/g COD, corresponding to 41.8 $kWhm^{-3}$.

To improve the removal efficiency, many catalysts were used to observe the oxidation ability. As such, **Sanchez et al. (2006)** showed the use of a new mineral iron dosage source (goethite,-FeOOH) for the electro-Fenton process that achieved a more efficient mineralization treatment. This new proposed Goethite catalyzed electro-Fenton (GEF) process yields 95% mineralization for an organic model pollutant such as aniline under optimum standard electro-Fenton (SEF) conditions. GEF process used only 2 ppm of soluble iron, compared with the 55 ppm of soluble iron used by SEF process. **Yuan et al. (2006)** studied the degradation of various nitrophenols by electro-Fenton and cathode reduction. Phenol (Poh), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP) and 2,4 –dinitrophenol (2,4-DNP) were treated in this study. Using 4-NP as a model nitrophenol, the electrochemical behavior on graphite cathode and Pt anode were analyzed by cyclic voltammetry. The degradation of 4-NP was much faster in the cathode cell than in the anodic cell. Treatment of high concentration of 4-NP in the undivided cell showed that more than 98% removal of 4-NP and about 13% removal of TOC were obtained for both processes. Intermediates such as hydroquinone and benzoquinone were detected by gas chromatography/mass spectrum. The degradation pathway of 4-NP in electro-Fenton process was proposed as a cathode reduction followed by hydroxyl oxidation.

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Zhang et al. (2006) treated the landfill leachate by electro-Fenton with a batch electrolytic reactor. The process was very fast in the first 30 min and then slow down until it was complete in 75 min. COD removal efficiency increased with the increasing current. COD removal was only 65% when hydrogen peroxide alone was applied to the electrolytic reactor. The presence of ferrous ion greatly improved COD removal. COD removal efficiency increased with the increase of ferrous ion dosage at a fixed hydrogen peroxide dose and was highest at 0.038 mol/l of ferrous ion concentration. Moreover, **Liu et al., (2007)** examined the electro-Fenton reaction by focusing on the kinetic modeling. They used phenol as the target compound and found that the degradation rate was three stages; a slow rate at the early stage of the reaction, a faster rate during the middle stage and a slow rate again at the last stage. The degradation of phenol obeyed first-order behavior.

In 2007, Liu et al. developed a novel electro-Fenton (EF) process in which the desired pH for an effective EF reaction and for a neutral treated media could be obtained by utilizing the reaction-released H^+ and OH^- instead of chemical addition. In the laboratory-scale process using three chambers, the substrate solution pH > 4.0 was designed to be adjusted in situ through three sequencing steps: (I) pH reduction, (II) pH keeping for the effective EF reaction, and (III) pH recovery to neutral while the EF reaction continued. The results revealed that the novel process was effective in reducing the dimethyl phthalate concentration and the total organic carbon at steps II and III. The initial dimethyl phthalate solution pH > 4.0 was reduced to 3.5 in Step I of the process. This pH adjustment not only allowed the EF reaction to occur in its favorable pH range, but also benefited any potential subsequent biological treatment process or a final discharge **(Liu et al., 2007). Sánchez-Sánchez et al., (2007)** used goethite (a new mineral iron dosage source) for electro-Fenton process to mineralize Aniline. It was found that by using goethite the degradation was yield to 95%. Only 2 ppm of soluble iron was needed by goethite catalyzed electro-Fenton compared to 55 ppm of soluble iron using by standard electro-Fenton process. The effect of goethite concentration, solution conductivity, pH, temperature and applied current density were examined in this study. A paper by **Sirés et al., (2007)** also studied the electro-Fenton degradation of antimicrobials triclosan and triclocarbon. They used boron-doped diamond anode and a carbon felt cathode. The results showed that the optimum pH for this study is pH3 and the reaction kinetic was second-order.

2.5 Photo-Fenton

Photo-Fenton process is already well known in many literatures as an effective and cheap method for wastewater treatment. By applying Ultra Violet light to Fenton reaction, photo-Fenton process, can enhance the oxidation rate of many organic compounds.

The UV light is a portion of the electromagnetic spectrum that lies beyond the “purple” edge of the visible spectrum and has wavelengths between 100 and 400 nm. The UV spectrum is further divided into ranges as listed in Table 2.14.

Table 2.14 Range of UV spectrum

Range Name	Wavelength Range (nm)
UVA	315 - 400
UVB	280 - 315
UVC	200 - 280
Vacuum UV	100 - 200

The UVA range causes “sun tanning” on human skin. The UVB range causes “sun burning”. The UVC range is absorbed by DNA and thus can cause cancer and mutations. This is also the range that is most effective in inactivating bacteria and viruses. The Vacuum UV range is absorbed strongly by water and air and thus can only be transmitted in a vacuum.Ultraviolet photons are particularly energetic and when absorbed in molecules can cause bonds to be broken (photochemistry). UV has many commercial applications in society. The major ones are: UV disinfection of water and air, UV curing of inks and coatings, UV disinfection of food, UV-based Advanced Oxidation destruction of pollutants in water and air. UV-based AOPs usually involve the generation of OH radicals by the photolysis of hydrogen peroxide (H_2O_2).

Photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures of ferric ion and hydrogen peroxide (known as Fenton-like reaction) have shown photon absorption up to 550 nm (Pignatello et al., 1999, Sun and Pignatello, 1993). In the presence of Fenton’s reagent, photochemical reactions can be driven with photons of low energy, photons that belong to the visible part of the spectrum. Light can play two different roles that would lead to an improvement o the reaction yields: (1) it drives photo-Fenton reaction, producing additional hydroxyl radicals and the recovery of ferrous ion needed in Fenton’s reaction. (2) It can drive ligand to metal charge transfer in the potentially photolabile complexes formed by ferric ion and organic compounds, a process that has been well proven for the complexes formed between ferric ion and the carboxylic acid moiety (Pérez et al., 2002, Hislop and Bolton, 1999). Large quantities of carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate. Therefore, photo-Fenton process is a potertial cost-reduced AOP that can be run under solar irradiation.

Production of hydroxyl radicals in a homogeneous reaction pathway out of hydrogen peroxide under photocatalytic conditions is the basis of this method. This process utilizes the photoreduction of produced ferric ions (Fe^{3+}) and ferric complexes (Equation 26-28) (Kim et al, 1997). In contrast to Fenton reaction (without photo-activation), ferrous ion (Fe^{2+}) is recycled continuously by irradiation of Fe^{3+} - H_2O, and therefore it is not depleted during the course of the oxidation reaction. Hence, the production of hydroxyl radicals is only limited by availability of UV/VIS radiation and H_2O_2.

$$Fe^{3+} + H_2O + hv \rightarrow Fe(OH)^{2+} + H^+ \quad (26)$$
$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH^{\bullet} \quad (27)$$
$$H_2O_2 + hv \rightarrow 2OH^{\bullet} \quad (28)$$

Moreover, a molecule of hydrogen peroxide can produce two molecules of hydroxyl radicals initiated by UV-light, according to Equation (28). Both two routes facilitate the formation of hydroxyl radicals and will promote the degradation rates of organic compounds.

2.5.1 The degradation of various chemicals by the Photo-Fenton process

The study of Fenton assisted by UV light has been studied a long time ago. It is a very promising water treatment method. Back in 1993, The oxidation of 2,5-dichlorophenoxyacetic acid by photoenhancement of Fenton-type using near-UV was studied. It was shown that photo-Fenton had more efficiency to degrade 2,4-D than conventional Fenton. The main mechanism that occurred in this experiment includes Fenton reaction and photolytic reactions that may contribute indirectly to the generation of hydroxyl radicals via production of ferric ion by the Fenton reaction **(Sun and Pignatello, 1993).** The large scale application of the light-enhanced Fenton reaction in treating highly contaminated wastewater which contained xylidines (dimethylaniline) was examined by **Oliveros et al.(1997).** They varied 2 factors, ferrous ion and hydrogen peroxide concentrations. The results showed that photo-Fenton is the most effective treatment process and it can be used as alternative to treat xylidines.

The prototype reactor for photo-Fenton process was applied on highly contaminated wastewaters up to a TOC of 1400 ppm and COD of 12,000 mg/l. The degradation rate was found to increase with the amount of Fe-catalyst. However, when the iron catalyst was applied beyond a maximum concentration, no further increase of degradation rate can be found **(Krutzler and Bauer, 1999).** In 2000, the degradation of aniline by Fenton and photo-Fenton processes were studied. The results showed that parameters such as ferrous ion, hydrogen peroxide concentration, pH, temperature and oxygen flow rate had an effect on the oxidation of aniline (**Utset et al., 2000). Fukushima et al.(2000)** studied on the degradation of aniline by light irradiation (ì > 370 nm), which contained Fe(III), humic acid (HA), and H2O2 showed that consumption of H2O2 and the reduction of Fe(III) to Fe(II) was consistent with the degradation of aniline via the photo-Fenton reaction, accompanied by the generation of hydroxyl radicals. HPLC analysis of the reaction mixture indicated the presence of p-aminophenol, p-hydroquinone, maleic and fumaric acids and the simultaneous release of NH^{4+} ion. **Contreras et al. (2001)** investigated the degradation of nitrobenzene using some advanced oxidation processes (O_3/UV, O_2/UV/ H_2O_2 and O_3/UV/Fe^{3+}). The combined O_3/UV process did not improve the degradation rate obtained by ozonation. The best TOC decrease was obtained when the O_3/UV process was carried out with low ferric concentration. **Sauleda et al. (2001)** studied on the mineralization of aniline and 4-chlorophenol in an acidic solution by ozonation catalyzed with Fe^{2+} and UVA light. The initial mineralization rate was enhanced as more oxidizing hydroxyl radicals were produced in the medium by the catalyzed ozonations. Each initial pollutant was destroyed with similar rates in all processes. P-Benzoquinone and nitrobenzene were identified as intermediates of aniline oxidation. Nitrate ion production was maximum under UVA irradiation, indicating that the generation of nitrobenzene from a selective attack of O_3 on the amino group of aniline was photocatalyzed.

Many kinds of wastewater degradation were examined by the photo-Fenton process. Textile wastewater is one of that. Fenton and photo-Fenton were compared for the removal efficiency of textile effluents from a Spanish textile manufacturer. The study from **Pérez et al. (2002)** showed that the important parameters for Fenton, Fenton-like and photo-Fenton were light intensity, temperature, pH, ferrous ion and

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hydrogen peroxide concentrations. The TOC,COD and color were measured and results revealed that Fenton processes are highly effective for the treatment of textile wastewater. The oxidation of explosives were also studied by comparing the conventional Fenton process and photo-Fenton process. It showed that photo-Fenton can be used to degrade these kinds of wastewater and the degradation of explosives obeyed a pseudo-first-order behavior. The study showed that the oxidation rate of explosives increased with an increasing concentration of ferrous ions. UV light has a higher promotion efficiency when there is a lower ferrous ion concentration **(Liou et al., 2003).** In 2004, Liou et al. also used the photo-Fenton process to degrade 2,4,6-trinitrotoluene or TNT. They found that the degradation followed first-order kinetic and increasing the intensity of UV light, ferrous ion an hydrogen peroxide concentrations will promoted the degradation rate (**Liou et al., 2004).**

Dyes are also one of the interesting target compounds of the photo-Fenton process. **Muruganandham, M. and Swaminathan, M. (2004)** carried out the experiment to decolorize Reactive Orange 4 using Fenton and photo-Fenton processes. The effects of pH, hydrogen peroxide dosage and ferrous ions were examined and the results revealed that photo-Fenton process was more efficient than Fenton process under the optimum conditions. In 2005, **Pérez-estrada et al. (2005)** studied on the removal of pharmaceuticals (diclofenac). These are new contaminants that are dangerous because many of them are not degraded under the typical biological treatments and represent a continuous input into the environment. They used photo-Fenton reaction. Results obtained show rapid and complete oxidation of diclofenac after 60 min and total mineralization after 100 min of exposure to sunlight. Although diclofenac precipitates during the process at low pH, its degradation takes place in the homogeneous phase which is governed by a precipitation-redissolution degradation process. 18 intermediates were found in two tentative degradation routes. **Daneshvar N. and Khataee A.R. (2006)** studied the decolorization of Acid Red 14 by hydrogen peroxide photolysis, Fenton, Fenton-like and photo-Fenton processes. For illumination, the UV-C lamp (30W) was selected. The results showed that at a reaction time of 2 min, the efficiency followed the decreasing order: UV/H_2O_2/Ferric ion/ oxalate > UV/ H_2O_2/Ferric ion > UV/ H_2O_2/Ferrous ion > UV/ H_2O_2. **Fares Al Momani (2006)** used photo-Fenton at laboratory scale to degrade nitrobenzene. The effect of reactants concentration, temperature, pH, hydrogen peroxide and ferrous ion were studied. It was found that at pH 3, an initial concentration of 65 ppm hydrogen peroxide and 10 ppm for ferrous ions could degrade all of the nitrobenzene in only 30 min. Increasing the concentration of iron ions led to an increase in degradation efficiency from 78% to 90%. The results from this study also reveal that after using photo-Fenton, biodegradability and toxicity were reduced.

The photo-Fenton was also used to oxidize formaline and methanol wastewater. The study showed that the oxidation reaction was in 3-stages. The first stage was the ferrous ion/hydrogen peroxide reaction where formaline was swiftly decomposed. The second and third stages had a less rapid degradation. pH 2.6 was found to be the optimum pH for this chemical degradation by photo-Fenton process. The experiments also revealed that the photo-Fenton process was the most effective treatment process among the studied AOPs such as UV/hydrogen peroxide, Fenton **(Kajitvichyanukul et al., 2006 and 2008).**

The degradation of tetracycline by photo-Fenton was also examined under black-light and solar radiation. The study revealed that total degradation was achieved after 1 min of irradiation of black-light when using $Fe(NO_3)_3$ as iron source. While under solar irradiation, the ferrioxalate favored the degradation of tetracycline. However, no significant difference in TOC removal was found between these two iron sources (**Bautitz and Noqueira, 2007).**

A study of anions on the degradation of organic compounds has been investigated. By using chloride ions as the anion and phenol as target compound, the study of **Machulek et al. (2007)** on the effect of chloride ion to the photo-Fenton process found that the inhibition of the photo-Fenton (Fe^{2+}/Fe^{3+}, H_2O_2, UV light) degradation of synthetic phenol wastewater solutions by chloride ions is shown to primarily affect the photochemical step of the process and having only a slight effect on the thermal or Fenton step. It also was shown that for synthetic phenol wastewater and an aqueous extract of Brazilian gasoline, the inhibition of the photo-Fenton degradation of the organic material in the presence of chloride ion can be circumvented by maintaining the pH of the medium at or slightly above 3 throughout the process even in the presence of significant amounts of added chloride ion (0.5 M).

2.6. Photoelectro-Fenton

The catalytic effect of Fe^{2+} in the electro-Fenton process can be enhanced by solution irradiation with UV light or visible light during or after electrolysis. Hence, it is called photoelectro-Fenton (PEF) process that can produce a large regeneration rate of Fe^{2+}. For photoelectro-Fenton process, the electro-Fenton process (which has a significant drawback is the parasitic reactions such as electrolysis of water often compete with the O_2 reduction and lower the energy efficiency) is combined with UV light. This way the advantages of both reactions occurred in the reactor. The photoelectro-Fenton process involves the additional irradiation of the solution with UV light to favor: (1) the photodecomposition of some intermediates, such as complexes of ferric ion with generated carboxylic acids (short-linear organic acids) and (2) the regeneration of ferrous ion with production of more hydroxyl radicals from the photoreduction of $Fe(OH)^{2+}$, which is the predominant ferric ion species in acid medium.

$$(Fe–OH)^{2+} + hv \rightarrow Fe^{2+} + OH^{\bullet} \qquad (29)$$

This reaction increases the oxidative capability of the process due to the rise of the $OH^{\bullet}$ in the Fenton’s reaction. In this context, the use of sunlight seems specially advantageous. In addition to all of these mechanisms in the photoelectro-Fenton process, two $OH^{\bullet}$ can be produced from H_2O_2 by the photocatalytic effect of UV light (253 nm).

$$H_2O_2 + hv \rightarrow 2OH^{\bullet} \qquad (30)$$

Environmental application of the PEF process is a fairly new topic and previous studies are quite limited. The most part of these studies have comprised treatability of some specific pollutants such as herbicides (Boye et al., 2002, Irmak et al., 2006, Boye et al., 2003, Brillas et al., 2003), dyes (Flox et al., 2006, Rao et al., 2006) and organics (Brillas et al., 2002, Boye et al., 2006). In addition, Flox et al. (Flox et al., 2007) have recently used solar energy as a photon source and substantially reduced operating costs of the process,

2.6.1 The degradation of various chemical by Photoelectro-Fenton process

The photoelectro-Fenton process was used by **Brillas et al. (1998)** on a study on aniline mineralization by Advanced Oxidation Processes through anodic oxidation, photocatalysis, electro-Fenton, and photoelectron-Fenton processes. The degradation of aniline at pH 3 under photocatalytic and electrochemical conditions were investigated. The electrochemical experiments performed in the presence of both species (electro-Fenton conditions) led to the fast mineralization of aniline which is increased by UVA irradiation (photoelectron-Fenton process). A general pathway for aniline mineralization is proposed in which products are formed via hydroxyl radical degradation. Later on 2003, Brillas et al. also had another study on photoelectro-Fenton. **Brillas et al. (2003)** studied the mineralization of an acidic aqueous solution with the herbicide 3,6 -dichloro-2-methoxybenzoic acid (dicamba) by electro-Fenton and photoelectron-Fenton using a Pt anode and an O_2-diffusion cathode. While electro-Fenton yield 60-70% mineralization, photoelectron-Fenton allows a fast and complete depollution of herbicide solution. In both treatment, the initial chlorine is rapidly released to the medium as a chloride ion. The dicamba decay follows a pseudo-first order reaction, as determined by reverse-phase chromatography. Formic, maleric and oxalic acids have been detected in the electrolyzed solution by ion-exclusion chromatography. In electro-Fenton, all formic acid is transformed into CO_2 and maleric is completely converted into oxalic acid, remaining stable Fe^{3+} - oxalate complexes in the solution.

Other study by **Boye et al. (2003)** was to compare anodic oxidation, electro-Fenton and photoelectro-Fenton treatment of 2,4,5-trichlorophenoxyacetic acid. The methods were carried out in an undivided cell with a Pt anode and O_2-diffusion cathode at pH 2-4 and operated at low current. Photoelectro-Fenton treatment yields fast and complete depollution of solution with 2,4,5-trichlorophenoxyacetic acid concentration up to about saturation. An electro-Fenton reaction leads to 60-65% of mineralization. The anodic oxidation is very poor mineralized the pollutant. The herbicide decay always follows a pseudo-first-order kinetic. Several intermediates can be detect such as 2,4,5-trichlorophenol, 2,5-dichlorohydroquinone, 4,6-dichlororesorcinol and the carboxylic acid group.

Casado et al. (2005) investigated on the degradation of aniline, nitrobenzene, and 4-chlorophenol by photoelectro-Fenton process in a pilot reactor. Using an oxygen diffusion cathode to produce H_2O_2 allowed mineralization of about half of the TOC content in 1 hr because anodic oxidation was coupled with Fenton reaction in the presence of Fe^{2+} catalyst. An intensity of 20 A was applied in a flow cell comprising a Ti/Pt anode and a carbon-PTFE cathode. After electrolysis the samples were exposed to sunlight and complete mineralization was achieved after 50 min. **Irmak et al. (2006)** studied the degradation of 4-chloro-2-methylphenol (PCOC) by electro-Fenton and photoelectro-Fenton processes. H_2O_2 produced by the reduction of oxygen at the carbon cathode reacted with dissolved metal ions to form hydroxyl radicals, which in turn reacted with PCOC sequentially to degrade the aromatic ring. It was found that the degradation rate was increased with increasing the $[Fe^{2+}]/[PCOC]_0$ ratio from 2 to 4. 41.7% TOC decay and complete dechlorination were observed after consuming only 141.4 C electrical charge during a 300 min photoelectro-Fenton treatment. In the case of electro-Fenton system, 280.7 C electrical charge was consumed during 450 min of electrolysis to attain a similar degradation of PCOC. 14.9% TOC removal and 89.3% dechlorination have been obtained in this system under the applied conditions.

The examination on Photoelectro-Fenton was also focused on the ability of sunlight as a source of light. **Casado et al. (2006)** treated benzoic acid, 2,4-dichlorophenoxyacetic acid and oxalic acid by electro-Fenton using electric current at 20 A. A reactor contained an anode and an oxygen diffusion cathode. Both had 100 cm^2 section. Pollutants were oxidized by hydroxyl radicals formed in solution from reaction of Fe^{2+} with electrogenerated H_2O_2, allowing mineralization of benzoic acid and 2,4-D. After electrolysis the samples were exposed to sunlight (Helielectro-Fenton process) and almost complete mineralization was reached after 30-50 min without additional cost. **Floz et al. (2006)** degraded the dye indigo carmine with concentrations up to 0.9 g/l by using electro-Fenton and photoelectro-Fenton with an undivided cell with a Pt or boron-doped diamond (BDD) anode and an O_2 -diffusion cathode at 35 ºC. Complete mineralization is feasible using electro-Fenton with a BDD anode and 1.0 mM Fe^{2+} and when 1.0 mM Fe^{2+} and 0.25 mM Cu^{2+} are combined as catalysts in photoelctro-Fenton with a Pt anode.

Sires et al. (2006) investigated on the degradation of acidic aqueous solution of clofibric acid, the bioactive metabolite of various lipid-regulating drugs by indirect electro-Fenton and photoelectro-Fenton with Fe^{2+} as catalyst using an undivided electrolytic cell with Pt anode and an O_2-diffusion cathode able to electrogenerate H_2O_2. At pH 3, about 80% mineralization was achieved from electro-Fenton process due to the production of hydroxyl radicals from Fenton’s reaction between Fe^{2+} and H_2O_2, but stable Fe^{3+} complexes are formed. The photoelectro-Fenton process was the photodecomposition of these species under UVA irradiation, reaching more than 96% of decontamination. Comparative degradation by anodic oxidation (without Fe^{2+}) yields poor decontamination. The ultimate product was oxalic acid, which forms very stable Fe^{3+} - oxalate complexes under electro-Fenton conditions. These complexes were photodecarboxylated in photoelectro-Fenton under the action of UVA light. **Brillas et al. (2007)** studied the degradation of 2-(2,4-dichlorophenoxy)-propionic acid by various AOPs methods such as anodic oxidation, electro-Fenton and photoelectro-Fenton with a Pt or boron-doped diamond anode. It described that the hydroxyl radicals formed from Fenton's reaction destroys aromatic products more rapidly making the electro-Fenton and photoelectro-Fenton processes more efficient than anodic oxidation. It also found that the decay of 2-(2,4-dichlorophenoxy)-propionic acid follows a pseudo-first-order kinetics.

The photoelectro-Fenton degradation of 2.5 l of solutions containing herbicide mecoprop up to 0.64 g/l, 0.05 M Na_2SO_4 and 0.5 mM Fe^{2+} of pH 3 has been studied using a flow plant with a one-compartment filter-press electrolytic reactor with a boron-doped diamond (BDD) anode and an O_2-diffusion cathode, both of 20 cm^2 area, coupled to either a UVA or solar photoreactor. Electrolyses performed in batch at low constant current density yield overall mineralization in both methods, although the process is much faster and less expensive with solar light. Under these conditions, the degradation rate and efficiency increase strongly with rising mecoprop content. The kinetics for the herbicide decay follows a pseudo-first-order reaction. Mecoprop reacts rapidly with hydroxyl radical ($OH^•$) produced from Fenton's reaction between Fe^{2+} and H_2O_2 electrogenerated at the cathode to yield 4-chloro-o-cresol, 2-methylhydroquinone and 2-methyl-pbenzoquinone as primary reaction products. Fe^{3+}-oxalato and Fe^{3+}-acetato complexes are detected as the most persistent final products. Overall mineralization is attained because Fe^{3+}-oxalato complexes are efficiently photodecomposed by solar irradiation, whereas Fe^{3+}-acetato complexes are slowly destroyed by $OH^•$ formed at the BDD anode from water oxidation. Photoelectro-Fenton with solar light appears to be a viable method to remove chlorophenoxy herbicides in wastewaters at an industrial scale **(Flox et al., 2007)**.

The photoelectro-Fenton process was used to remove COD, color and phosphate from the landfill leachates. The results from Ahmet Altin showed that this process was improved by combining the different type of electro-Fenton process with UV irradiation.

In addition, photoelectro-Fenton was compared with other treatment processes such as electro-coagulation , electro-Fenton and UV/H_2O_2 in terms of treatment efficiency. The high removal efficiencies were observed at the initial pH 3, initial H_2O_2 concentration of 3000 mg L^{-1}, current at 2.5 A and treatment time at 20 min. Removal of COD, color and phosphate under the reported conditions were 94%, 97%, 96%, respectively. The results from the comparative experiments revealed that the photoelectro-Fenton process is more effective than the other treatment processes for the landfill leachate **(Altin 2008).**

Skoumal et al. studied about the degradation of biocide chloroxylenol. They found that at pH 3 biocide can be completely decontaminated using anodic oxidation with a boron-doped diamond (BDD) anode, as well as photoelectro-Fenton with a Pt or BDD anode. The PEF procedure with a BDD anode is the most powerful method leading to total mineralization in about 300 min, practically independent of current density. When current density rises, the degradation rate of processes increases, but they become less efficient due to the larger enhancement of waste reactions of oxidants. Chloroxylenol is much more rapidly removed in EF and PEF than in AO. 2,6-dimethylhydroquinone, 2,6-dimethyl-p-benzoquinone and 3,5-dimethyl-2-hydroxy-p-benzoquinone are identified as aromatic by-products, and maleic, malonic, pyruvic, acetic and oxalic acids are found as generated carboxylic acids. A general pathway for chloroxylenol mineralization is proposed **(Skoumal et al., 2008).**

The mineralization of an azo dye Acid Red 14 (AR14) by the photoelectro-Fenton process was studied in an undivided electrochemical reactor with a RuO_2/Ti anode and an activated carbon fiber (ACF) cathode able to electrochemically generate H_2O_2. Results indicate that the electro-Fenton process yielded about 60–70% mineralization of AR14, while the photoelectro-Fenton could mineralize AR14 more effectively (more than 94% total organic carbon (TOC) removal) even at low current densities assisted with UV irradiation after 6 h of electrolysis. The mineralization current efficiency (MCE) of the PEF process increased with increasing AR14 concentrations. In addition, the initial solution pH ranging from 1.49 to 6.72 had little influence on the TOC removal probably due to the formation of organic carboxylic acids which balanced the pH increase caused by the cathodic generation of hydrogen gas. The ACF cathode showed long-term stability during multiple experimental runs for degradation of AR14, indicating its good potential for practical applications in treating refractory organic pollutants in aqueous solutions (**Wang et al, 2008).**

From the previous literature review, the study of 2,6-dimethylaniline degradation has not been investigated yet. Therefore, it is interesting to determine whether 2,6-dimethylaniline can also be effectively oxidized by AOPs, namely, the Fenton process and the electro-Fenton process. Moreover, in this study, a novel photoelectro-Fenton method was employed in which Fenton’s reagent was utilized to produce hydroxyl radical in the electrochemical cell and ferrous ion was regenerated via the reduction of ferric ion on the light source and cathode. Effects of initial pH, Fe^{2+} dosage, H_2O_2 concentration, electric current and UV light numbers on the processes were investigated. The aniline degradation was also examined by a novel photoelectro-Fenton process. The comparison of various AOPs on the degradation of 2,6-dimethylaniline and aniline was examined by using Photolysis, Electrolysis (Anodic Oxidation), Hydrogen peroxide oxidation, Fenton process, electro-Fenton process, Photo-Fenton process and photoelectro-Fenton process. In addition, in order to define the degradation ability of each process, the study also determined the removal efficiency, the TOC removal, COD removal, and the kinetic study of 2,6-dimethylaniline and aniline. Moreover, the identification of intermediates and a possible degradation pathway for 2,6-dimethylaniline is proposed in this study.

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CHAPTER III

METHODOLOGY

3.1. Experimental Chemicals and Instruments

3.1.1. Chemicals

All chemical substances used in this study were analytical reagent grade. Aqueous solutions were prepared from using de-ionized water from a Millipore system with a resistivity of 18.2 MΩ cm^{-1}

1. Target organic compounds

Name	Formula	Company
2,6-Dimethylaniline (98%)	$C_8H_{11}N$	MERCK
Aniline (99.5%)	$C_6H_5NH_2$	MERCK

2. Fenton’s reagent

Name	Formula	Company
Ferrous sulfate heptahydrated	$FeSO_4.7H_2O$	MERCK
Hydrogen peroxide (35%)	H_2O_2	MERCK

3. For pH adjustment

Name	Formula	Company
Perchloric acid (70-72%)	$HClO_4$	MERCK

4. For terminate the reaction

Name	Formula	Company
Sodium hydroxide (99%)	NaOH	MERCK

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5. GC analysis

Name	Formula	Company
Acetone (98%)	CH_3COCH_3	MERCK
Nitrogen gas (99.99%)	N_2	-
Hydrogen gas (99.99%)	H_2	-
Air	-	-

6. COD measurement

Name	Formula	Company
Silver sulfate	$AgSO_4$	MERCK
Mercury Sulfate	$HgSO_4$	MERCK
Sulfuric acid (95-97%)	H_2SO_4	MERCK
Ammonium iron(III) sulfate hexahydrate	$FeH_8N_2O_8S_2$ .6 H_2O	MERCK
Potassium dichromate	$Cr_2K_2O_7$	MERCK
Ferroin indicator solution	-	MERCK

7. Ferrous ion measurement

Name	Formula	Company
Hydrochloric Acid	HCl	MERCK
Ammonium Acetate	$NH_4C_2H_3O_2$	MERCK
1,10 – phenanthroline monohydrate	$C_{12}H_8N_2.H_2O$	MERCK

8. Hydrogen peroxide measurement

Name	Formula	Company
Potassium iodide	KI	MERCK
Ammomium molybdate	$(NH_4)_6Mo_7O_{24}.4H_2O$	MERCK
Ammonium nitrate	NH_4NO_3	MERCK
Starch	-	MERCK
Sodium thiosulfate	$Na_2S_2O_3$	MERCK

9. HPLC measurement

Name	Formula	Company
Acetonitrile (99.9%)	CH_3CN	MERCK

3.1.2. Experimental Instruments

1. pH meter: a SUNTEX pH/mV/TEMP (SP-701) meter.

2. UV-VIS Spectrophotometer: SHIMADZU UV-1201

3. Thermometer: 0-100 °C; ± 1 °C

4. Auto Pipette: 1,000 µl and 5,000 µl

5. Weighing Machine (4-Digits Balance): METTLER TOLEDO (AB 204-5)

6. Magnetic Stirrer: Fargo (MS-90)

7. Magnetic Bar: 30 x 8 mm

8. Glassware

9. Clock Timer

10. Membrane Filter 0.45 µm and 0.2µm

11. GC Syringe: 20 µl

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12. Total organic carbon analyzer: liquiTOC (elementar) with high temperature combustion method
13. High performance liquid chromatography (HPLC): with SpectraSYSTEM model SN4000 pump and Asahipak ODP-506D column (150mm × 6mm × 5µm).
14. Gas chromatography (GC): equipped with flame ionization detector (FID) and a SUPELCO Equity^{TM} – 5 Capillary Column (length: 15m; id: 0.15 µm).
15. Atomic absorption spectrophotometer (AAS): Ferrous anaysis at 510 nm
16. Ion Chromatograph (IC): (Dionex DX-120) equipped with RFC-30 EGCII (KOH), IonPac®AG11 guard column(4x50mm), IonPac®AS11 analytical column (4x250mm), ASRS®-ULTRA II (4mm) suppressor and conductivity detector.
17. UV light: The UV light bought from SUNBEAM with tube diameter 3 mm, length 100 mm. The input voltage of inverter is 12 V, output is 1.80 v, current 5 mA. The brightness is between 28000 to 30000 cd/m^2 with the lifetime 30,000 hrs.
18. Electrode:
    -Anode : Mesh-type titanium metal coated with IrO_2/RuO_2:size 15 cm x 20 cm (DSA - Dimensionally Stable Anodes) with area 600 cm^2
    -Cathode: Stainless steel mesh:size 15 cm x 20 cm with area 900 cm^2
19. Power supply: The electrodes were connected to a Topward 33010D power supply operated at the desired electric current.
20. Power supply for UV light:
    The UV light were connected to the power supply E-safe 2003, Switching Power Supply (Max. 300W), Model : LC-B300ATX

3.2. Analytical Methods

3.2.1. Measurement of 2,6-Dimethylaniline and Aniline by GC and HPLC

Firstly, the liquid samples were filtered through 0.45 µm syringe microfilters (when using GC and 0.2 µm when using HPLC) to separate precipitated iron from the solutions. Next, the analysis of residual sample was addressed by using a gas chromatograph (GC) (HP 4890II) equipped with flame ionization detector (FID) and a SUPELCO Equity^{TM} – 5 Capillary Column (length: 15m; id: 0.15 µm). The chromatographic conditions for 2,6-dimethylaniline and aniline were as follows : the initial oven temperature at 85^{o}C for 1.50 minutes, final oven temperature was 200^{o}C with and increasing rate of 65^{o}C/minutes were operated for the chromatographic condition of 2,6-Dimethylaniline. Operation also included injector temperature of 250^{o}C, and nitrogen carrier gas, flow rate at 14.6 ml/minutes. The retention time for 2,6-dimethylaniline detection is 2.7-2.8 minute and aniline is around 2.2 minute.

GC condition for analyze 2,6-dimethylaniline: flow rate: 10 psi or 50 kPa

Temperature	**°C**
initial	85
Rate/min	65
injector temperature	250
detector temperature	250

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Aniline concentrations were determined by high performance liquid chromatography (HPLC) where the mobile phase was 29%Acetonitrile with DI water 71%. The column were operated between 18 and 22 ℃. The pump was Spectra

SYSTEM model SN4000 with the operating flow rate at 1 ml/min through an Asahipak ODP-506D column (150mm × 6mm × 5μm). The 254 nm outputs from UV1000 detector was measured. 20 μL of sample was injected.

3.2.2. Analysis of total organic carbon

The TOC analyzer was used for analyzing the total organic carbon. TOC were analyzed by liquiTOC (elementar) with high temperature combustion method. Before the analysis, all supernatants were diluted 10 times by DI water and pH was adjusted to 10 with ammonium, and then the solutions were filtered with 0.45 μm microfilters to separate the iron sludge from the solutions.

3.2.3. Analysis of chemical oxygen demand

COD was measured by closed reflux titrimetric method as described in Appendix A.

3.2.4. Analysis of total iron concentration

The samples were digested by nitric acid and diluted by DI water. Then, the samples were filtered with 0.45 μm microfilters to separate small particles from the solutions. Next, the total iron concentration was analyzed using an atomic absorption spectrophotometer.

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3.2.5. Analysis of ferrous concentration

The samples were analyzed by phenanthroline method in Appendix A. Deionized water was added to making up volume of 50 ml.

3.2.6. Analysis of hydrogen peroxide

The concentration of hydrogen peroxide was determined by standard iodometric method where potassium iodide with $Na_2S_2O_3$ solution was used as a reactant as described in Appendix A.

3.2.7. Analysis of Anion

Anion were determined by Ion Chromatograph (Dionex DX-120) equipped with RFC-30 EGCII (KOH), IonPac$^{®}$AG11 guard column(4x50mm), IonPac$^{®}$AS11 analytical column(4x250mm), ASRS$^{®}$-ULTRA II (4mm) suppressor and conductivity detector. The intermediate (oxalic acid, citric acid, formic acid, acetic acid, lactic acid, maleic acid, nitrate, nitrite, ammonium, sulphate, chloride, perchloric acid) were determined.

3.2.8. Intermediate analysis

The identification of other organic intermediates in the AOPs's reaction was determined by using GC-MS. GC-MS (Agilent 6890,Agilent 5975) equipped with DB-5MS capillary column (30 m x 0.25 mm i.d., 0.25 mm film, from J&W, USA) was used. The GC temperature program was as follows: 40 °C for 2 min, followed by a 15 °C/min ramp to 280 °C, and hold for 5 min.

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3.3. Fenton, Electro-Fenton and Photoelectro-Fenton Reactors

3.3.1. Fenton reactor

The reactor was made of acrylic (15cm x 21cm x 20cm). The dimensions of the reactor are shown in Figure 3.1, 3.2 and 3.3. Mixers were installed in the reactor to provide agitation.

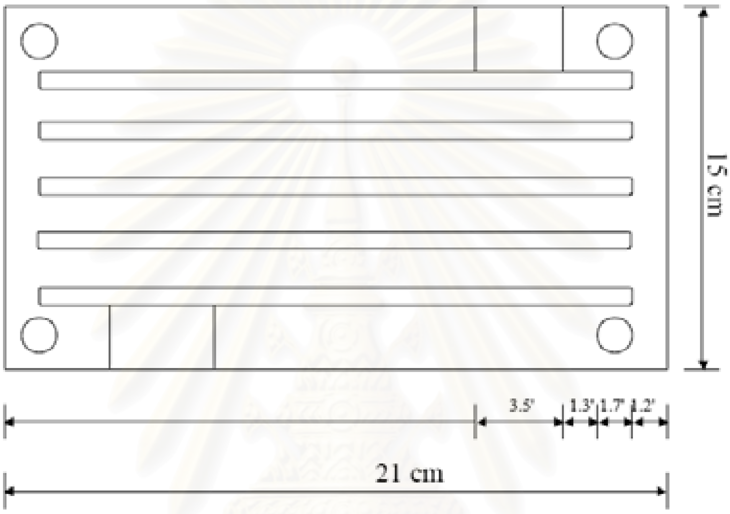

Figure 3.1 Reactor top view

Figure 3.2 Reactor side view

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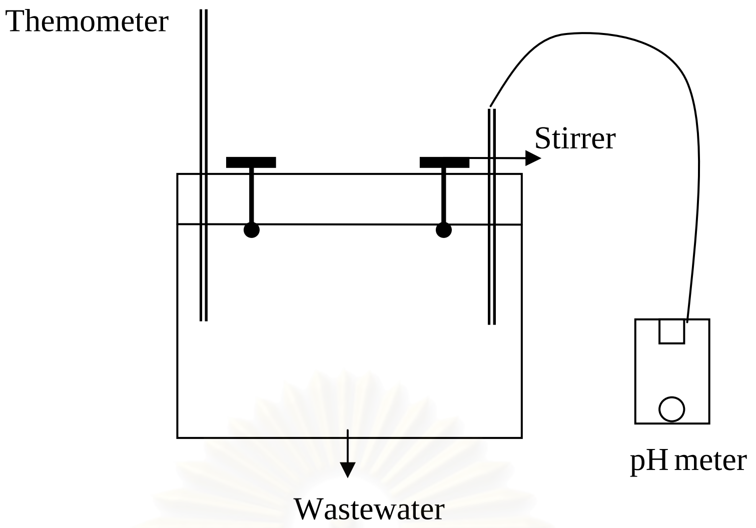

Figure 3.3 Fenton Reactor configuration

3.3.2. Electro-Fenton reactor

The electro-Fenton anode is special net made from Ti/Pt or DSA and the cathode was stainless steel. The anode and cathode were connected with DC power supply.

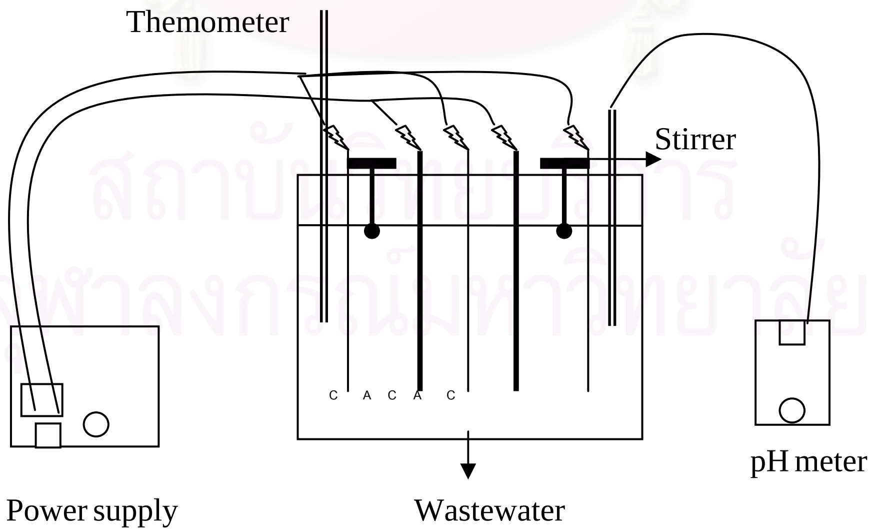

Figure 3.4 Electro-Fenton Reactor configuration

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3.3.3. Photo-Fenton and Photoelectro-Fenton Reactor

The photoelectro-Fenton reactor was same as in the electro-Fenton process but it has the addition of UV light as shown in Figure 3.5. For the photo-Fenton reactor, electrodes, both anodes and cathodes are removed. Only UV lights are needed in the system.

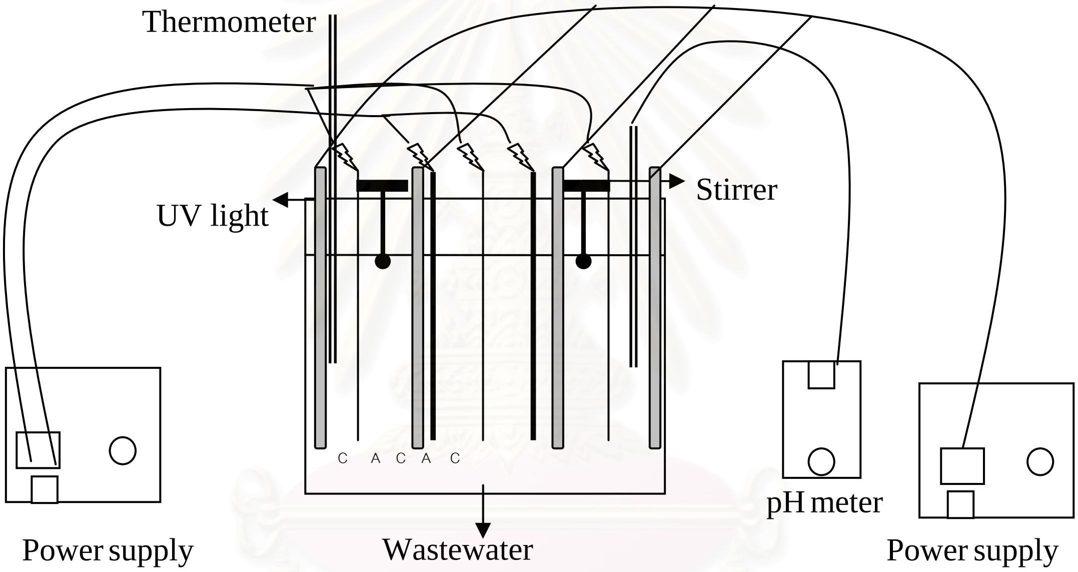

Figure 3.5 Photoelectro-Fenton (UV) Reactor configuration

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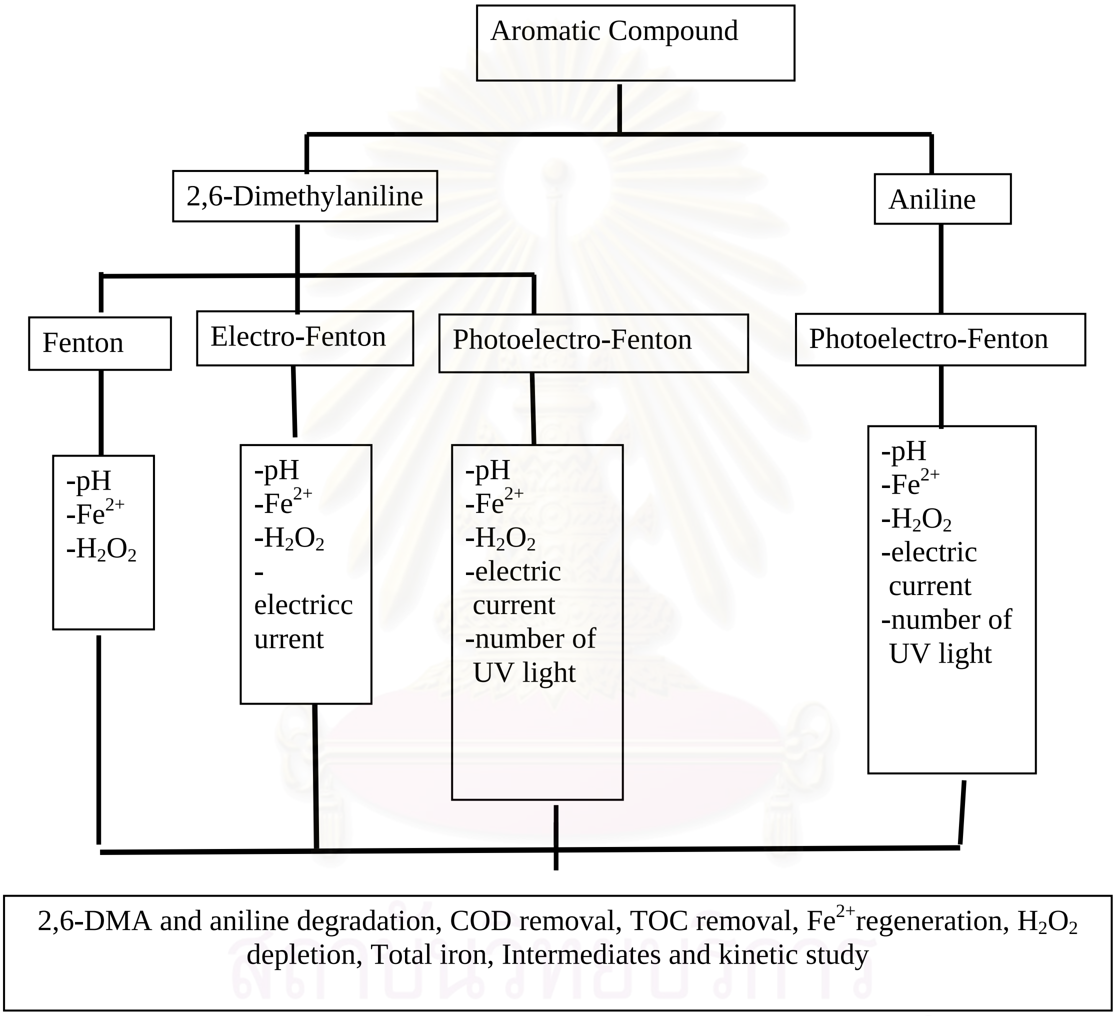
3.4. Experimental Procedures

The experimental procedure for the degradation of 2,6-dimethylaniline and aniline by Fenton, electro-Fenton and photoelectron-Fenton processes were followed scheme 1.



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Scheme 1. The experimental procedures

- The experiments were divided into 2 sections:

  1. 2,6-Dimethylaniline degradation by Fenton processes
  2. Aniline degradation by Fenton processes

3.4.1. 2,6-Dimethylaniline degradation by Fenton processes

3.4.1.1. Effect of initial condition on the decomposition of 2,6-dimethylaniline by Fenton process

The studied conditions include:

- effect of initial pH
- effect of initial hydrogen peroxide concentration
- effect of initial ferrous ion concentration
- effect of initial 2,6-dimethylaniline concentration

The experiments started with a low concentration of 2,6-dimethylaniline (1mM). The pH values were varied as 1, 1.5, 2, 2.5, 3, 3.5, and 4, while 1mM of 2,6-dimethylaniline was used as initial concentration, in evaluating the effect of initial pH value. From these studies, the optimum condition for treating 2,6-dimethylaniline was obtained.

To study the effect of hydrogen peroxide dosage on the degradation of 2,6-dimethylaniline, H_2O_2 concentration were varied as 5 mM, 10 mM, 20 mM, 40 mM, 60 mM, 100 mM, 120 mM and 150 mM for 1 mM of 2,6-dimethylaniline. To investigate the effect of ferrous ion on pollutant removal, amounts of ferrous ion were varied as 0.1 mM, 0.25 mM, 0.5 mM, 1 mM, 2 mM and 2.5 mM for 1 mM of 2,6-dimethylaniline concentration. The effect of initial 2,6-dimethylaniline concentration was also determined by varying 2,6-dimethylaniline concentration from 0.5 mM, 1 mM and 5 mM, while, hydrogen peroxide was 20 mM, ferrous ion was 1 mM and pH was 2.

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Experiment procedures - All the solutions with the 2,6-dimethylaniline was prepared in the reactor. Then, ferrous sulfate heptahydrate was completely mixed with the prepared solution in the reactor. The initial pH was adjusted to the desire pH with $HClO_4$ and NaOH. The reaction was initiated by adding the hydrogen peroxide. The procedures were shown in (3.6). For all experiments, 1 ml samples were withdrawn at a selected time and the Fenton reaction was stopped by adding 9 ml of 0.1 M NaOH. After adding NaOH, the solutions were filtered by 0.45 µm syringe microfilters before analysis.

The samples were taken at 0, 2, 5, 10, 20, 40, 60, 90, 120, 180, 240 and 300 min while the pH and temperature were recorded. Besides, 1 ml samples were taken for residual hydrogen peroxide analysis and 2 ml was taken for residual ferrous ion analyzing.

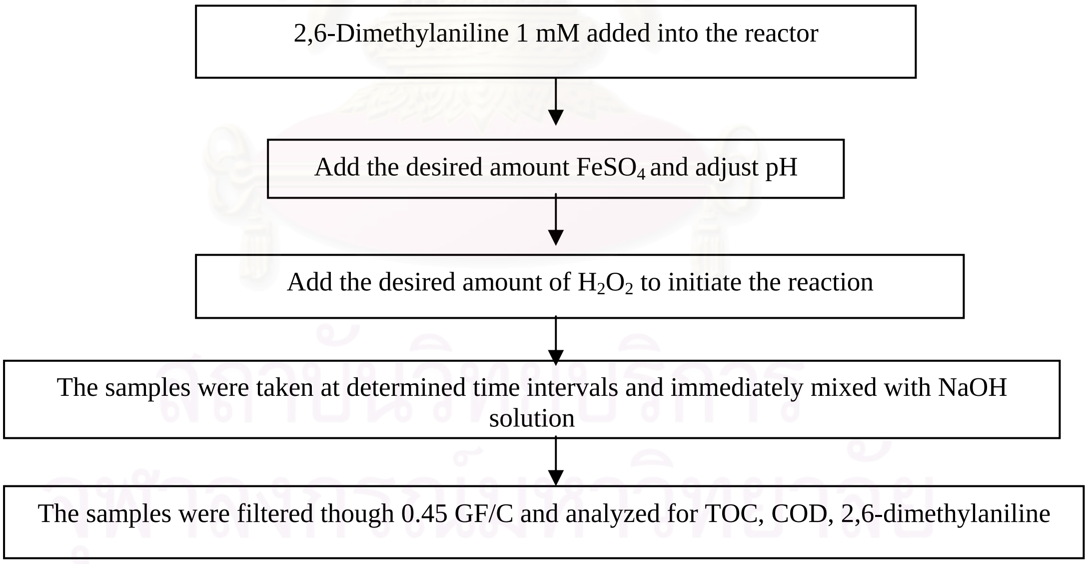

Figure 3.6 Effect of initial condition study procedures

3.4.1.2. Effect of initial condition on the decomposition of 2,6-dimethylaniline by electro-Fenton process

The studied conditions include:

- effect of initial pH
- effect of initial hydrogen peroxide concentration
- effect of initial ferrous ion concentration
- effect of initial 2,6-dimethylaniline concentration
- effect of electrical current application

The study of the effect of initial pH, hydrogen peroxide concentration, ferrous ion concentration, 2,6-dimethylaniline concentration were the same as that of the Fenton process which is mentioned above. For the effect of electrical current application, the electric current was varied from 0.5 A, 1 A, 1.43 A, 4 A and 6 A.

3.4.1.3. Effect of initial condition on the decomposition of 2,6-dimethylaniline by Photoelectro-Fenton process

The studied conditions include:

- effect of initial pH
- effect of initial hydrogen peroxide concentration
- effect of initial ferrous ion concentration
- effect of initial 2,6-dimethylaniline concentration
- effect of electrical current applied
- effect of number of UV lamps

The experiments started with a low concentration of 2,6-dimethylaniline (1mM). The pH values were varied as 1.5, 2.0, 2.5 and 3.0 while 1 mM of 2,6-dimethylaniline was used as initial concentration in evaluating the effect of initial pH value. From these studies, the optimum condition for treating 2,6-dimethylaniline by Photoelectro-Fenton was obtained.

To study the effect of hydrogen peroxide dosage on the degradation of 2,6-dimethylaniline, H_2O_2 concentration were varied as 5 mM, 20 mM, 40 mM, 100 mM and 120 mM. To investigate the effect of ferrous ion on pollutant removal, amount of ferrous ion were varied as free Fe^{2+}, 0.1 mM, 0.25 mM, 0.5 mM, 1 mM and 2 mM for 1 mM of 2,6-dimethylaniline concentration. The effect of initial 2,6-dimethylaniline concentration was also determined by vary 2,6-dimethylaniline concentration from 0.5 mM, 1 mM and 5 mM. The effect of numbers of UV lamps were varied from 4, 8 and 12 lamps.

Experimental procedures - All the solutions with the 2,6-dimethylaniline was prepared in the reactor. Ferrous sulfate heptahydrate was completely mixed with the prepared solution in the reactor. The initial pH was adjusted to the desired pH with $HClO_4$ and NaOH. The reaction was initiated by opening the UVA lamps and adding the hydrogen peroxide.

3.4.2. Aniline degradation by Fenton processes

3.4.2.1. Effect of initial condition on the decomposition of aniline by Fenton process

This part of experiment was using the information from a previous study. The study of **Parichat, 2003** showed that for removal of aniline 1 mM, 20 mM of hydrogen peroxide, 0.5 mM of ferrous ion at pH 3 is needed. This condition could degrade 100% of the aniline in 2 hours. This study also used this condition as a control experiment.

3.5.2.2. Effect of initial condition on the decomposition of aniline by electro-Fenton process

From the previous study of **Parichat, 2003.** on the degradation of aniline, the optimum condition for aniline removal was used. Initial aniline concentration at 1mM, 20 mM of hydrogen peroxide, 0.5 mM of ferrous ion and pH 3 were used in this part of experiment. For the effect of electric current, 1 A of electricity was used. The previous experiment shows that aniline can be degraded on this condition in 90 min.

3.5.2.3. Effect of initial condition on the decomposition of aniline by Photoelectro-Fenton process

The studied conditions include:

- effect of initial pH
- effect of initial hydrogen peroxide concentration
- effect of initial ferrous ion concentration
- effect of electrical current applied
- effect of number of UV lamps

The pH values were varied as 2, 2.5, 3 and 3.5 while 1 mM aniline was used as the initial concentration in evaluating the effect of initial pH value. From these studies, the optimum condition for treating aniline by Photo-Fenton was obtained. To study the effect of hydrogen peroxide dosage on the degradation of aniline, H_2O_2 concentration were varied as 5 mM, 20 mM, 40 mM, 100 mM and 120 mM. To investigate the effect of ferrous ion on pollutant removal, amounts of ferrous ion were varied as free Fe^{2+}, 0.1 mM, 0.25 mM, 0.5 mM, 1 mM and 2 mM for 1 mM of 2,6-dimethylaniline concentration. For the effect of electrical current application, the electric current was varied from 0.5 A, 1.0 A, 1.43 A and 4.0 A. The effect of UVA lamps amounts were varied from 4, 8 and 12 lamps.

Experimental procedures - All the solutions with aniline was prepared in the reactor. Ferrous sulfate heptahydrate was then completely mixed with the prepared solution in the reactor. The initial pH was adjusted to the desired pH with $HClO_4$ and NaOH. The reaction was initiated by opening the UVA lamps and adding the hydrogen peroxide.

3.4.3 Fenton Experiment

The 2,6-dimethylaniline and aniline solution were adjusted to the desired pH by an addition of $HClO_4$. After that, a predetermined amount of catalytic ferrous sulfate was added and thoroughly agitated by a mechanical mixer until the solid particles were completely dissolved. The solution pH was rechecked again prior to the addition of H_2O_2 solution and the reaction was simultaneously started. The H_2O_2 was supplied into the solution. Samples of 1 ml were taken at every predetermined time interval and was immediately injected into a tube containing 9 ml of 1 N NaOH to stop the reaction. Samples were analyzed for COD, TOC, aniline and 2,6-dimethylaniline concentration.

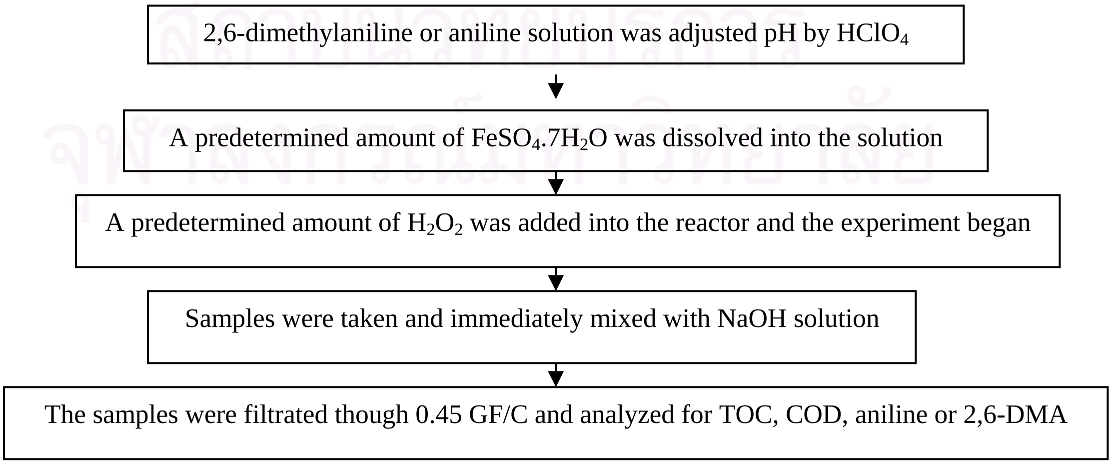

Figure 3.7 Flow chart for Fenton experiment

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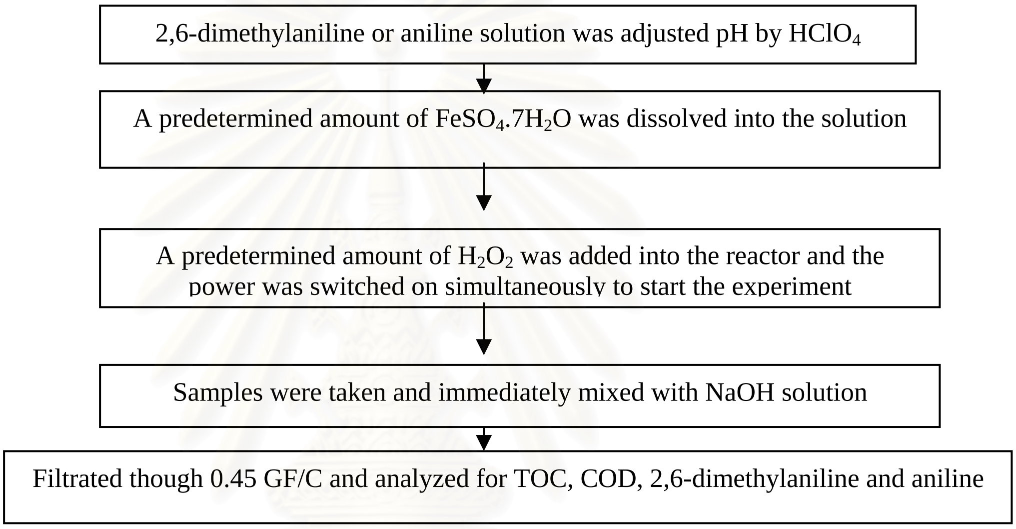
3.4.4. Electro-Fenton Experiment

In this experiment, an electrical supply unit which consisted of a stainless steel cathode, a $Ti/IrO_2/RuO_2$ anode, and a regulator DC power supply were installed additionally in the reactor. Most procedures were similar to those of typical Fenton reaction, however, in this scenario, the electrical current was delivered through out the experimental period.



2,6-dimethylaniline or aniline solution was adjusted pH by $HClO_4$

A predetermined amount of $FeSO_4.7H_2O$ was dissolved into the solution

A predetermined amount of H_2O_2 was added into the reactor and the power was switched on simultaneously to start the experiment

Samples were taken and immediately mixed with NaOH solution

Filtrated though 0.45 GF/C and analyzed for TOC, COD, 2,6-dimethylaniline and aniline

Figure 3.8 Flow chart for electro-Fenton experiment

3.4.5. Photo-Fenton Experiment

In this experiment, the process in the beginning was similar to Fenton process but will including the photo process with UVA lamps.

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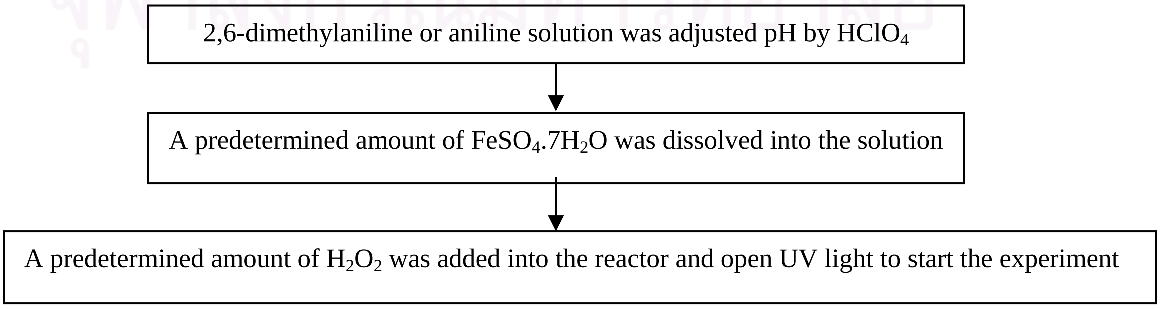


2,6-dimethylaniline or aniline solution was adjusted pH by $HClO_4$

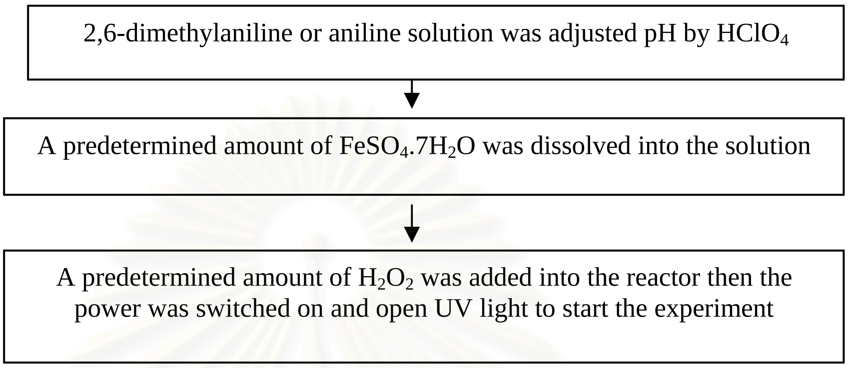
A predetermined amount of $FeSO_4.7H_2O$ was dissolved into the solution

A predetermined amount of H_2O_2 was added into the reactor and open UV light to start the experiment

Figure 3.9 Flow chart for photo-Fenton experiment

3.4.6. Photoelectro-Fenton process

In this experiment, the process in the beginning was similar to electro-Fenton process but will including the photo process with UVA lamps.



2,6-dimethylaniline or aniline solution was adjusted pH by $HClO_4$

A predetermined amount of $FeSO_4.7H_2O$ was dissolved into the solution

A predetermined amount of H_2O_2 was added into the reactor then the power was switched on and open UV light to start the experiment

Figure 3.10 Flow chart for photoelectro-Fenton experiment

3.5. Experimental Scenarios

Scenario A Determination of effects of parameters on the degradation of 2,6-dimethylaniline by Fenton and electro-Fenton process as shown in Table 3.1

Table 3.1 Detail for scenario A

2,6-Dimethylaniline (mM)	Control parameters
1	pH , Fe^{2+}, H_2O_2 , Electrical current

Scenario B Determination of effect pH on the degradation of 2,6-dimethylaniline by Fenton and electro-Fenton processes with the conditions as shown in Table 3.2

Table 3.2 Detail for scenario B

2,6-Dimethylaniline (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	pH
1	20	1	2, 2.5, 3, 3.5, 4

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Scenario C Determination of effect of Fe^{2+} concentration on the degradation of 2,6-dimethylaniline by Fenton and electro-Fenton with the conditions as shown in Table 3.3

Table 3.3 Detail for scenario C

2,6-Dimethylaniline (mM)	pH	H_2O_2(mM)	Fe^{2+} (mM)
1	3.0	20	0.1 , 0.25, 0.5 , 1 , 2 , 2.5

Scenario D Determination of effect of H_2O_2 concentration on the degradation of aniline and 2,6-dimethylaniline by Fenton and electro-Fenton process with the conditions as shown in Table 3.4

Table 3.4 Detail for scenario D

2,6-Dimethylaniline (mM)	pH	Fe^{2+} (mM)	H_2O_2 (mM)
1	From scenario B	From scenario C	5, 10, 20, 40, 60, 100, 120 , 150

From scenario A-D, the optimum condition for Fenton process of 2,6-dimethylaniline at low concentration 1 mM will be obtained .

Scenario E Determination of effect of electrical current on the degradation of 2,6-dimethylaniline by electro-Fenton process with the conditions as shown in Table 3.5

Table 3.5 Detail for scenario E

2,6-Dimethylaniline (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	pH	Electrical current (A)
1	From scenario D	From scenario C	From scenario B	0.5, 1.0, 1.43, 4.0, 6.0

Scenario F Determination of effect of number of UV lamp on the degradation of 2,6-dimethylaniline by photo-Fenton process with the conditions as shown in Table 3.6

Table 3.6 Detail for scenario F

2,6-Dimethylaniline (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	pH	Number of UV lamps
1	From scenario D	From scenario C	From scenario B	4, 8 , 12

Scenario G Determination of effect of number of UV lamp on the degradation of 2,6-dimethylaniline by photoelectro-Fenton process with the conditions as shown in Table 3.7

Table 3.7 Detail for scenario G

2,6-Dimethylaniline (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	pH	Electrical current (A)	Number of UV lamps
1	From scenario D	From scenario C	From scenario B	From scenario E	4, 8, 12

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Scenario H Determination of effects of parameters on the degradation of aniline by photo-Fenton and photoelectro-Fenton process as shown in Table 3.8

Table 3.8 Detail for scenario H

2,6-Dimethylaniline (mM)	Control parameters
1	pH, Fe^{2+}, H_2O_2 , Electrical current, Number of UVA lamps

From the previous study, the optimum condition for degradation of aniline by Fenton and electro-Fenton are: aniline = 1mM, ferrous ion = 0.5 mM, hydrogen peroxide = 20 mM, pH 3 and electroical current = 1 A.

Scenario I Determination of effect of number of UV lamp on the degradation of aniline by photo-Fenton process with the conditions as shown in Table 3.9

Table 3.9 Detail for scenario I

Aniline (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	pH	Number of UV lamps
1	20	0.5	3	4, 8 , 12

Scenario J Determination of effect of number of UVA lamps on the degradation of aniline by photoelectro-Fenton process with the conditions as shown in Table 3.10

Table 3.10 Detail for scenario J

Aniline (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	pH	Electrical current (A)	Number of UV lamps
1	20	0.5	3	1	4, 8, 12

And the intermediate products from Fenton, electro-Fenton, photo-Fenton and photoelectro-Fenton process also were identified.

CHAPTER IV
RESULTS AND DISCUSSION

4.1. 2,6-Dimethylaniline degradation by Fenton processes

The degradation of 2,6-dimethylaniline were studied by using three main processes including Fenton, electro-Fenton and photoelectro-Fenton processes in order to compare the efficiency of each processes on the oxidation of 2,6-dimethylaniline. In this section, the detailed explanation on each factor such as pH, ferrous ion, hydrogen peroxide, electric current and number of UV lights will be shown.

4.1.1. Effect of initial condition on the decomposition of 2,6-dimethylaniline by various processes

4.1.1.1. Fenton process

Fenton process is one of AOPs which is known for more than a century and consider as a successful treatment for industrial wastewater (Rios-Enriquez et al., 2004). It involves the production of hydroxyl radicals ($OH^{\bullet}$) which is a highly reactive oxidant (E° = 2.8 V) that can oxidize and mineralize almost all the organic pollutants (Zhang et al., 2006, Sun et al., 2007, Muruganandham et al., 2004).

Fenton’s reagent is an aqueous mixture of ferrous ion and hydrogen peroxide that has a rapid oxidation rate, relatively cheap and easily to operated and maintained (Walling C., 1975). The Fenton’s reagent was first described in 1894 and is generally occurred in acidic medium between pH 2 -4 (Rodriguez et al., 2003, 10 Utset et al., 2000) and can involve the steps as shown in the flow chart below that described the fate of Fenton’s reaction on the degradation of organic compounds including equations (1-8).

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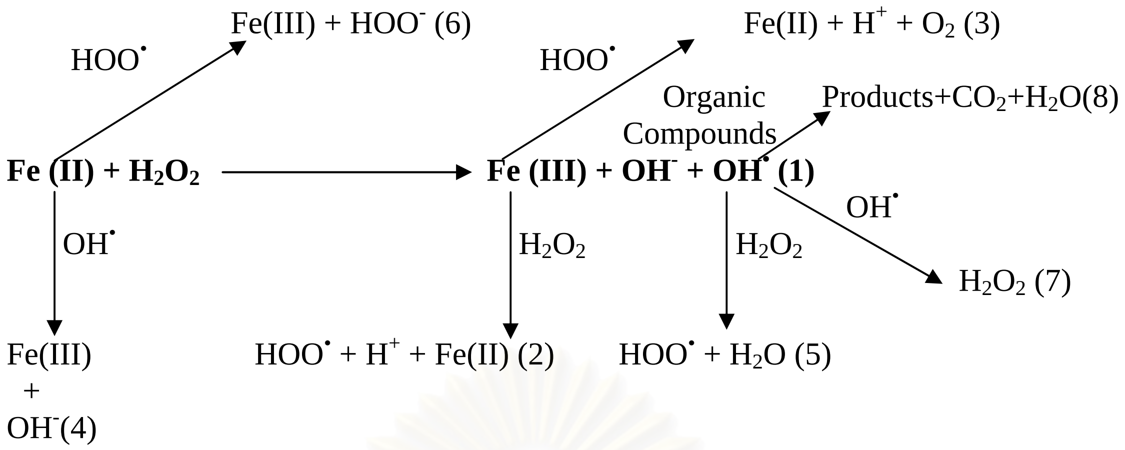

Figure 4.1. Fate of Fenton's reaction on the degradation of organic compounds.

During Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals and would degrade the organic compounds. However, the rate constant of reaction (1) is around 63 $M^{-1}s^{-1}$ (Kang et al., 2002), while the rate of reaction (2) is only 0.01-0.02 $M^{-1}s^{-1}$(Martinez et al., 2003). This indicated that ferrous ions are consumed more rapidly than they are produced. The hydroxyl radicals ($OH^\bullet$) will degrade organic compounds through equation (8) and hydrogen peroxide can also react with Fe^{3+} via reaction (2).

1) Effect of initial pH on the degradation of 2,6-dimethylaniline

The pH is the important parameter of the treatment efficiency in Fenton's reaction. Normally, the Fenton reaction has the highest efficiency when the pH is around 2-4.In the 2,6-dimethylaniline degradation by the Fenton process, the pH dropped as time progressed. The initial and final pH of solutions are listed in Table 4.1.

Table 4.1. The initial and final pHs of 2,6-dimethylaniline solution during Fenton process at the different initial pH ; [2,6-dimethylaniline] = 1 mM, [H_2O_2] = 20 mM, Fe^{2+} = 1 mM.

pH $_{\text{initial}}$	pH $_{\text{final}}$
1	0.92
1.5	1.43
2	1.96
2.5	2.47
3	2.90
3.5	3.21
4	3.56

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Figure 4.2 shows that the pH had an effect on 2,6-dimethylaniline degradation. When the pH was 1, the removal efficiency was 39.62%. The removal efficiency was 51.55% when using pH 1.5. The degradation of 2,6-dimethylaniline increased as pH increased to pH 2 with 64% removal efficiency. When the pH was further increased the degradation decreased as also illustrated in Figure 4.2. As pH was increased from 2.5 to 4, the degradation efficiency decreased from 63% to 31%. Figure 4.2 indicates that the initial pH that induces the best Fenton's reaction is around 2.

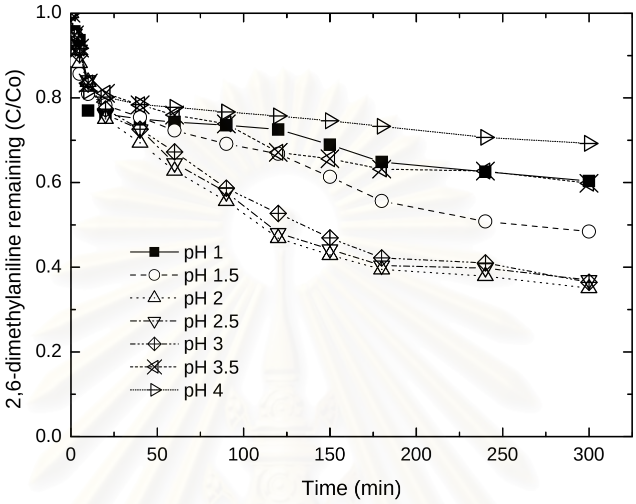

Figure 4.2. The effect of initial pH on 2,6-dimethylaniline removal

COD removal efficiency followed the same trend as 2,6-dimethylaniline removal. COD removal increased from 18.3%, 23.1% to 28% as pH increased, from 1, 1.5, and 2. The highest COD removal about 28%, was achieved at pH 2. When pH was further increased, COD removal decreased. It is shown in Figure 4.3. that at pH 2.5, 3, 3.5 and 4, COD removal decreased from 24.6%, 21.5%, 16.3% and 16%, respectively.

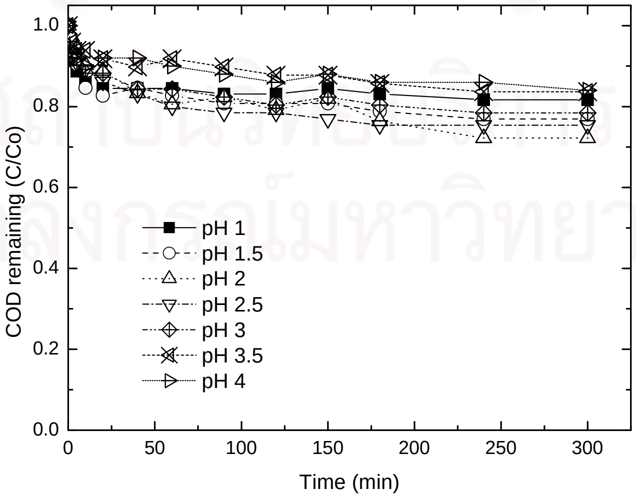

Figure 4.3. The effect of initial pH on COD removal

The degradation of 2,6-dimethylaniline can also be monitored by measuring the total organic carbon (TOC) reduction during Fenton process. TOC analysis was performed in order to know the amount of organic compounds that were depleted to carbon dioxide during the chemical oxidation (Chamarro et al., 2001). The highest TOC removal by Fenton process was around 26% when the pH was 2. The decrease of TOC can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton's reaction. The removal efficiency of 2,6-dimethylaniline and COD were shown in Figure 4.4.

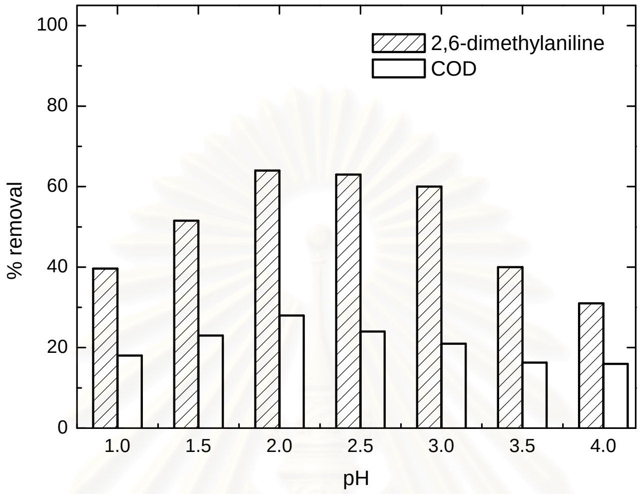

Figure 4.4. 2,6-Dimethylaniline and COD removal vs. $[pH]_I$ by Fenton process

Moreover, the initial degradation rate of 2,6-dimethylaniline at different initial pHs also show that at the optimum pH (pH 2) the highest initial rate of 0.0170 $mMmin^{-1}$ was achieved. At pHs 1 to 4, the initial rates are 0.0123, 0.0148, 0.0170, 0.0168, 0.0163, 0.0159 and 0.0153 $mMmin^{-1}$ when the initial pH was adjusted from 1, 1.5, 2, 2.5, 3, 3.5 and 4, respectively (as shown in Table 4.2). This phenomenon followed the same trend as 2,6-dimethylaniline removal, COD and TOC removal.

Table 4.2. Effect of initial pH on 2,6-dimethylaniline initial degradation rate at the different initial pH ; [2,6-DMA] = 1 mM, $[H_2O_2]$ = 20 mM, Fe^{2+} = 1 mM

$pH_{initial}$	**Initial degradation rate ($mMmin^{-1}$)**
1	0.0123
1.5	0.0148
2	0.0170
2.5	0.0168
3	0.0163
3.5	0.0159
4	0.0153

The decrease in 2,6-dimethylaniline degradation at low pH is probably due to the formation of $Fe(OH)^+$. It is formed at low pH and its activity is higher than Fe^{2+} in Fenton oxidation. The $Fe(OH)^+$ reacts more slowly with hydrogen peroxide and produces less hydroxyl radicals. This reduces the degradation efficiency. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant at a very low pH and also the reaction of Fe^{3+} with hydrogen peroxide is inhibited. (Pignatello J.J., 1992, Wang S., 2007). On the contrary, ferrous ions are unstable at a pH > 4.0 and they easily form ferric ions, which have a tendency to produce ferric hydroxo complexes or ferric oxyhydroxides (Wang S., 2007). At higher pH, the oxidation efficiency of Fenton's reagent may decrease because ferric ions could form $Fe(OH)_3$, which has a low activity and will not react with hydrogen peroxide. The ferric ions in the solution that can react with hydrogen peroxide are so reduced via equation (9) with the rate constant 0.001-0.01 $M^{-1}s^{-1}$ (Neyen et al., 2003).

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (9)$$

Hydrogen peroxide is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability. Thus, hydrogen peroxide and ferrous ions have difficulty in establishing an effective redox system and their degradation is also less effective (Kuo WG., 1992). Hence, the optimum initial pH for this Fenton process should be pH 2.

2) Effect of initial ferrous ion concentration on the degradation of 2,6-dimethylaniline

Ferrous ion is main specie in Fenton's reagent. It can catalyst hydrogen peroxide to produce hydroxyl radical with powerful oxidizing abilities to degrade certain toxic contaminants (Watts et al., 1996). However, ferrous ion also can be scavengers of hydroxyl radicals as shown in the equation below (Pignatello, 1992):

$$Fe^{2+} + OH^{\bullet} \rightarrow OH^- + Fe^{3+} \qquad (10)$$

In the excess amount of ferrous ion, it can react with hydroxyl radical. Thus, the hydroxyl radical in the system will be decreased and the organic degradation will be reduced also. To evaluate the effect of ferrous ion, the experiments were conducted on various amounts of ferrous ion as 0.25 to 2.5 mM as shown in Figure 4.5. Initial concentration 1 mM of 2,6-dimethylaniline, 20 mM of hydrogen peroxide and an initial pH 2 were used as the initial conditions.

The results show that increasing the initial Fe^{2+} concentration from 0.25 mM to 2 mM enhanced the 2,6-dimethylaniline removal. The removal of 2,6-dimethylaniline increased from 24%, 51%, 63%, 62% to 70% when ferrous ions were applied from 0.25, 0.50, 1.00, 1.50 to 2.00 mM, respectively. The highest removal efficiency of 2,6-dimethylaniline was achieved when an initial Fe^{2+} concentration of 2 mM was applied.

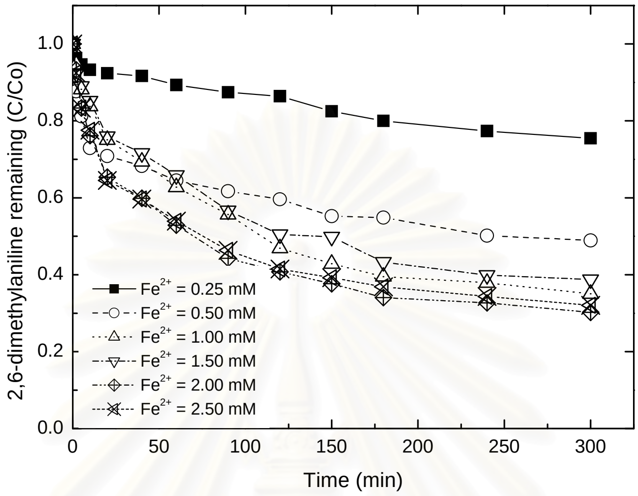

Figure 4.5. The effect of initial ferrous ion on 2,6-dimethylaniline removal

The results show that increasing the initial Fe^{2+} concentration from 0.25 mM to 2.5 mM enhanced COD removal. COD removal also increased as the ferrous ion concentration increased from 0.25, 0.50, 1.00, 1.50 to 2.00 mM as shown in Figure 4.6. The COD increased from 15.4%, 21.7%, 27.8%, 28.8% to 29.6%. The highest COD removal of 29.6% was observed when the initial Fe^{2+} concentration of 2 mM was added to the reactor.

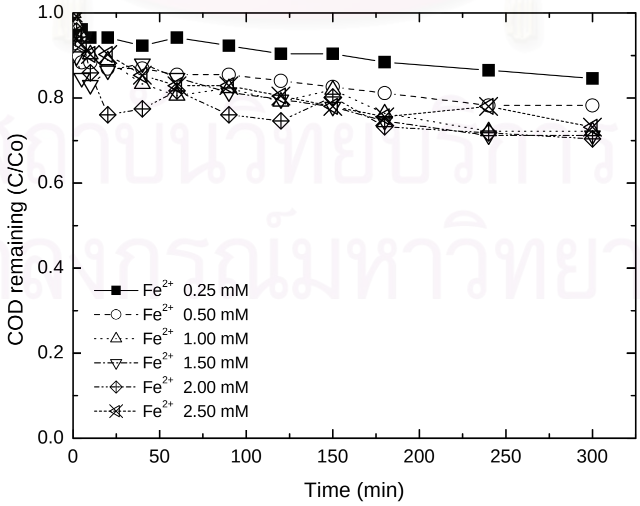

Figure 4.6. The effect of initial ferrous ion on COD removal

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Figure 4.7 illustrates the effect of initial Fe^{2+} concentration on the 2,6-dimethylaniline and COD removal efficiencies.

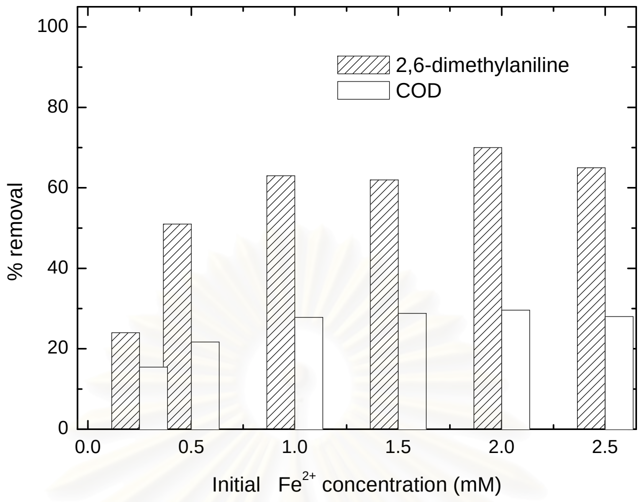

Figure 4.7. 2,6-Dimethylaniline and COD removal vs. $[Fe^{2+}]_i$ by Fenton process

TOC was also examined in this part. TOC removal when using 2 mM of ferrous ion was 30%. However, the COD removal efficiency started going down at concentrations higher than 2 mM. The initial degradation also had the same trend as 2,6-dimethylaniline removal and COD removal, as listed in Table 4.3. The results show that initial degradation rate increased from 0.006 to 0.031 $mMmin^{-1}$ when increases initial ferrous ion concentration from 0.25 to 2 mM.

Table 4.3. Initial degradation rate of 2,6-dimethylaniline at different initial Fe^{2+} concentration; [2,6-dimethylaniline] = 1 mM, $[H_2O_2]$ = 20 mM, pH = 2

Fe^{2+} (mM)	$\frac{[H_2O_2]}{[Fe^{2+}]}$ (mM)	2,6-DMA initial degradation rate ($mMmin^{-1}$)
0.25	80	0.006
0.50	40	0.016
1.00	20	0.021
1.50	13	0.025
2.00	10	0.031
2.50	8	0.026

The increase in the 2,6-dimethylaniline removal, COD removal and initial degradation rate can explain by the rate constant of reaction (1) being 63 $M^{-1}s^{-1}$, while that for

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reaction (2) is only 0.01 $M^{-1}s^{-1}$ (Kang et al., 2002). This means that ferrous ions are consumed faster than they are produced. Accordingly, increasing in the initial Fe^{2+} concentration promoted the hydroxyl radical formation through reaction (1) and enhanced the 2,6-dimethylaniline removal and COD removal via reaction (8). An increase in initial Fe^{2+} concentration was needed to improve the organic compounds degradation and decomposition (Anotai et al., 2006).

The 2,6-dimethylaniline removal and COD removal decreased to 65% and 28%, respectively, when the initial Fe^{2+} concentration was increased to 2.5 mM. There was also a decrease in the initial degradation rate at this high initial Fe^{2+} concentration. The initial degradation rate was 0.026 $mMmin^{-1}$ when applied 2.5 mM of ferrous ion in this process. The low 2,6-dimethylaniline removal, COD removal and initial degradation rate at low initial Fe^{2+} concentration might due to the side reaction between H_2O_2 and $OH^{\bullet}$ through reaction (5), i.e. there was not enough Fe^{2+} to react with the available H_2O_2 such that the unreacted H_2O_2 reacted with the hydroxyl radical. Thus, the concentration of the hydroxyl radicals that could react with the organic compounds was reduced. Moreover, it may due to the formation of iron complexes via reaction (2). Alternatively, ferrous ions can also react with hydroxyl radicals through reaction (4) which has a rate constant of $3.2 \times 10^{8}\ M^{-1}s^{-1}$ (Kang et al., 2002). From the study, the optimum initial ferrous ion concentration for degradation of 1 mM of 2,6-dimethylaniline at pH 2 was 2 mM.

3) Effect of initial hydrogen peroxide concentration on the degradation of 2,6-dimethylaniline

Hydrogen peroxide plays the role of an oxidizing agent in the Fenton reaction. Usually it has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide (Pignatello J.J., 1992, Lin et al., 1999). It is the precursor in generating the hydroxyl radical ($OH^{\bullet}$) in the combination with Fe^{2+} (equation 1). Moreover, hydrogen peroxide can also react with Fe^{3+} to regenerate Fe^{2+}. Nevertheless, in the presence of excess amount of hydrogen peroxide, oxidation reaction can be limited by the generation of O_2 instead of hydroxyl radicals and inhibition due to H_2O_2 consuming hydroxyl radicals as shown on the equation 11 and 12.

$$\text{Reductant} + H_2O_2 \rightarrow O_2 + \text{Products} \qquad (11)$$

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + OH^{\bullet}_2 \tag{12}$$

This part of the experiment was performed in order to study the effects of H_2O_2 concentration on the Fenton reaction for the treatment of 2,6-dimethylaniline. In this part, 1 mM of 2,6-dimethylaniline, 1 mM of Fe^{2+}, and an initial pH = 2.0 ± 0.1 were fixed as the initial conditions, while H_2O_2 concentrations were varied as 5 mM, 10 mM, 20 mM, 30 mM, 40 mM, 60 mM, 100 mM, 120 mM and 150 mM.

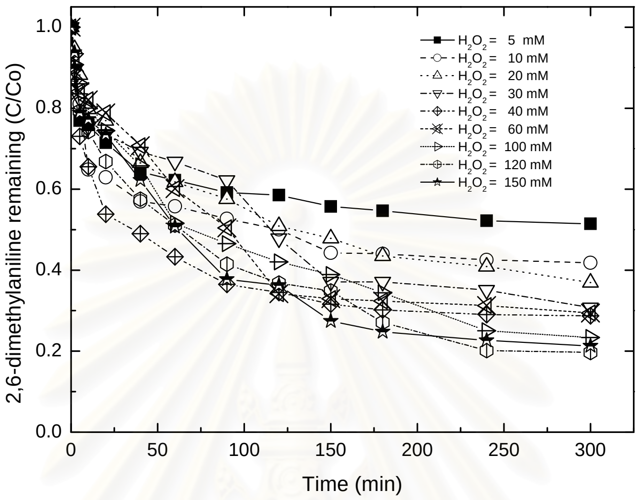

Figure 4.8. The effect of initial H_2O_2 concentration on 2,6-dimethylaniline removal

The degradation of 2,6-dimethylaniline by Fenton process is shown in Figure 4.8. The results indicate that increasing in the initial H_2O_2 concentration from 5 mM to 150 mM can enhance 2,6-dimethylaniline removal. When an initial H_2O_2 concentration of 5 mM was added, 48.6% degradation of 2,6-dimethylaniline was achieved, as listed in Table 4.4. Increasing the initial H_2O_2 concentration up to 120 mM could degrade 80% of 2,6-dimethylaniline. This was probably due to the presence of excess H_2O_2 available that can react with ferrous ions for the production of more hydroxyl radicals, as illustrated in equation (1) with the rate constant about 76 $M^{-1}s^{-1}$ (Sun et al., 2007).

2,6-Dimethylaniline degradation in this system underwent a two-stage reaction. The degradation was fast during the initial 10 minutes of the reaction then slowed down until the end of the reaction time as illustrated in Figure 4.8. The first stage or first 10 minutes, the degradation rate of 2,6-dimethylaniline was high, it is probably due to the reaction between ferrous ion and hydrogen peroxide. The second stage is the reaction that took place after 10 minutes. The degradation rate of 2,6-dimethylaniline in this reaction stage was slower, it is possibly a reaction of ferric ion and hydrogen peroxide.

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After initial 10 minutes, the initial rate increase with the hydrogen peroxide concentration. It showed that the higher the concentration of hydrogen peroxide, the faster 2,6-dimethylaniline degraded. For the Fenton process, the oxidation of 2,6-dimethylaniline did not inhibited by increasing the concentration of hydrogen peroxide. The same results were also found in other researches (Pignatello, 1992, Li et al., 1997). The reason might be that the amount of hydrogen peroxide added in this study has not yet reached the degree of inhibition when using Fenton process (Rahhal and Ritchter, 1988).

Table 4.4. Effect of H_2O_2 on the initial rate of 2,6-dimethylaniline degradation and 2,6-dimethylaniline removal efficiency by Fenton process; [2,6-dimethylaniline] = 1 mM, [Fe^{2+}] = 1 mM, pH = 2

H_2O_2 (mM)	**Initial degradation rate** ($mMmin^{-1}$)	**2,6-dimethylaniline removal efficiency** (%)
5	0.0168	48.56
10	0.0184	58.00
20	0.0199	63.05
30	0.023	69.28
40	0.0249	71.27
60	0.0271	70.59
100	0.0303	76.65
120	0.0305	80.32
150	0.0249	78.72

The initial degradation rate also follows the same trend as 2,6-dimethylaniline removal efficiency. The initial degradation rate increased from 0.0168 to 0.0305 $mMmin^{-1}$ when initial hydrogen peroxide was increased from 5 mM to 120 mM. This increase in initial degradation rate was due to the presence of higher concentration of H_2O_2 forming non-hydroxyl radicals and hydroxyl radicals when reacted with Fe^{2+}. The higher $OH^{\bullet}$ concentration increases the degradation rate since there are more available $OH^{\bullet}$ to react with the organics in the solution.

However, decreasing in 2,6-dimethylaniline removal efficiency and initial degradation rate were observed at high H_2O_2 concentration. The removal efficiency was decreased from 80.3% to 78.7% when increased hydrogen peroxide concentration from 120 mM to 150 mM as also shown in Table 4.4. And the initial degradation rate was decreased from 0.0305 to 0.0249 $mMmin^{-1}$ when increased hydrogen peroxide concentration from 120 mM to 150 mM. This was probably due to the competition of intermediates with 2,6-

dimethylaniline on hydroxyl radicals. The higher concentration of H_2O_2 might have favored the side reactions that scavenged the $OH^{\bullet}$ to form hydroperoxyl radicals ($OH^{\bullet}{}_2$) via reaction (5). This has a rate constant of about (1.2 – 4.5) x 10^7 $M^{-1}s^{-1}$ (Lu et al., 1999, Sun et al., 2007, Watts et al., 2005).

The H_2O_2 efficiency for 2,6-dimethylaniline was also determined in the study and it shows in Table 4.5. The H_2O_2 efficiency for 2,6-dimethylaniline removal was calculated using the amount of H_2O_2 consumed for the amount of 2,6-dimethylaniline removed.

Table 4.5. Comparison of the effect of H_2O_2 concentrations on 2,6-dimethylaniline removal and H_2O_2 efficiency using Fenton process

H_2O_2 (mM)	**Fenton**	
	2,6-dimethylaniline removal (%)	**H_2O_2 efficiency** (%)
5	48.6	34.6
10	58.0	20.7
20	63.0	10.8
30	69.3	8.23
40	71.3	6.35
60	70.6	4.19
100	76.6	2.73
120	80.3	2.39
150	78.7	1.87

From Table 4.5, it can be seen that increasing the H_2O_2 concentration had the effect of decreasing the H_2O_2 efficiency. As initial H_2O_2 concentration increased from 5 mM to 150 mM decreased H_2O_2 efficiency of 2,6-dimethylaniline removal from 34.62% to 1.87% where as the percent removal increased from 48.6% to 78.7%. Theoretically, the highest H_2O_2 efficiency of 100% for 2,6-dimethylaniline removal would mean that 1 mol of 2,6-dimethylaniline was removed by 1 mol of H_2O_2. The H_2O_2 efficiency for 2,6-dimethylaniline removal at 5 mM of H_2O_2 was 34.6%. This means that not all of the H_2O_2 consumed were used to degrade 2,6-dimethylaniline only. The H_2O_2 consumed could be used for the degradation of intermediates of 2,6-dimethylaniline or by scavenging reactions.

The increasing of initial H_2O_2 concentration also increased the COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize 2,6-dimethylaniline and its intermediates. For Fenton process, the results show that increasing in the initial

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H_2O_2 concentration from 5 mM to 150 mM could promote COD removal. COD removal increased from 14.1% to 27.77% as the H_2O_2 concentration increased. The COD removal had reached 27.77% when using 20 mM of H_2O_2 by Fenton process, as shown in Figure 4.9.

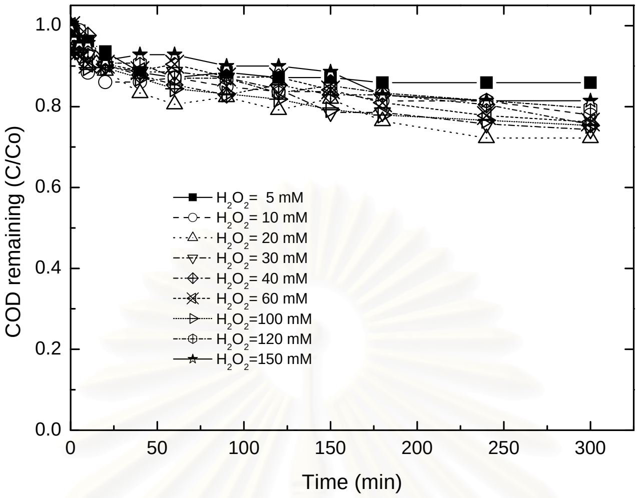

Figure 4.9. The effect of the initial H_2O_2 concentration on the 2,6-dimethylaniline and COD removal efficiencies.

Increasing of COD removal was not significant when applying initial H_2O_2 concentration from 20 mM to 120 mM. Increasing of COD removal efficiencies was due to the increase in available H_2O_2 for the production of hydroxyl radicals. At higher H_2O_2 concentrations, the produced $OH^{\bullet}$ might have followed other reaction pathways instead of equation (8) after 2,6-dimethylaniline was degraded. Higher H_2O_2 concentrations might have favored the side reactions that scavenged the hydroxyl radical to form hydroperoxyl radicals ($OH^{\bullet}_2$).

The COD removal efficiency and the H_2O_2 efficiency for COD removal followed the same trend as that of the 2,6-dimethylaniline removal. The efficiency of hydrogen peroxide on COD removal can be define by the equation below,

$$\eta = \left[\frac{\Delta COD\ (mg/l)}{available\ \ O_2(mg/l)} \right] x\ 100 \qquad (13)$$

where the available oxygen is the theoretical amount of reactive oxygen in the added hydrogen peroxide. The efficiency of hydrogen peroxide on the COD removal by Fenton process decreased when increasing hydrogen peroxide concentrations.

Table 4.6. Comparison of the effect of H_2O_2 concentrations on COD removal and H_2O_2 efficiency by Fenton process

H_2O_2 (mM)	Fenton COD removal (%)	Fenton H_2O_2 efficiency (%)
5	14.1	113.8
10	22.1	98.3
20	27.8	48.3
30	25.7	29.9
40	24.4	13.2
60	23.8	12.7
100	24.7	9.4
120	20.4	4.8
150	18.6	4.6

When increasing the initial hydrogen peroxide concentration from 5 mM to 150 mM, the H_2O_2 efficiency for COD removal decreased from 113.79% to 4.57% by using Fenton process. H_2O_2 efficiencies higher than 100% were possible in this study since COD removal was not only attributed to Fenton’s reaction. COD could not be completely eliminated even though hydrogen peroxide concentration was higher than the theoretical dosage. The similar result also found when treated landfill leacheate by electro-Fenton process (Zhang et al., 2006). This was probably due to the intermediate from the change in this chemical structure such as from aromatic to aliphatic structure by the ring opening reactions. These intermediates may have more resistant to degradation.

The TOC removal was also determined in this study. The highest TOC removal was 22% when 120 mM of hydrogen peroxide was used. The low COD and TOC removals may indicate that, although 2,6-dimethylaniline might be highly oxidizable, some of its derivatives and intermediates might not be as readily oxidized.

Based on the Fenton’s reactions, an increase in initial H_2O_2 concentration would also increase the production of hydroxyl radicals that could react with the organics in the solution via equation (8). Thus, the 2,6-dimethylaniline and COD removal efficiencies were increased. Increasing the initial H_2O_2 concentration also increases the COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize the by products of 2,6-dimethylaniline degradation.

4.1.1.2 Electro-Fenton process

According to the classical Fenton's reaction, hydroxyl radicals are produced in the solution by chemical reaction between ferrous ion and hydrogen peroxide. This is explained by the series of reaction mechanisms that might occur during the Fenton reaction (Lu et al., 1999):

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \tag{1}$$
$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{2}$$
$$OH^{\bullet} + \text{organics} \rightarrow \text{products} \tag{3}$$
$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{4}$$
$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \tag{5}$$
$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^{+} \tag{6}$$
$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \tag{7}$$
$$HO_2^{\bullet} + Fe^{2+} \rightarrow HO_2^{-} + Fe^{3+} \tag{8}$$
$$HO_2^{\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^{+} \tag{9}$$

Equation (1) shows that hydrogen peroxide may be consumed when it reacts with ferrous ion (Fe^{2+}). This produces hydroxyl radicals ($OH^{\bullet}$) that may degrade organic compounds through equation (3). Hydrogen peroxide can also react with Fe^{3+} via reaction (6).The major advantage of the Fenton process is the complete destruction of contaminants to harmless compounds, for instance, carbon dioxide, water and inorganic salts (Neyen E. et al., 2003). The main advantage of Fenton process is its simplicity (Arnold et al., 1995). However, its application has been limited due to the generation of the excess amount of ferric hydroxide sludge that requires additional separation processes and disposal (Chang P.H., 2004). Therefore, the electro-Fenton (EF) process is developed to eliminate or minimize the disadvantages of the conventional Fenton process.

The electro-Fenton process is one of the electrochemical processes that can be generally divided into three groups depending on the objective of current supply. The "EF- H_2O_2" method uses Fe^{2+} and electro-generated H_2O_2 from an oxygen sparging cathode (Tzedakis et al., 1989) whereas the "EF-Feox" utilizes H_2O_2 and electro-generated Fe^{2+} which is produced via the oxidation of sacrificial iron anode. And last group is Fenton sludge recycling (FSR) system. FSR system is somehow quite similar to the process used in this study. FSR system uses the electrical current to induce the reduction of ferric hydroxide sludge to form ferrous ions. Hence, it reduces the sludge disposal cost which is one of the major drawbacks of conventional Fenton process (Anotai et al., 2006, Gnann et al., 1993).

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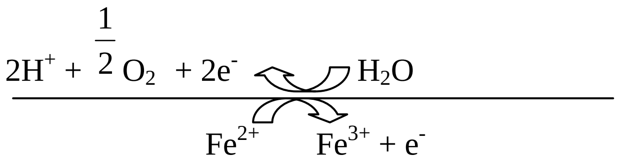
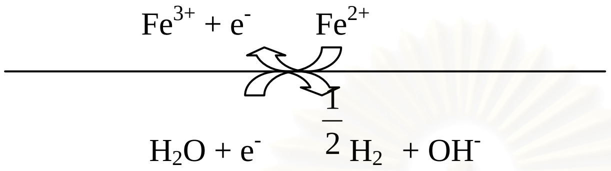
The proposed reactions in the electrolytic system are as follows:
On the anode side:



$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O \qquad (10)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad (11)$$

On the cathode side:



$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (12)$$

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \qquad (13)$$

From the reactions above, it can be seen that the ferric ion can be transformed to ferrous ion by the reaction to an electron produced on the cathode side. The regenerated ferrous ion will then react with hydrogen peroxide and produced more hydroxyl radicals that can destroy the target compounds. This reaction will not only minimize the ferric sludge, which is the major disadvantage of the Fenton process, but it will also enhance the degradation rate of target compounds. Therefore, it is interesting to determine whether 2,6-dimethylaniline can also be effectively oxidized by the electro-Fenton process.

1) Removal of 2,6-dimethylaniline by different processes

To verify the effect of electro-Fenton method (combining electrochemical method and Fenton’s reaction), the control experiments were carried out by compared three different processes (electrochemical alone, Fenton process and electro-Fenton process). The degradation of a 1 mM of 2,6-dimethylaniline solution at pH 2 by electrochemical alone, Fenton process and electro-Fenton show in Figure 4.10. Results showed that electrochemical method can hardly remove 2,6-dimethylaniline or around 21% after 4 hours of reaction. Fenton process has higher degradation efficiency compared to electrochemical alone. The removal efficiency by Fenton process can reach to 63% when using 1 mM of ferrous ion and 20 mM of hydrogen peroxide at pH 2. The utmost removal efficiency was found when applied electro-Fenton. At the same conditions, electro-Fenton process achieved 100% removal when applied electric current at 1.43 A. This indicates a slow degradation rate of 2,6-dimethylaniline and its reaction products by electrochemical alone, while the destruction of pollutants is notably accelerated in

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the presence of ferrous ion and hydrogen peroxide (so called Fenton process). This increased in the degradation was due to the fast homogeneous reaction of 2,6-dimethylaniline with hydroxyl radical generated from the reaction. Complete degradation of 2,6-dimethylaniline was achieved using the electro-Fenton process. This could be ascribed to two different effects, firstly, an increase in ferrous ion concentration in the reactor due to the effect of electric current on the regeneration of ferrous ion from ferric ion (Equation 12), which causes an increase in the rate of reaction (1) and then enhances the rate of reaction of 2,6-dimethylaniline with hydroxyl radical. Secondly, the increased of 2,6-dimethylaniline degradation was due to the effect of Fenton's reaction in the solution.

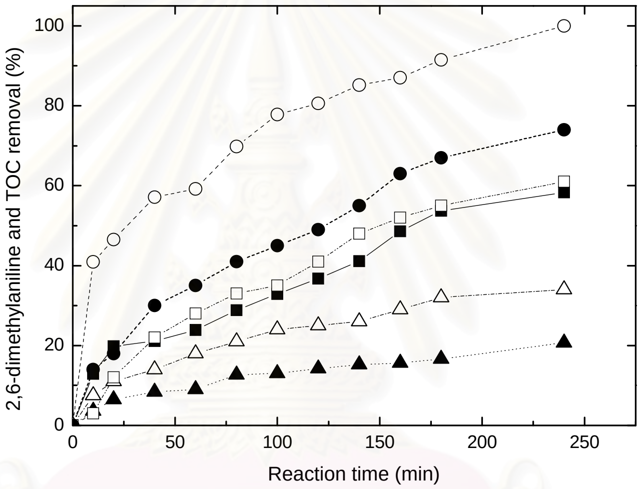

Figure 4.10. 2,6-dimethylaniline and TOC removal efficiency in various AOPs processes. When, (○) = 2,6-dimethylaniline removal by electro-Fenton, (●) = TOC removal by electro-Fenton process, (□) = 2,6-dimethylaniline removal by Fenton process, (■) = TOC removal by Fenton process, (△)= 2,6-dimethyl aniline removal by Anodic oxidation and (▲) = TOC removal by Anodic oxidation. Anodic oxidation: I = 1.43 A, pH = 2; Fenton Process: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM, pH = 2; Electro-Fenton: $[H_2O_2]$ = 20 mM, $[Fe^{2+}]$ = 1 mM, I = 1.43 A, pH = 2. All systems were using [2,6-dimethylaniline] = 1 mM.

Figure 4.10 also shows the TOC decay of a 1 mM 2,6-dimethylaniline solution at pH 2. The results for electrochemical alone, Fenton and electro-Fenton processes followed the same trend as 2,6-dimethylaniline. The results also reveal that electrochemical alone can remove TOC only 37%, while Fenton process was able to remove about 63% and 80% for electro-Fenton process after 6 hours. The final TOC removal obtained by electro-Fenton process was about 17% higher than conventional Fenton process at the same experimental conditions. This indicates that electro-Fenton had higher TOC removal efficiency. The rate for TOC removal is similar under Fenton process and electro-Fenton process.

During the first 20 minutes, the removal of TOC was rapidly decreased. Afterwards, the rate for TOC decay was slowly decreased, which can be attributed to the depletion of ferrous ion in the solution. This information is similar to the experiment that treated 4-nitrophenol by electro-Fenton (Zhang et al., 2006).

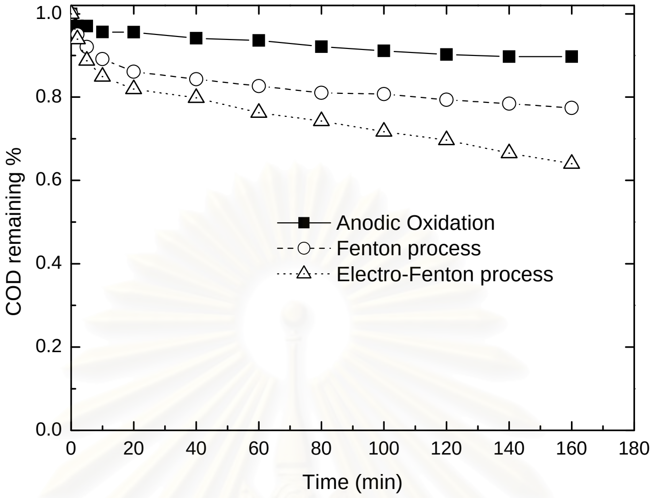

Figure 4.11. COD removal efficiency in different system. Anodic oxidation: I = 1.43 A, pH = 2; Fenton Process: [Fe^{2+}] = 1 mM, [H_2O_2] = 20 mM, pH = 2; Electro-Fenton: [H_2O_2] = 20 mM, [Fe^{2+}] = 1 mM, I = 1.43 A, pH = 2. All systems were using [2,6-dimethylaniline] = 1 mM

Figure 4.11 shows the COD removal of a 1 mM 2,6-dimethylaniline solution at pH 2. The results for anodic oxidation, Fenton and electro-Fenton processes followed the same trend as 2,6-dimethylaniline. The results show that anodic oxidation can remove COD only 10%, while Fenton process was able to remove about 22% and 38 % for electro-Fenton process after 6 hours. The final COD removal obtained by electro-Fenton process was about 16% higher than Fenton process at the same experimental conditions. This indicates that electro-Fenton had higher COD removal efficiency. During the first 20 minutes, the removal of COD was rapidly decreased. Afterwards, the rate for COD was slowly decreased, which can be attributed to the depletion of ferrous ion in the solution. Hydroxyl radical formed from Fenton's reaction destroys more rapidly aromatic products, making the Fenton and electro-Fenton processes much more efficient than anodic oxidation

2) Degradation of 2,6-dimethylaniline by electro-Fenton process

The results for 2,6-dimethylaniline degradation by using the electro-Fenton process shown that 2,6-dimethylaniline was able to oxidized even at low initial hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) concentration. Most of the 2,6-dimethylaniline was degraded in 5 hours of the reaction, thus the degradation rate constant was significant for this experiment. 2,6-dimethylaniline degradation follows the first-order behavior.

2.1) Effect of initial pH on the degradation of 2,6-dimethylaniline

Figure 4.12 shows that the pH had an effect on 2,6-dimethylaniline degradation. When the pH was 1, the removal efficiency was 61.88%. The degradation of 2,6-dimethylaniline increased as pH increased to 2. 2,6-Dimethylaniline was completely degraded after 4 hours at pH 2. When the pH was further increased the degradation decreased as also illustrated in Figure 4.12.

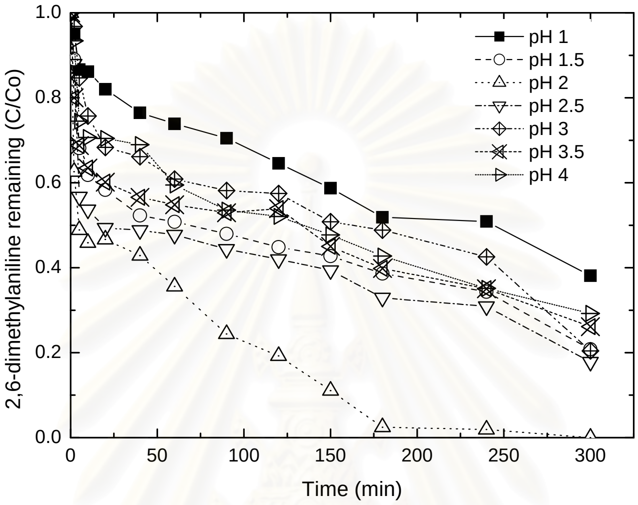

Figure 4.12. The effect of initial pH on 2,6-dimethylaniline removal

As pH was increased from 2.5 to 4, the degradation efficiency decreased from 82.19%, 79.57%, 73.86% and to 70.76%. Table 4.7 indicates that the initial pH that induces the best electro-Fenton reaction is around 2.

Table 4.7. Effect of initial pH on 2,6-Dimethylaniline removal efficiency, COD removal efficiency and 2,6-dimethylaniline initial degradation rate at the different initial pH ; [2,6-dimethylaniline] = 1 mM, [H_2O_2] = 20 mM, $Fe2^+$ = 1 mM, I = 1.43 A

pH initial	**pH** final	**2,6-dimethylaniline removal efficiency** (%)	**COD removal efficiency** (%)	**Initial degradation rate** ($mMmin^{-1}$)
1.0	0.94	61.88	18.03	0.0157
1.5	1.38	79.20	25.93	0.0373
2.0	1.89	100.00	35.71	0.0468
2.5	2.46	82.19	28.72	0.0448
3.0	2.79	79.57	27.60	0.0351
3.5	3.25	73.86	25.00	0.0332
4.0	3.56	70.76	23.62	0.0265

In the 2,6-dimethylaniline degradation by the electro-Fenton process, the pH dropped as time progressed. The initial and final pH of solutions are listed in Table 4.7. The COD removal efficiency was shown in Figure 4.13. COD removal efficiency followed the same trend as 2,6-dimethylaniline removal. COD removal increased as pH increased, from 1 to 2. The highest COD removal about 35.71%, was achieved at pH 2. When pH was further increased, COD removal decreased. It is shown in Table 4.7 that at pH 2.5, 3, 3.5 and 4, COD removal decreased from 28.72%, 27.6%, 25% and 23.62%, respectively.

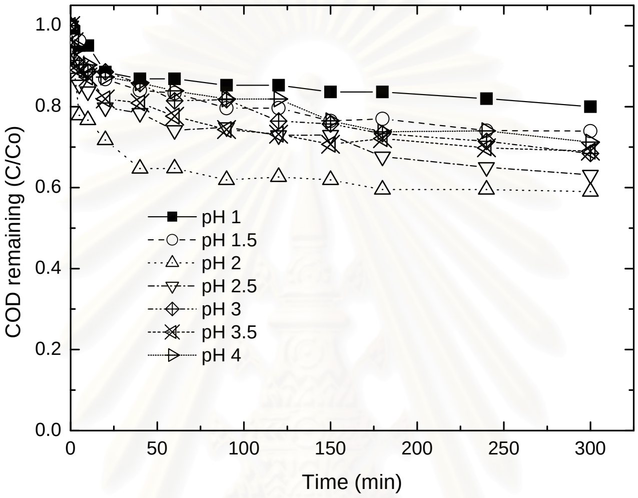

Figure 4.13. The effect of initial pH on COD removal

The degradation of 2,6-dimethylaniline can also be monitored by measuring the total organic carbon (TOC) reduction during electro-Fenton process. TOC analysis was performed in order to know the amount of organic compounds that were depleted to carbon dioxide during the chemical oxidation (Chamarro et al., 2001). The highest TOC removal by electro-Fenton process was around 45% when the pH was 2. The decrease of TOC can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton’s reaction and from electrochemically generated ferrous ion from ferric ion via equation (12) during electro-Fenton processes. The regenerated ferrous ions were then reacted with available hydrogen peroxide in the solution and thus produced hydroxyl radicals through equation (1) (Andreozzi et al., 1999).

Moreover, the initial degradation rate of 2,6-dimethylaniline at different initial pHs also show that at the optimum pH (pH 2) the highest initial rate of 0.0468 mMmin^{-1} was achieved. At pHs 1 to 4, the initial rates are 0.0157, 0.0373, 0.0468, 0.0448, 0.0351, 0.0332 and 0.0265 mMmin^{-1} when the initial pH was adjusted from 1, 1.5, 2, 2.5, 3, 3.5

and 4, respectively (as shown in Table 4.7). This phenomenon followed the same trend as 2,6-dimethylaniline removal, COD and TOC removal. The removal efficiency of 2,6-dimethylaniline and COD were shown in Figure 4.14.

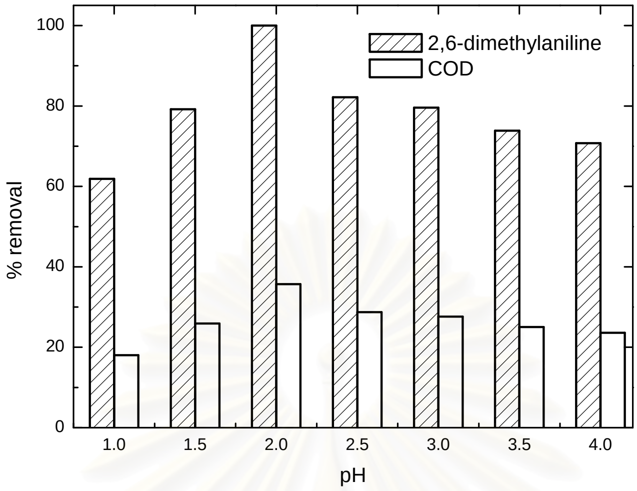

Figure 4.14. 2,6-Dimethylaniline and COD removal vs. $[pH]_i$

The decrease in 2,6-dimethylaniline degradation at low pH is probably due to the formation of $Fe(OH)^+$. It is formed at low pH and its activity is higher than Fe^{2+} in Fenton oxidation. The $Fe(OH)^+$ reacts more slowly with hydrogen peroxide and produces less hydroxyl radicals. This reduces the degradation efficiency. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant at a very low pH and also the reaction of Fe^{3+} with hydrogen peroxide is inhibited. (Pignatello J.J., 1992, Wang S., 2007). On the contrary, ferrous ions are unstable at a pH > 4.0 and they easily form ferric ions, which have a tendency to produce ferric hydroxo complexes or ferric oxyhydroxides (Wang S., 2007). At higher pH, the oxidation efficiency of Fenton's reagent may decrease because ferric ions could form $Fe(OH)_3$, which has a low activity and will not react with hydrogen peroxide. The ferric ions in the solution that can react with hydrogen peroxide are so reduced via equation (5) with the rate constant 0.001-0.01 $M^{-1}s^{-1}$ (Neyen et al., 2003).

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (14)$$

Hydrogen peroxide is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability. Thus, hydrogen peroxide and ferrous ions have difficulty in establishing an effective redox system and their degradation is also less effective (Kuo WG., 1992). Hence, the optimum initial pH for this electro-Fenton process should be pH 2.

2.2) Effect of initial ferrous ion concentration on the degradation of 2,6-dimethylaniline

Usually, the rate of degradation increases with an increase in the concentration of Ferrous ions (Fe^{2+}) (Gogate P.R., 2004). The results show that increasing the initial Fe^{2+} concentration from 0.25 mM to 2.5 mM enhanced both the 2,6-dimethylaniline removal and COD removal. The removal of 2,6-dimethylaniline increased from 66% to 100% when ferrous ions were applied from 0.25 to 2.5 mM, respectively, as shown in Figure 4.15. One hundred percent of 2,6-dimethylaniline degradation was achieved when an initial Fe^{2+} concentration of 1 mM was applied.

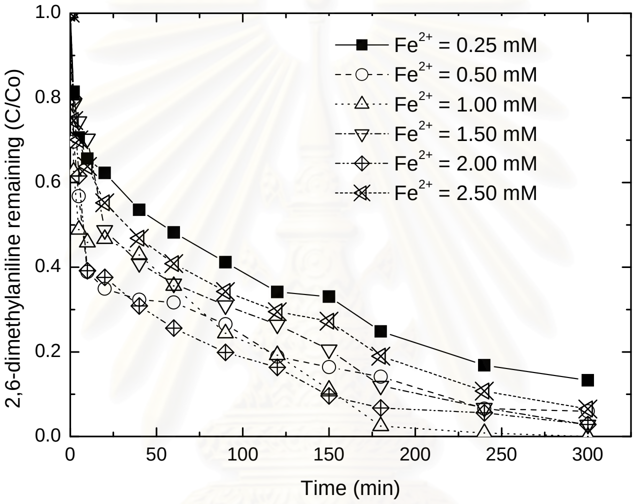

Figure 4.15. The effect of initial ferrous ion concentration on 2,6-dimethylaniline removal

Figure 4.16 shows the effect of initial ferrous ion on COD removal efficiency of 2,6-dimethylaniline. COD removal also increased as the ferrous ion concentration increased from 0.25 mM to 2 mM. The COD increased from 23% to 38.5%. The highest COD removal of 38.23% was observed when the initial Fe^{2+} concentration of 2 mM was added to the reactor. TOC was also examined in this part. TOC removal when using 2 mM of ferrous ion was 40%. However, the COD removal efficiency started going down at concentrations higher than 2 mM and leveled off when the initial Fe^{2+} concentrations were between 1 mM and 2 mM, as shown in Figure 4.16.

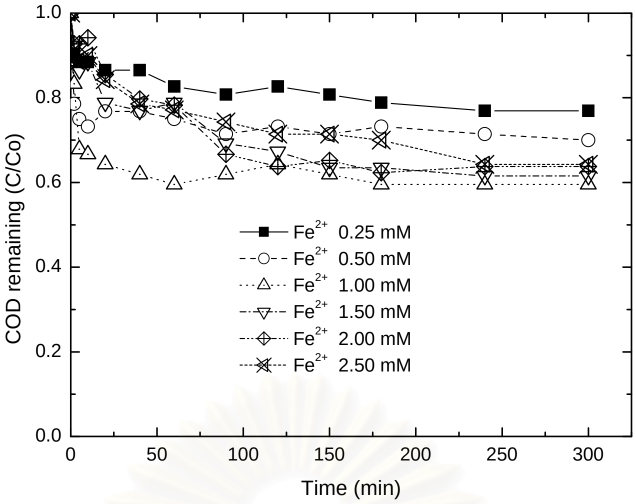

Figure 4.16. The effect of initial ferrous ion concentration on COD removal

The initial degradation rate and the H_2O_2 efficiencies for both 2,6-DMA and COD also had the same trend, as listed in Table 4.8. The initial degradation rate was followed the same trend as 2,6-dimethylaniline removal and COD removal efficiencies. The intial degradation rate increased from 0.0313 to 0.521 $mMmin^{-1}$ when increased ferrous ion concentration from 0.25 to 2 mM as shown in Table 4.8. The highest H_2O_2 efficiency for 2,6-dimethylaniline removal was about 17.82% and the COD removal was at 85.42% when an initial Fe^{2+} concentration of 2 mM was applied.

Table 4.8. 2,6-Dimethylaniline initial degradation rate, hydrogen peroxide to ferrous ion ratio and H_2O_2 efficiency of 2,6-dimethylaniline and COD when the increasing initial Fe^{2+} concentration [2,6-dimethylaniline] = 1 mM, $[H_2O_2]$ = 20 mM, I = 1.43 A, pH = 2

Fe^{2+} (mM)	**$[H_2O_2]$ / $[Fe^{2+}]$** (mM)	**2,6-DMA initial degradation rate** ($mMmin^{-1}$)	**H_2O_2 efficiency**	
			2,6-DMA (%)	**COD** (%)
0.25	80	0.0313	15.45	30.30
0.50	40	0.0464	16.76	41.65
1.00	20	0.0468	17.82	85.42
1.50	13.33	0.0482	17.32	71.61
2.00	10	0.0521	17.31	68.74
2.50	8	0.0510	16.66	61.37

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The 2,6-dimethylaniline removal and COD removal decreased to 98.5% and 37%, respectively, when the initial Fe^{2+} concentration was increased to 2.5 mM as shown in Figure 4.17. There was also a decrease in the initial degradation rate and the H_2O_2 efficiencies for both 2,6-DMA removal and COD at this high initial Fe^{2+} concentration. The initial degradation rate and H_2O_2 efficiencies for 2,6-dimethylaniline and COD were 0.051 $mMmin^{-1}$, 16.66% and 61.37%, respectively.

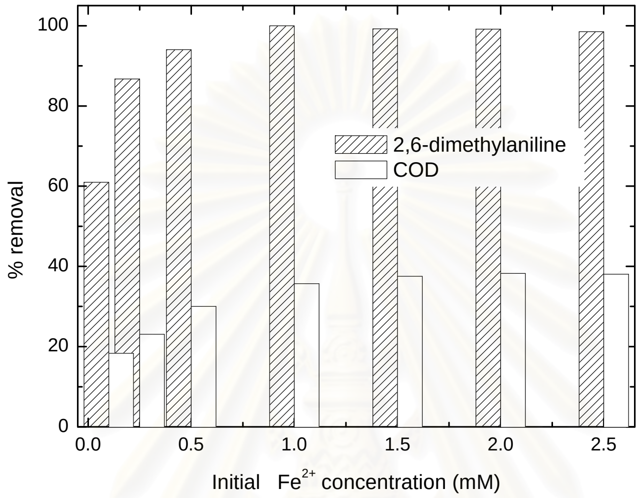

Figure 4.17. The effect of initial Fe^{2+} concentration on the 2,6-dimethylaniline and COD removal efficiencies.

The increase in the 2,6-dimethylaniline removal and COD removal may be explained by the rate constant of reaction (1) being 63 $M^{-1}s^{-1}$, while that for reaction (6) is only 0.01 $M^{-1}s^{-1}$ (Kang et al., 2002). This means that ferrous ions are consumed faster than they are produced. Accordingly, increasing in the initial Fe^{2+} concentration promoted the hydroxyl radical formation through reaction (1) and enhanced the 2,6-dimethylaniline removal and COD removal via reaction (3). An increase in initial Fe^{2+} concentration was needed to improve the organic compounds degradation and decomposition (Anotai et al., 2006).

The low 2,6-dimethylaniline removal and COD removal at low initial Fe^{2+} concentration might due to the side reaction between H_2O_2 and $OH^{\bullet}$ through reaction (4), i.e. there was not enough Fe^{2+} to react with the available H_2O_2 such that the unreacted H_2O_2 reacted with the hydroxyl radical. Thus, the concentration of the hydroxyl radicals that could react with the organic compounds was reduced.

The decrease in rate constant, removal efficiencies and H_2O_2 efficiencies at high Fe^{2+} concentration may be attributed to the formation of iron complexes via reaction (6) and (7). Alternatively, ferrous ions can also react with hydroxyl radicals through reaction (2) which has a rate constant of $3.2 \times 10^{8}\ M^{-1}s^{-1}$ (Kang et al., 2002). The excess amount of ferrous ions may have a scavenging effect on the hydroxyl radical at the high initial Fe^{2+} concentration of 2.5 mM as indicated by the decreased of the intial degradation rate to 0.051mMmin^{-1}. This resulted in a decrease of 2,6-dimethylaniline removal and COD removal as well as the H_2O_2 efficiencies for both 2,6-DMA removal and COD removal.

2.3) Effect of initial hydrogen peroxide concentration on the degradation of 2,6-dimethylaniline

Hydrogen peroxide plays the role of an oxidizing agent in the Fenton reaction. Usually it has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide (Pignatello J.J., 1992, Lin et al., 1999). As shown in Figure 4.18, increasing in the initial H_2O_2 concentration from 5 mM to 120 mM could promote the 2,6-dimethylaniline removal and also COD removal. The 2,6-dimethylaniline removal was 88.9% when the hydrogen peroxide concentration was 5 mM. When using an initial H_2O_2 concentration of 20 to 150 mM, 100% degradation of 2,6-dimethylaniline was achieved, as shown in Figure 4.18.

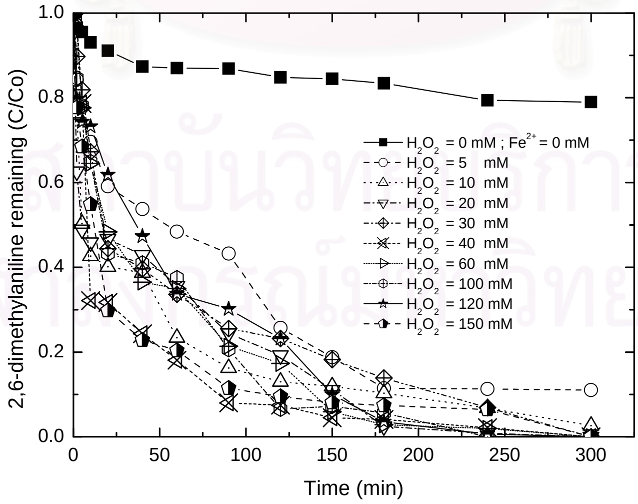

Figure 4.18. The effect of initial hydrogen peroxide concentration on 2,6-dimethylaniline removal

The 2,6-dimethylaniline removal efficiency of 100% was observed when higher than 20 mM of H_2O_2 were used. This was due to the presence of excess H_2O_2 available for the production of more hydroxyl radicals. The consequences are consistent with the experiments using aniline (Anotai et al., 2006) and m-phenylenediamine (Lu et al., 2006) in Electro-Fenton process when the initial H_2O_2 concentration was increased. Therefore it can be state that the percentage degradation of the 2,6-dimethylaniline increased with an increase in the dosage of hydrogen peroxide (Gogate et al., 2004)

The same trend was found when measuring COD removal efficiency as shown in Figure 4.19. The COD removal increased from 28% to 42.57% as hydrogen peroxide dosage was increased from 5 mM to 120 mM. However, further increase to 150 mM showed a decrease in removal efficiency. The COD removal decreased to 41.54% when 150 mM of hydrogen peroxide was applied. This could be explained by the series of reaction mechanisms that might occur during the Fenton’s reaction (Lu et al., 1999).

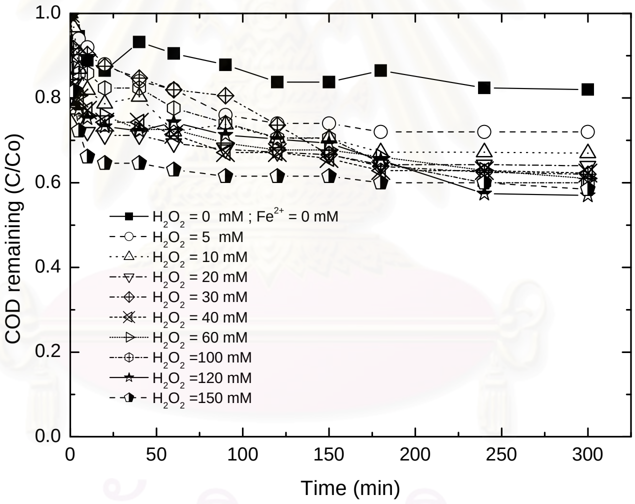

Figure 4.19. The effect of initial hydrogen peroxide concentration on COD removal

The results show that only 20 mM of H_2O_2 is required to achieve 100% 2,6-dimethylaniline removal. However, the COD removal at this initial H_2O_2 concentration was still very low. This is probably due to the production of intermediates that are not as oxidizable as 2,6-dimethylaniline. Increasing the initial H_2O_2 concentration also increases the COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize the by products of 2,6-dimethylaniline degradation. The COD removal had reached 40.27% after using 120 mM of H_2O_2 as shown in Figure 4.19.

This Electro-Fenton process had an 2,6-dimethylaniline removal efficiency of 20.6% through direct anodic oxidation experiment as also shown in Figure 4.19.

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Based on the Fenton's reactions, an increase in initial H_2O_2 concentration would also increase the production of hydroxyl radicals that could react with the organics in the solution via equation (3). Thus, the 2,6-dimethylaniline and COD removal efficiencies were increased. Although 100% 2,6-dimethylaniline degradation was achieved at an initial H_2O_2 concentration of 20 mM, the COD removal was still low. This is probably due to the production of intermediates that are not as oxidizable as 2,6-dimethylaniline. Increasing the initial H_2O_2 concentration also increases the COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize the by products of 2,6-dimethylaniline degradation. The COD removal reached 42.57 % after using 120 mM of H_2O_2. This is also shown in Figure 4.19. The results reveal that complete degradation of 2,6-dimethylaniline was achieved after 4 hours of electro-Fenton process when 20 mM of hydrogen peroxide was applied. The effect of initial hydrogen peroxide concentration on 2,6-dimethylaniline and COD removal efficiencies are shown in Figure 4.20.

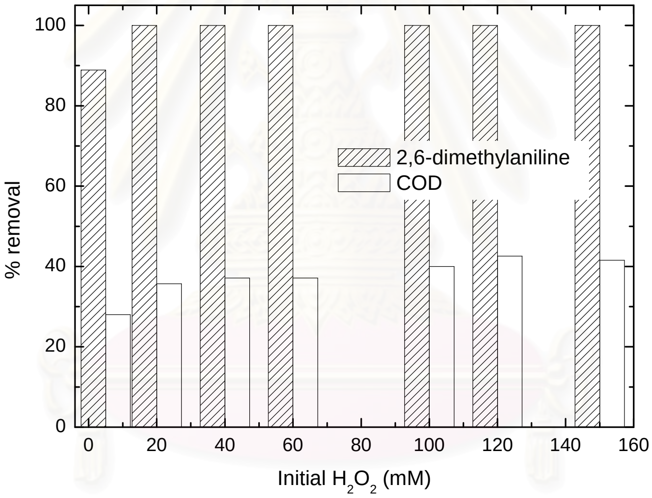

Figure 4.20. The effect of initial hydrogen peroxide concentration on the 2,6-dimethylaniline and COD removal efficiencies.

Table 4.9 shows the initial degradation rate of 2,6-dimethylaniline and the H_2O_2 efficiency of 2,6-dimethylaniline and COD removal. From the table, it can be seen that the initial degradation rate followed the same trend as that of the COD removal efficiency, i.e. the initial degradation rate increased from 0.0275 $mMmin^{-1}$ to 0.0602 $mMmin^{-1}$ as the H_2O_2 concentration was increased from 5 mM to 120 mM but decreased to 0.0589 $mMmin^{-1}$ when H_2O_2 concentration was further increased to 150 mM. This increase in initial degradation rate was due to the presence of higher concentration of H_2O_2 forming non-hydroxyl radicals and hydroxyl radicals when reacted with Fe^{2+}. The higher $OH^{\bullet}$ concentration increases the degradation rate since there are more available

$OH^{\bullet}$ to react with the organics in the solution. However, a high H_2O_2 concentration could also affect the degradation rate constant when the unreacted H_2O_2 might favor the side reactions that scavenged the $OH^{\bullet}$ to form hydroperoxyl radicals ($OH^{\bullet}_2$) via reaction (4)(Martinez et al., 2003). This has a rate constant of about (1.2 – 4.5) x 10^7 $M^{-1}s^{-1}$ (Sun et al., 2007, Watts et al., 2005).

The H_2O_2 efficiencies for 2,6-dimethylaniline and COD removal were also determined in the study and are also shown in Figure 4.21. The H_2O_2 efficiency for 2,6-dimethylaniline removal was calculated using the amount of H_2O_2 consumed for the amount of 2,6-dimethylaniline removed. From Table 4.9, it can be seen that increasing the H_2O_2 concentration had the effect of decreasing the H_2O_2 efficiency. The hydrogen peroxide efficiency for 2,6-dimethylaniline removal decreased from 63% to 2 % when increased initial hydrogen peroxide concentration from 5 to 150 mM. This is probably due to the scavenging effect of the excess H_2O_2 as illustrated by reaction (4).

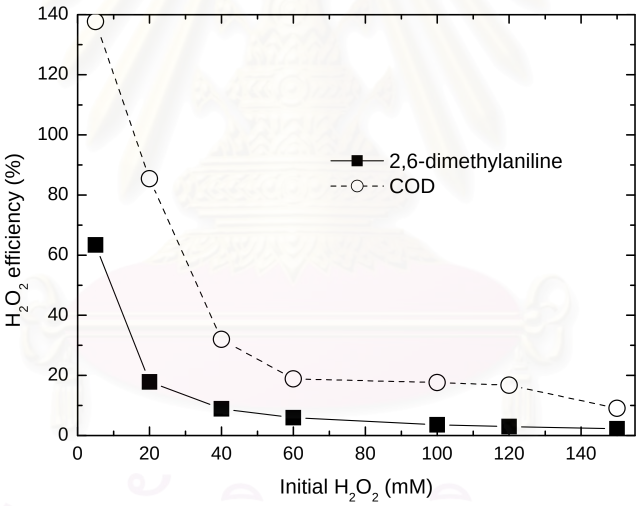

Figure 4.21. The effect of initial hydrogen peroxide concentration on the H_2O_2 efficiencies for 2,6-dimethylaniline and COD removal

Theoretically, the highest H_2O_2 efficiency of 100% for 2,6-dimethylaniline removal would mean that 1 mol of 2,6-dimethylaniline was removed by 1 mol of H_2O_2. The H_2O_2 efficiency for 2,6-dimethylaniline removal at 5 mM of H_2O_2 was 63.42%. This means that not all of the H_2O_2 consumed were used to degrade 2,6-dimethylaniline only. The H_2O_2 consumed could be used for the degradation of intermediates of 2,6-dimethylaniline or by scavenging reactions.

Table 4.9. Initial rate and H_2O_2 efficiency of 2,6-dimethylaniline and COD removal when the increasing initial H_2O_2 concentration ; [2,6-dimethylaniline] = 1 mM, [Fe^{2+}] = 1 mM, I = 1.43 A, pH = 2

H_2O_2 (mM)	**Initial degradation rate** (mM min^{-1})	**H_2O_2 efficiency (η)** **2,6-DMA** (%)	**COD** (%)
5	0.0275	63.42	137.7
10	0.0312	34.70	109.2
20	0.0468	17.82	85.43
30	0.0509	11.88	55.78
40	0.0559	8.91	31.97
60	0.0563	5.94	18.85
100	0.0572	3.56	17.62
120	0.0602	2.95	16.72
150	0.0589	2.22	9.04

*2,6-dimethylaniline = 2,6-DMA

The effects of H_2O_2 on COD removal efficiencies were also determined in this study and are shown in Table 4.9. COD removal efficiencies increased from 28% to 42.57% as the H_2O_2 concentration. The COD removal efficiency and the H_2O_2 efficiency for COD removal followed the same trend as that of the 2,6-dimethylaniline removal. The H_2O_2 efficiency for COD removal decreased from 138% to 9% when increasing hydrogen peroxide concentration from 5 to 150 mM. H_2O_2 efficiencies higher than 100% were possible in this study since COD removal was not only attributed to Fenton's reaction. The efficiency of hydrogen peroxide on COD removal is defined by the equation below,

$$\eta = \left[\frac{\Delta COD \ (mg/l)}{available \ O_2 (mg/l)} \right] x \ 100 \qquad (15)$$

where the available oxygen is the theoretical amount of reactive oxygen in the added hydrogen peroxide. COD could not be completely eliminated even though hydrogen peroxide dosage was higher than the theoretical dosage. A similar result also found when landfill leachate was treated by electro-Fenton process (Zhang et al., 2006). When large quantities of hydrogen peroxide are present, it will acts as a scavenger for the generated hydroxyl radicals. At higher H_2O_2 concentrations, the $OH^\bullet$ produced might have followed other reaction pathways instead of equation (3) after 2,6-dimethylaniline was degraded. Higher H_2O_2 concentrations might have favored the side reactions that scavenged the hydroxyl radical to form hydroperoxyl radicals ($OH^\bullet_2$).

This could be supported by a decrease in the degradation rate constants from 0.0589 $mMmin^{-1}$ of the 150 mM initial H_2O_2 concentration compared with 0.0602 $mMmin^{-1}$ of 120 mM initial H_2O_2 concentration. Additionally, a similar COD removal trend, a decrease in COD removal from 42.57% to 41.54%, was observed at higher initial H_2O_2 concentrations. The TOC removal was also determined in this study. The highest TOC removal was 52% when 120 mM of hydrogen peroxide was used. The low COD and TOC removals may indicate that, although 2,6-dimethylaniline might be highly oxidizable, some of its derivatives and intermediates might not be as readily oxidized.

2.4) Effect of applied electric current on the degradation of 2,6-dimethylaniline

Figure 4.22 illustrates the effect of applied electric current on the 2,6-dimethylaniline removal efficiency. Results showed that increasing the applied electric current from 0.5 to 4 A can promote the removal of 2,6-dimethylaniline from 93.12% to 100%.

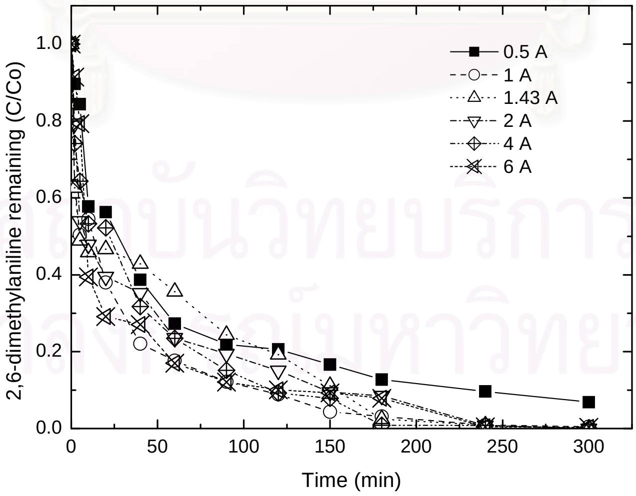

Figure 4.22. The effect of applied electric current on 2,6-dimethylaniline removal

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Figure 4.23 shows the effect of applied electric current on the COD removal efficiency. COD removal also increased when the applied current from 31.58% to 40.32%, indicating an enhancement of the degradation power. This observation was similar to the experiment on the removal of 4-nitrophenol by varying the electric current from 0.5 to 1 A (Zhang et al., 2007).

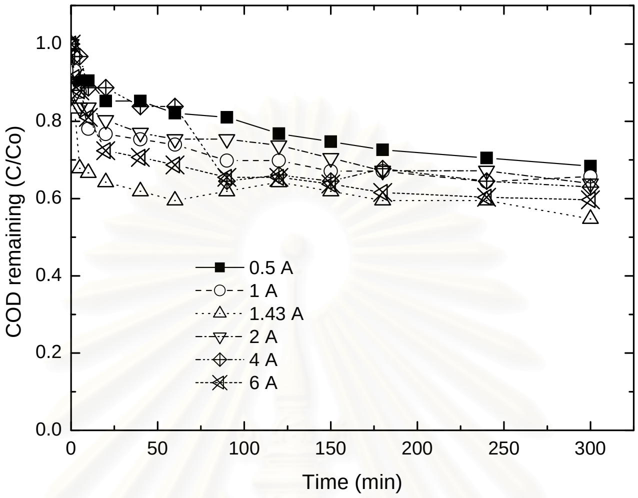

Figure 4.23. The effect of applied electric current on COD removal efficiency

The effect of applied electric current on 2,6-dimethylaniline and COD removal efficiencies were shown in Figure 4.24.

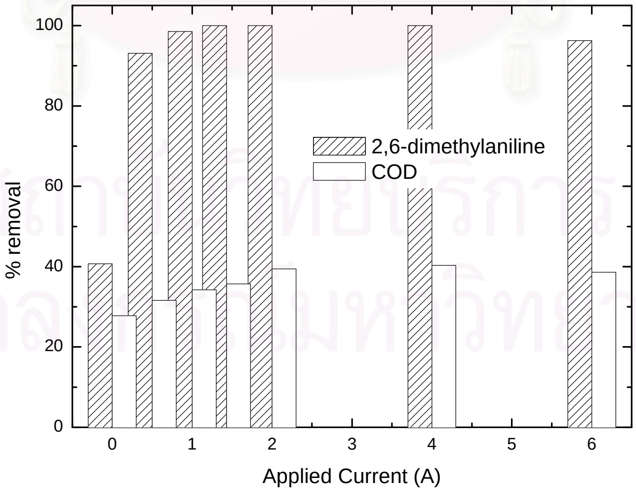

Figure 4.24. The effect of applied electric current on the 2,6-dimethylaniline and COD removal efficiencies.

In addition, the current impact (EF efficiency/CF efficiency) at 4 A was 2.46 for 2,6-dimethylaniline removal and 1.94 for COD removal as shown in Table 4.10. This means that electro-Fenton at 4A is highly superior in 2,6-dimethylaniline degradation when it is compared to the conventional Fenton (CF) process (no electric current applied) operated at the same conditions. This was probably due to the higher electro-regeneration rate of ferrous ions from ferric ions with increased current, which also increased the efficiency of the Fenton chain reactions.

The effect of applied electric current on the regeneration of ferrous ion was also examined in this study as shown in Figure 4.25. The results show that increased the applied electric current from 0.5, 1.43 to 4.00 A was able to increase the ferrous ion regeneration. This was due to the regeneration of Fe^{2+} induced at the cathode via reaction (17) which promotes hydroxyl radical production through reaction (1)

However, both 2,6-dimethylaniline removal and COD removal decreased to 96.25% and 38.59%, respectively, when an electric current of 6 A was applied. The same trend were also observed for the H_2O_2 efficiency of both 2,6-DMA removal and COD removal and their corresponding current impacts. The TOC removal at 4 A was also found to be the highest and it is about 45%.

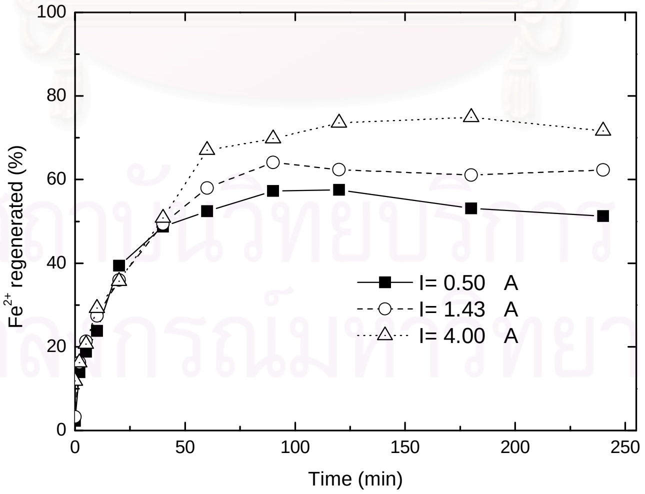

Figure 4.25. Effect of electric current on the regeneration of ferrous ion. $[Fe^{3+}]$ = 1 mM, pH = 2

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The H_2O_2 efficiency for the 2,6-dimethylaniline removal was 17.15% and the current impact was 2.36%. The H_2O_2 efficiency and current impact for COD removal were 26.06% and 1.15%, respectively. The performance of the electro-Fenton process was evaluated by the instantaneous current efficiency (η), which is defined as

$$\eta = (FV/A)\frac{dFe^{2+}}{dt} x\ 100\% \qquad (16)$$

Where F denotes the Faraday constant, Fe^{2+} represents the molar concentration of generated ferrous ion, V is the volume of the solution, A denotes the operating current, and t represents the reaction time. Since the current was kept constant, the amount of Fe^{2+} generated was proportional to the time of electrolysis. Current efficiency for 0.5 A, 1.43 A and 4 A after 90 minutes are 35.79%, 38.3 % and 39.85%, respectively.

The initial degradation rate increased from 0.0421 $mMmin^{-1}$ to 0.0474 $mMmin^{-1}$ when the electric current was increased from 0.5 A to 6 A. However, when this is compare to the initial degradation rate of the Fenton process, the electro-Fenton process has a faster degradation.

Table 4.10. Rate constants, 2,6-dimethylaniline and COD removal efficiency and H_2O_2 efficiency with different values of the applied electric current ; [2,6-dimethylaniline] = 1 mM, $[H_2O_2]$ = 20 mM, $[Fe^{2+}]$ = 1 mM, pH = 2

Current (A)	Voltage (V)	2,6-DMA initial degradation rate ($mMmin^{-1}$)	[Δ 2,6-DMA] / $[\Delta H_2O_2]$ (%)	Current Impact E_{EF}/E_{CF}	[ΔCOD] / $[\Delta H_2O_2]$ (%)	Current Impact E_{EF}/E_{CF}	Energy cost (kWh/m^3)
0.00	0.0	0.0111	7.26	-	48.30	-	0
0.50	1.4	0.0421	16.59	2.29	72.82	1.51	1.77
1.00	1.9	0.0434	17.57	2.42	76.75	1.59	4.44
1.43	2.0	0.0468	17.82	2.46	85.42	1.77	6.41
2.00	2.3	0.0468	17.82	2.46	89.91	1.86	9.33
4.00	3.0	0.0473	17.82	2.46	93.60	1.94	23.81
6.00	3.7	0.0474	17.15	2.36	55.38	1.15	46.01

The increase in 2,6-dimethylaniline removal and COD removal when the applied electric current was increased. This is probably due to the increased regeneration of Fe^{2+} induced at the cathode via reaction (17) which promotes hydroxyl radical production through reaction (1)

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (17)$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (18)$$

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$$2H^+ + 2e^- \rightarrow H_2 \qquad (19)$$

The electro-Fenton process did not have to depend on reaction (11) for the regeneration of ferrous ions. On the other hand, at a higher electric current of 6 A, the competitive reactions such as the discharge of oxygen gas at the anode via reaction (18) and the evolution of hydrogen gas at the cathode via reaction (19) become more pronounced (Zhang et al., 2007). Hence, the initial degradation rate constant decreased and H_2O_2 was not efficiently used. The energy cost for electro-Fenton process was also discussed and shown in Figure 2.6.

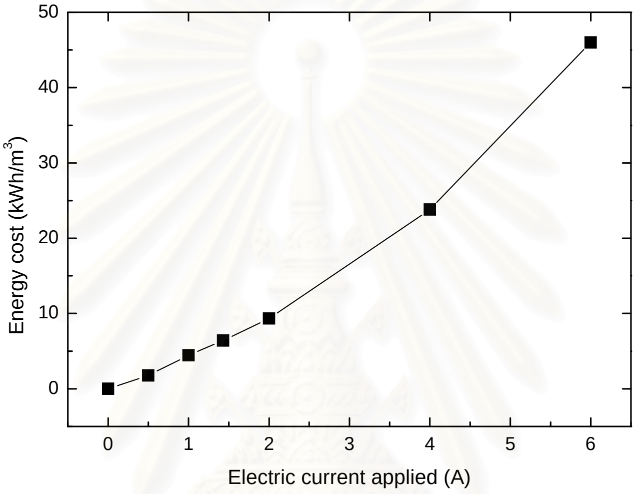

Figure 4.26. Effect of electric current on the energy cost

The equation applied for calculate the energy cost is:

$$\text{Energy cost :}\ (kWh/m^3) = [\ V\ x\ I\ x\ t/volume\ ]\ x\ [COD_o/\Delta COD_{exp.}] \qquad (20)$$

where V is the voltage applied until time t (Volt), I is the electric current (Ampere) used in the study, t is the given time (minute), volume is the amount of organic solution used in the experiment (liter), COD_o is the initial COD of the organic chemical and $\Delta\ COD_{exp}$ is the difference between the initial COD and the final COD after treatment. By using equation (20), the energy cost was increased when increasing the initial electric current and time applied. Consequently, the energy cost should be considered when applied electricity into Fenton's reaction.

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From the overall study of electro-Fenton process, it can be seen that initial pH, initial ferrous ion concentration, initial hydrogen peroxide concentration and applied electric current are the important parameters in order to achieve the highest removal efficiency of 2,6-dimethylaniline, COD and TOC.

It is obvious that, with electricity supply, the ferrous ion dose and reaction time can be reduced substantially. In fact, the ferric hydroxide sludge precipitating after pH neutralization can also reduce significantly. This clearly shows the advantage of electro-Fenton over convention Fenton process. Increasing electric current could sufficiently rectify ferrous regeneration. Electro-Fenton process at its optimum conditions should be able to completely remove 2,6-dimethylaniline at a much lower ferrous ion concentration than conventional Fenton process

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4.1.1.3 Photoelectro-Fenton process

From the previous experiments on 2,6-dimethylaniline degradation by Fenton process and electro-Fenton process, it can be seen that the formation of ferric oxyhydroxide sludge is still a problem here. The sludge can be electrochemically reduced to ferrous ion, but this requires a step in which the pH is lowered around 1 (Chou et al., 1999). In principle, the ferric ion could reduce to ferrous ion at the cathode in electro-Fenton process. However, the ferrous ion regeneration is slow even at optimum electric current applied. Both current density and current efficiency drop off precipitously above pH ~ 2.5 (Qiang et al., 2003). Therefore, the new method which can promote the ferrous ion regeneration was focused in this part of experiment.

The photoelectro-Fenton process involves the additional irradiation of the solution with UVA light. UVA light can favor (1) the regeneration of ferrous ion with production of more amount of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$, which is the predominant ferric ion species in acid medium (Sun and Pignatello, 1993) and (2) the photodecomposition of complexes of ferric ion with generated carboxylic acids (Flox et al., 2006)

According to the classical Fenton's reaction, hydroxyl radicals are produced in the solution by chemical reaction between ferrous ion and hydrogen peroxide. This is explained by the series of reaction mechanisms that might occur during the Fenton reaction (Lu et al., 1999):

$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+}$ (1)
$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-}$ (2)
$OH^{\bullet} + \text{organics} \rightarrow \text{products}$ (3)
$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$ (4)
$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$ (5)
$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^{+}$ (6)
$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+}$ (7)
$HO_2^{\bullet} + Fe^{2+} \rightarrow HO_2^{-} + Fe^{3+}$ (8)
$HO_2^{\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^{+}$ (9)

The reactions in the electrolytic system are as follows:

On the anode side:

$2H^{+} + \frac{1}{2}O_2 + 2e^{-} \rightarrow H_2O$ (20)

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$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (11)

On the cathode side:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (12)

$H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$ (13)

Moreover, under UVA irradiation, the overall efficiency of the process increases due mainly to the regeneration of ferrous ions and formation of additional hydroxyl radical. The action of this irradiation is complex and can be described by:

(1) the production of greater amount of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$, the predominant Fe^{3+} species in acid medium. Under light irradiation, Fe(III) is continuously reduced to Fe(II):

$FeOH^{2+} + h\nu \rightarrow Fe(II) + OH^{\bullet}$ (14)

(2) the photolysis of complexes of Fe(III) with generated carboxylic acids (Pignatello et al., 2006; Exposito et al., 2007).

$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe(II) + CO_2 + R^{\bullet}$ (15)

The maximum adsorption wavelength of $Fe(OH)^{2+}$ species is less than 360 nm, visible irradiation may not drive the reaction of equation (1). An interesting and potentially useful modification of the photoreduction reaction takes advantage of the photo-lability of Fe(Ⅲ)-oxalate complexes, which is efficiency up to 500 nm (Pignatello et al., 2006). Under these conditions, it is also feasible to used sunlight as an alternative inexpensive source of UVA light using the solar photoelectro-Fenton process (Casado et al., 2005, Flox et al., 2007;).

It is known that hydrogen peroxide has a maximum absorbance at 210-230 nm and these wavelength fall away of the wavelength of the used UVA lamp (~360 nm). This type of lamps was used, in this study, to serve the following reasons (Momani, 2006):

(1) Hydrogen peroxide proteolysis can take place to a small limit at wavelength ~360 (Pignatello et al., 1999).

(2) Iron photo-redox is known to take place under high wavelength (~ 360 nm).

(3) From the economical point of view, the use of cheap black light, compared with the expensive high pressure mercury lamp (254 nm), enhance the treatment feasibility.

(1) Degradation of 2,6-dimethylaniline by different processes

Electrolysis, Fenton, electro-Fenton and photoelectro-Fenton experiments were conducted to investigate the synergistic effect of combined photo and electrochemical methods. As shown in Figure 4.27, the results show that electricity alone could remove 20% of 2,6-dimethylaniline in 2 hr. In the electrolysis method, 2,6-dimethylaniline would be destroyed by reaction with adsorbed hydroxyl radical generated at the surface of a high oxygen-overvoltage anode from water oxidation. The same tendency can be found in the research of Brillas et al (Brillas et al., 1998). Fenton process has higher degradation efficiency compared to electrolysis. The removal efficiency by Fenton process can reach to 45% when using 1 mM of ferrous ion and 20 mM of hydrogen peroxide at pH 2. The main reason is that ferrous ions reacted very quickly with hydrogen peroxide to produce some hydroxyl radicals.

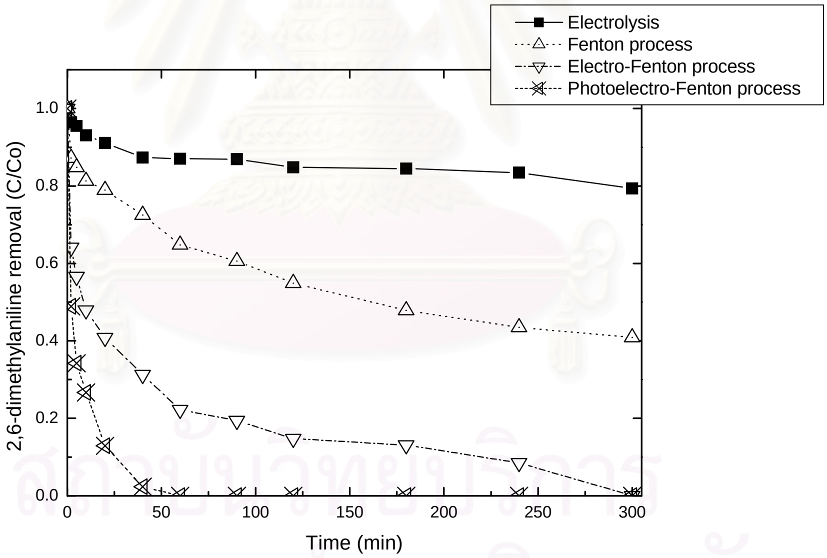

Figure 4.27. Effect of different processes on 2,6-dimethylaniline removal efficiency. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

The 85% removal efficiency achieved by the electro-Fenton process was nearly 40% higher than that of the Fenton's reagent alone. The reason that electro-Fenton process can remove 2,6-dimethylaniline more than the Fenton process is due to the ability of electricity that can produced hydroxyl radicals from water oxidation as described in equation (16).

$H_2O \rightarrow OH^{\bullet} + H^+ + e^-$ (16)

Hydroxyl radical is the main oxidizing agent of organics. Furthermore, when electro-Fenton process was applied, the ferrous ions were regenerated by the reduction of ferric ions with hydrogen peroxide, hydroperoxyl radical ($HO_2^{\bullet}$) or organic radical intermediates (Özcan et al, 2008) as shown in equation (6, 9 and 17).

$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^+$ (17)

Meanwhile, the utmost removal efficiency was found when applied photoelectro-Fenton process, 2,6-dimethylaniline was removed completely during the first 60 minutes. The photoelectro-Fenton process achieved a removal efficiency that was 15% higher than that of the electro-Fenton process. This indicates that the photoelectro-Fenton method had a synergistic effect for 2,6-dimethylaniline degradation.

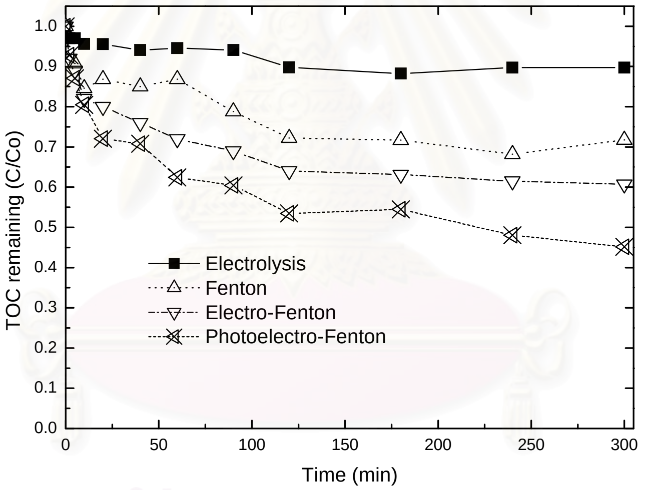

Figure 4.28. Effect of different processes on TOC removal efficiency. 2,6-dimethylaniline = 1 mM; $[Fe^{2+}]$ = 1 mM; $[H_2O_2]$ = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

The degradation of 2,6-dimethylaniline was monitored by measuring the total organic carbon (TOC) reduction. For TOC removal, by electrolysis, Fenton, electro-Fenton and photoelectro-Fenton processes, the same trend was found for 2,6-dimethylaniline degradation as shown in Figure 4.28.

The results reveal that electrolysis can remove COD only 13%, while Fenton process was able to remove about 26% and 36% for electro-Fenton process as shown in Figure 2. The highest TOC removal was found when applied photoelectro-Fenton. It was about 55% and TOC removal by photoelectro-Fenton process was 20% higher than electro-Fenton at the same experimental condition. The decrease of TOC can be attributed to the mineralization of 2,6-dimethylaniline by the hydroxyl radicals from Fenton's reaction, from the electrochemically generated Fenton's reagent during electro-Fenton and photoelectro-Fenton processes and the production of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$ in photoelectro-Fenton process.

(2) ***Degradation of 2,6-dimethylaniline by Photoelectro- Fenton process***

1) Control experiment

Photolysis, UV + hydrogen peroxide, Photo-Fenton and Photoelectro-Fenton experiments were conducted to investigate the effect of UVA lamp, Fenton's reagent and electrochemical methods. Figure 4.29 shows that photolysis could remove 40% of 2,6-dimethylaniline in 5 hr. In the UV + hydrogen peroxide method, 2,6-dimethylaniline would be destroyed 60%. When applied UVA combined with Fenton's reagent, 100% removal was found in 3 hour. This was due to the formation of additional hydroxyl radical from the Fenton's reaction and the regeneration of ferric ion to ferrous ion (equation 14). The utmost removal efficiency was found when applied photoelectro-Fenton process, 2,6-dimethylaniline was removed completely during the first 60 minutes as mentioned before in previous section.

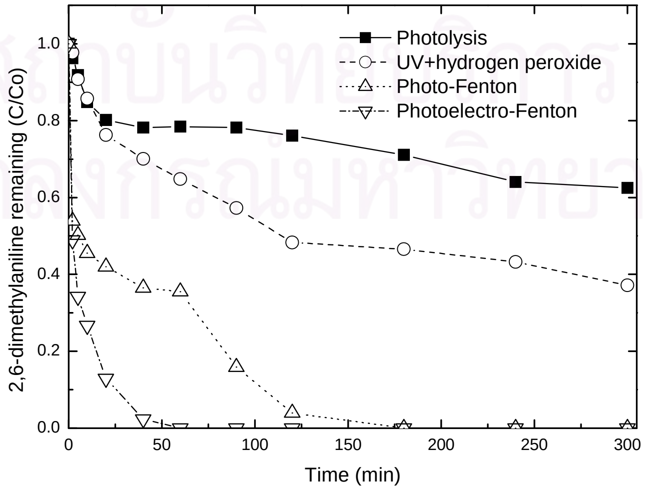

Figure 4.29. Effect of different control processes on 2,6-dimethylaniline removal efficiency. 2,6-dimethylaniline = 1 mM; $[Fe^{2+}]$ = 1 mM; $[H_2O_2]$ = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

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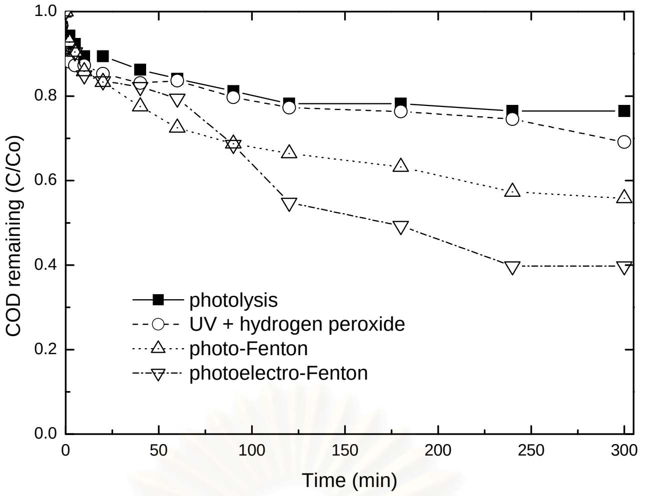

Figure 4.30. Effect of different control processes on COD removal efficiency. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

Figure 4.30 shows the COD removal of a 1 mM 2,6-dimethylaniline solution at pH 2. The results for Photolysis, UV + hydrogen peroxide, Photo-Fenton and Photoelectro-Fenton followed the same trend as 2,6-dimethylaniline. The results show that photolysis can remove COD only 11%, while UV + hydrogen peroxide method was able to remove about 20% and 44 % for photo-Fenton process after 5 hours. The final COD removal obtained by photoelectro-Fenton process was about 60% the same experimental conditions. This indicates that photoelectro-Fenton had higher COD removal efficiency. During the first 20 minutes, the removal of COD was rapidly decreased. Afterwards, the rate for COD was slowly decreased, which can be attributed to the depletion of ferrous ion in the solution. Hydroxyl radical formed from Fenton’s reaction, electricity and UVA lamp destroys more rapidly aromatic products, making the photo-Fenton and photoelectro-Fenton processes much more efficient than others.

2) Effect of initial pH on 2,6-dimethylaniline degradation

pH is an important parameter for Fenton’s reaction. Hence, the pH of the solution controls the production of the hydroxyl radical and the concentration of ferrous ions (Pignatello et al., 2006, Sun et al., 2007). A very acid solution or a neutral-basic media slows down the process. The effect of pH on the degradation of 2,6-dimethylaniline is shown in Figure 4.31. Increasing the pH from 1.5 to 2.0 increased the removal from 89% to 100% in 1 hour. A further increase of pH from 2 to 3 decreased the removal from 100% to 88%. Above this pH, Fe^{3+} started to be precipitated in the form of

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amorphous $Fe(OH)_3$. The formation of $Fe(OH)_3$ not only decreased the dissolved Fe^{3+} concentration, but also inhibited Fe^{2+} regeneration by partially coating the electrode surface. The optimum pH was found to be about 2. It is in good agreement with early reports (Lu et al., 2003, Chou et al., 1999, Qiang et al., 2003).

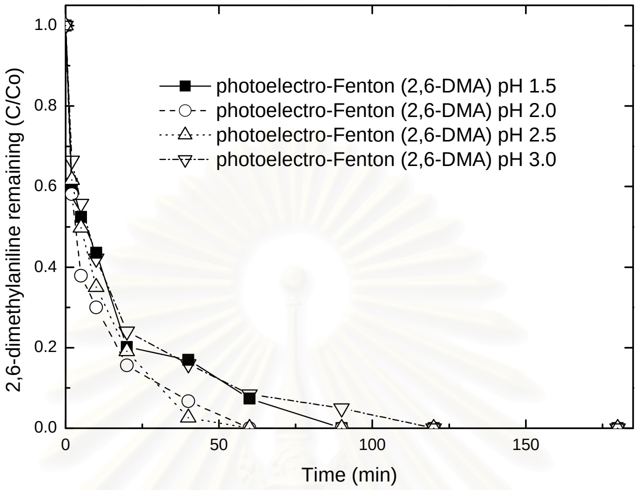

Figure 4.31. Effect of pH_i on the 2,6-DMA degradation by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; $[Fe^{2+}]$ = 1 mM; $[H_2O_2]$ = 20 mM; I = 1.43 A, UVA lamp = 12.

This indicates that photoelectro-Fenton had higher COD removal efficiency. During the first 20 minutes, the removal of COD was rapidly decreased. Afterwards, the rate for COD was slowly decreased, which can be attributed to the depletion of ferrous ion in the solution. Hydroxyl radical formed from Fenton’s reaction, electricity and UVA lamp destroys more rapidly aromatic products, making the photo-Fenton and photoelectro-Fenton processes much more efficient than others.

COD removal efficiency followed the same trend as 2,6-dimethylaniline removal. Figure 4.32 shows that COD removal increased as pH increased, from 1 to 2. 55% COD removal was found at pH 1.5. The highest COD removal about 63% was achieved at pH 2. When pH was further increased, COD removal decreased. At pH 2.5 and 3, COD removal decreased from 60% to 59 %, respectively.

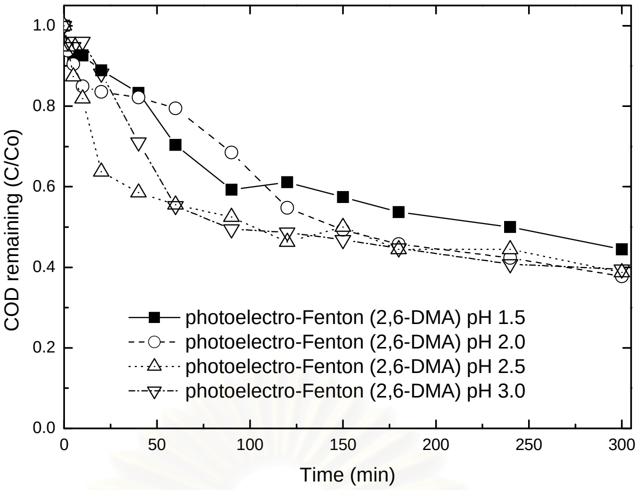

Figure 4.32. Effect of pH_i on the COD removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; I = 1.43 A, UVA lamp = 12.

The degradation of 2,6-dimethylaniline can also be monitored by measuring the total organic carbon (TOC) reduction during photoelectro-Fenton process (Figure 4.33). TOC analysis was performed in order to know the amount of organic compounds that were depleted to carbon dioxide during the chemical oxidation. At pH 1.5, the TOC removal was 46%. The highest TOC removal by photoelectro-Fenton process was 55% when the pH was 2.

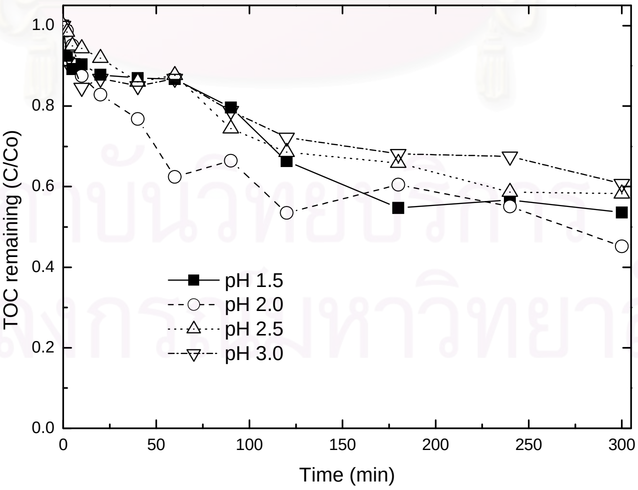

Figure 4.33. Effect of pH_i on the TOC removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; I = 1.43 A, UVA lamp = 12.

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The TOC removal decreased from 42% to 39% when increased pH from 2.5 to 3. The TOC removal efficiency can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton's reaction, from electrochemically generated ferrous ion from ferric ion via equation (12) during electro-Fenton processes and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 14). The regenerated ferrous ions were then reacted with available hydrogen peroxide in the solution and thus produced hydroxyl radicals through equation (1).

To further compare the 2,6-dimethylaniline degradation, all experimental data were analyzed using initial degradation rate, which presented in Table 4.11.

Table 4.11. Effect of initial pH on 2,6-Dimethylaniline removal efficiency, COD removal efficiency and 2,6-dimethylaniline initial degradation rate at the different initial pH by photoelectro-Fenton; [2,6-dimethylaniline] = 1 mM, [H_2O_2] = 20 mM, Fe2$^+$ = 1 mM, I = 1.43 A, UVA lamp = 12

pH initial	pH final	2,6-dimethylaniline removal efficiency* (%)	COD removal efficiency (%)	Initial degradation rate** (mMmin^{-1})
1.5	1.3	89	55	0.0512
2.0	1.81	100	63	0.0625
2.5	2.41	100	60	0.0572
3.0	2.63	88	59	0.0478

* After 60 minute of reaction ** After 10 minutes of reaction

The results in Table 4.11 show that the initial degradation rate of 2,6-dimethylaniline degradation was significantly influenced by the pH value and that the optimal pH was observed at pH 2.0. The initial degradation rate was followed the same trend as 2,6-dimethylaniline removal, COD removal and TOC removal. The value of initial degradation rate increased from 0.0512 to 0.0625 mMmin^{-1} when the pH increased from 1.5 to 2.0, suddenly decrease to 0.0572 and 0.0478 mMmin^{-1} when the pH is raised from 2.0 to 3.0. As a result, the initial degradation rate of 2,6-dimethylaniline at different initial pH also show that at the optimum pH (pH 2) the highest initial rate at 0.0625 mMmin^{-1} was achieved.

A very acid or a neutral-base media slows down the process. The decrease of activity detected for pH values below the optimum is understandable taking into account that Fe(III) forms different complex species ($Fe(OH)^+$) in solution. It is formed at low pH and its activity is higher than Fe^{2+} in Fenton oxidation. The $Fe(OH)^+$ reacts more slowly with hydrogen peroxide and produces less hydroxyl radicals. This reduces the degradation efficiency. Moreover, the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant at a very low pH and also the reaction of Fe^{3+} with hydrogen peroxide is inhibited. (Pignatello J.J., 1992, Wang S., 2007). The quantum yield of light absorption by Fe(III) is directly depending on the specific species responsible for the absorption (Pérez et al., 2002).

On the contrary, the low activity detected for high pH values can be explained by the formation and precipitation of $Fe(OH)_3$, which has a low activity and will not react with hydrogen peroxide, a process that hamper the development of photoelectr-Fenton reaction. Ferrous ions are unstable at a pH > 4.0 and they easily form ferric ions, which have a tendency to produce ferric hydroxo complexes or ferric oxyhydroxides (Wang S., 2007).

2) Effect of initial ferrous ion concentration

Ferrous ion is main specie in Fenton process. It can catalyze hydrogen peroxide to produce hydroxyl radical with powerful oxidizing abilities to degrade certain toxic contaminants (Spacek et al., 1995, Pignatello, 1992). Usually, the rate of degradation increases with an increase in the concentration of ferrous ions (Gogate P.R., 2004). Figure 4.34 illustrates the effect of initial Fe^{2+} concentration on the 2,6-dimethylaniline removal efficiency. From the results, it can be seen that the removal of 2,6-dimethylaniline was very fast in the first 10 minutes and then the reaction was relatively slow until the end of reaction time. The results show that increasing the initial Fe^{2+} concentration from 0.25 to 5 mM enhanced the 2,6-dimethylaniline removal. The removal of 2,6-dimethylaniline increased from 90% to 100% when applied ferrous ion from 0.5 to 2.5 mM. One hundred percent of 2,6-dimethylaniline degradation was achieved after 60 minutes when an initial Fe^{2+} concentration of 1mM was applied.

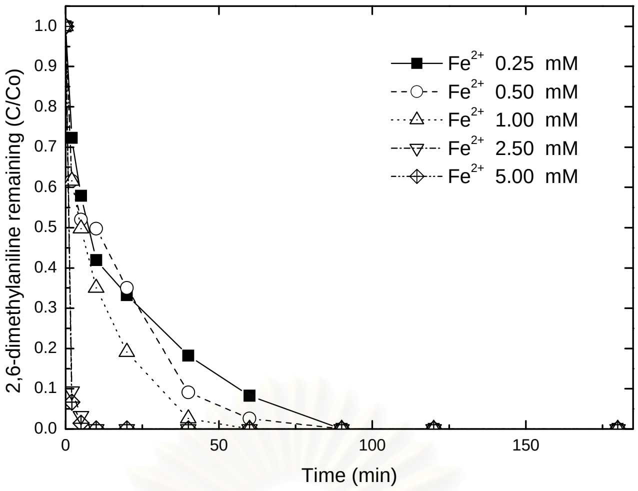

Figure 4.34. Effect of initial Fe^{2+} concentration on the 2,6-DMA degradation by photoelectro-Fenton. 2,6 - dimethylaniline = 1 mM; $[H_2O_2]$ = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

It was found that the improvement of the degradation efficiency can be enhanced by UVA lamp. UVA lamp produces additional hydroxyl radicals as described in equation 14. This result is agree with the result reported by Casero et al. (1997). They found that the degradation of aromatic amine essentially depended on ferrous ion concentration. From this experiment at the 1.0, 2.5 and 5.0 mM of ferrous ion, the removal efficiency were almost the same within 60 minute. Thus the optimum initial ferrous ion concentration obtained from this experiment was 1 mM.

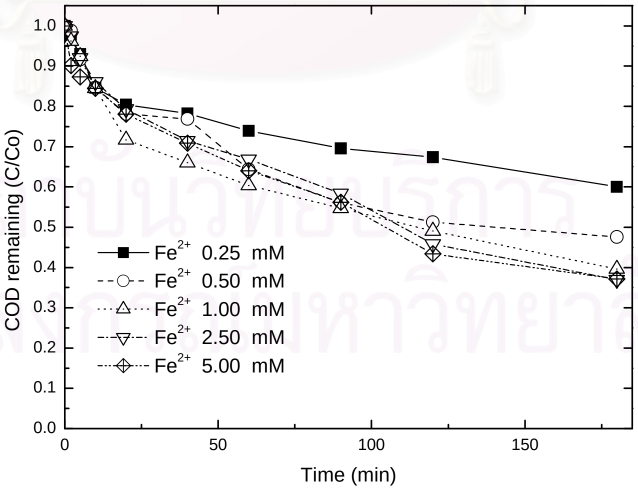

Figure 4.35. Effect of initial Fe^{2+} concentration on the COD removal by photoelectro-Fenton. 2,6 - dimethylaniline = 1 mM; $[H_2O_2]$ = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

COD removal efficiency followed the same trend as 2,6-dimethylaniline removal. Figure 4.35 shows that COD removal increased from 40, 55, 60, 63 and 64% as ferrous ion concentration increased from 0.25, 0.50, 1.00, 2.50 and 5.00 mM. The highest COD removal about 64% was achieved when using 5 mM of ferrous ion. However, the different of removal efficiency of ferrous ion from 1 mM to 5 mM was not significant.

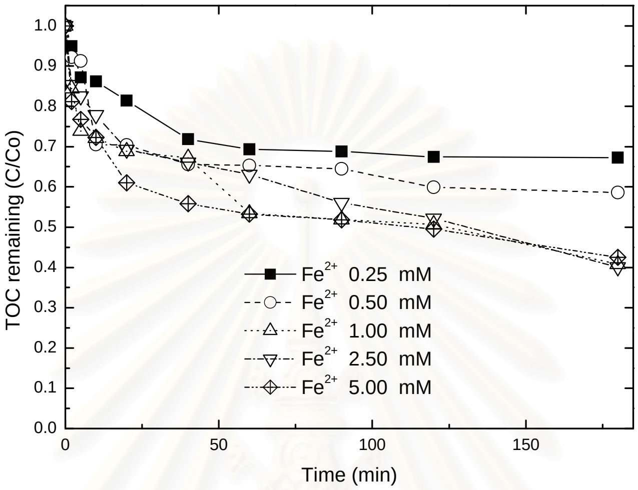

Figure 4.36. Effect of initial Fe^{2+} concentration on the TOC removal by photoelectro-Fenton. 2,6 - dimethylaniline = 1 mM; $[H_2O_2]$ = 20 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

The degradation of 2,6-dimethylaniline can also be monitored by measuring the total organic carbon (TOC) reduction during photoelectro-Fenton process. The TOC removal followed the same trend as COD removal. Figure 4.36 shows that TOC removal increased from 32, 40, 56, 57 and 56% as ferrous ion concentration increased from 0.25, 0.50, 1.00, 2.50 and 5.00 mM. The TOC removal efficiency can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton's reaction, from electrochemically generated ferrous ion from ferric ion via equation (12) during electro-Fenton processes and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 14).

To further compare the 2,6-dimethylaniline degradation, all experimental data were analyzed using initial degradation rate, which presented in Table 4.12.

Table 4.12. Effect of initial ferrous ion on 2,6-dimethylaniline removal efficiency, COD removal efficiency and 2,6-dimethylaniline initial degradation rate by photoelectro-Fenton; [2,6-dimethylaniline] = 1 mM, pH =2, [H_2O_2] = 20 mM, I = 1.43 A, UVA lamp = 12

[Fe^{2+}] (mM)	**2,6-dimethylaniline removal efficiency*** (%)	**COD removal efficiency** (%)	**Initial degradation rate**** ($mMmin^{-1}$)
0.25	90	40	0.0534
0.50	97	55	0.0572
1.00	100	60	0.0625
2.50	100	63	0.0782
5.00	100	64	0.0773

* After 60 minute of reaction ** After 10 minutes of reaction

The effect of Fe^{2+} concentration on the initial degradation rate for 2,6-dimethylaniline degradation was also studied by varying ferrous ion from 0.25 to 5.00 mM. The results are presented in Table 4.12. It can be seen that the initial degradation rate of 2,6-dimethylaniline increased from 0.0534 $mMmin^{-1}$ to 0.0782 $mMmin^{-1}$ when increasing Fe^{2+} concentration from 0.25 to 2.5 mM. Accordingly, increasing in the initial Fe^{2+} concentration promoted the hydroxyl radicals formation through reaction (1) and enhanced the 2,6-dimethylaniline removal. Moreover, this is also due to the fact that Fe^{2+} plays a very important role in initiating the decomposition of H_2O_2 to generate the $OH^{\bullet}$ in the Fenton process. When the concentrations of Fe^{2+} and $OH^{\bullet}$ are high, Fe^{2+} can react with the $OH^{\bullet}$ according to equation (2). However, it is not a good idea to use over high concentration of Fe^{2+}. By reason of a large quantity of ferric oxide sludge will be generated, resulting in much more requirement of separation and disposal of the sludge.

It can be concluded from the study that increasing the relative concentration of Fe^{2+} with respect to the organic compound increases the rate of formation of hydroxyl radicals, which in turn enhances the degradation rate, but this takes place at the expense of consuming more electrical charge due to the enhancement of some competing reactions during electrolysis. Increasing of Fe^{2+} concentration led less H_2O_2 accumulation in the reaction medium and efficient formation of hydroxyl radicals by reaction with H_2O_2 according to Fenton reaction. However, an increase in the Fe^{2+} concentration inhibits the degradation rate of organic substrates because of competitive reaction as shown in equation 2. It is evident from our results that increasing ferrous ion do not cause that inhibition effect in these experimental conditions since [Fe^{2+}] used was not excess.

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3) Effect of initial hydrogen peroxide concentration

Hydrogen peroxide is an important parameter in Fenton process. It is the precursor in generating the hydroxyl radical in combination with ferrous ion (equation 1). Furthermore, hydrogen peroxide can also react with ferric ion to regenerate ferrous ion (equation 6). It has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide (Pignatello J.J., 1992, Lin et al., 1999).

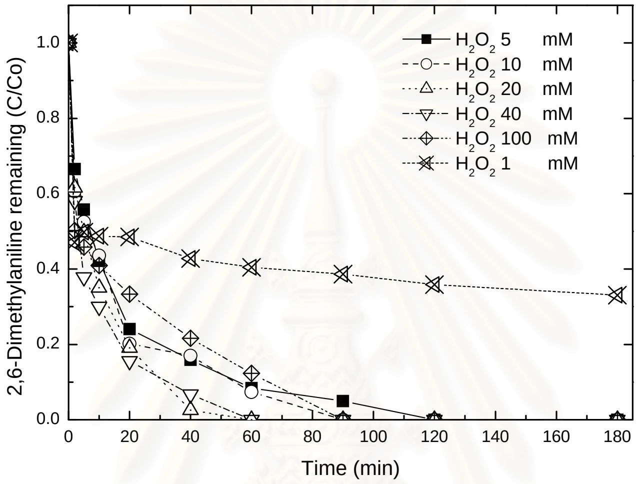

Figure 4.37. Effect of initial hydrogen peroxide concentration on the 2,6-DMA degradation by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

Figure 4.37 shows the effect of the initial H_2O_2 concentration on the 2,6-dimethylaniline removal efficiency. The results show that increasing in the initial H_2O_2 concentration could promoted the 2,6-dimethylaniline removal. When using theoretical condition which is 1 mM of 2,6-dimethylaniline:1mM of ferrous ion: 1 mM of hydrogen peroxide, the result showed that the 2,6-dimethylaniline could be removed about 65%. The removal of 2,6-dimethylaniline was fast during the first 10 minutes because of the hydroxyl radicals that formed from the Fenton’s reaction. However, after that the removal was decreased and stable, this was due to the fact that no more hydrogen peroxide available in the solution so the hydroxyl radical could not be produced and thus making the reaction stopped or slowed down**.** In order to get rid this problem, the higher concentration of hydrogen peroxide was applied in this study from 5 mM to 100 mM and the results were shown in figure 4.37.

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After 60 minutes, the removal efficiency of 2,6-dimethylaniline was 88%, 90%, 100%, 100% and 86% with 5 mM, 10 mM, 20 mM, 40 mM and 100 mM of initial hydrogen peroxide concentration, respectively. Additionally, 2,6-dimethylaniline was completely degraded with 20 mM and 40 mM of initial hydrogen peroxide concentration at 60 minutes. This phenomenon was due to an increase in initial H_2O_2 concentration can increase the productions of hydroxyl radicals that could react with the organics in the solution. The results agreed with the experiment by Lu, 1999. The decomposition rate of organic contaminants increased with the increasing of hydrogen peroxide concentration.

However, further increase to 100 mM showed a decrease in removal efficiency. In the presence of excess amount of hydrogen peroxide concentration, oxidation reaction can be limited by the generation of O_2 instead of hydroxyl radicals as shown in equation 18 and inhibition due to hydrogen peroxide consuming hydroxyl radicals as shown in equation 4.

$$\text{Reductant} + H_2O_2 \rightarrow O_2 + \text{Products} \qquad (18)$$

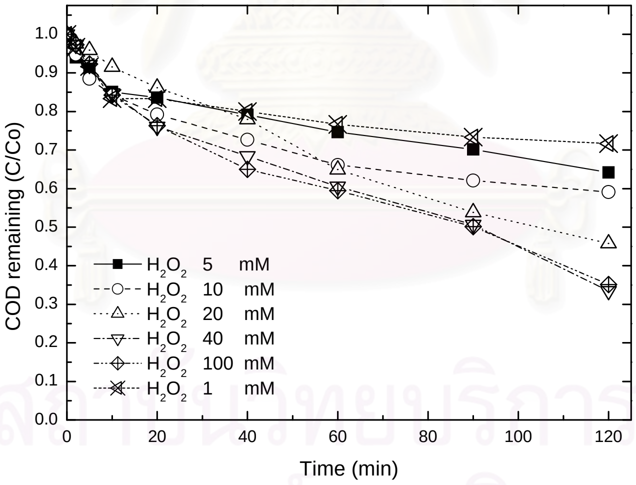

Figure 4.38. Effect of initial hydrogen peroxide concentration on the COD removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

COD removal efficiency followed the same trend as 2,6-dimethylaniline removal. Figure 4.38 shows that COD removal increased from 25, 35, 40, 57, 67 and 65% as hydrogen peroxide concentration increased from 1, 5, 10, 20, 40 and 100 mM. The highest COD removal about 67% was achieved when using 40 mM of initial hydrogen peroxide concentration. The increasing of initial H_2O_2 concentration also increased the

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COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize 2,6-dimethylaniline and its intermediates. At higher H_2O_2 concentrations, the produced $OH^•$ might have followed other reaction pathways instead of equation (8) after 2,6-dimethylaniline was degraded. Higher H_2O_2 concentrations might have favored the side reactions that scavenged the hydroxyl radical to form hydroperoxyl radicals ($OH^•_2$).

The TOC removal followed the same trend as COD removal. TOC removal of 2,6-dimethylaniline at different initial hydrogen peroxide showed that the faster removal of TOC take place at initial hydrogen peroxide 100 mM. It was clearly showed that Fenton’s reagent assisted electric current under irradiation of UVA can improve TOC removal. Figure 4.39 shows that TOC removal increased when increasing the initial hydrogen peroxide concentration. TOC removal efficiency increased from 34, 43, 46, 55 and 55% as initial hydrogen peroxide concentration increased from 5, 10, 20, 40 and 100 mM.

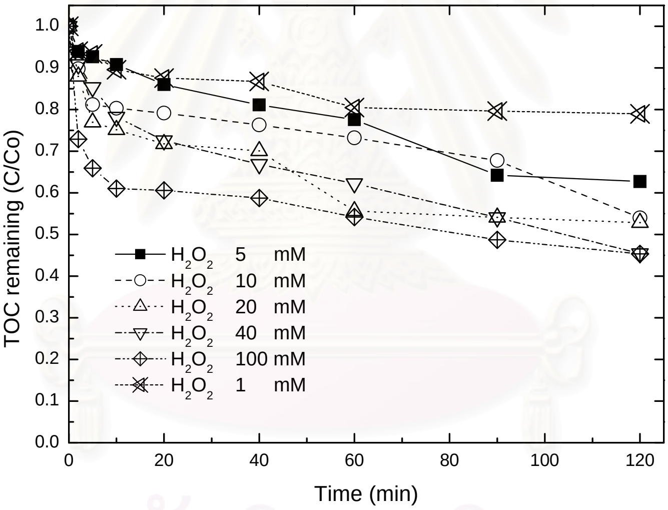

Figure 4.39. Effect of initial hydrogen peroxide concentration on the TOC removal by photoelectro-Fenton. 2,6 - dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; pH = 2; I = 1.43 A, UVA lamp = 12.

In this case, it is clear that increasing amounts of hydrogen peroxide lead to larger TOC removal. However, excess of hydrogen peroxide might be detrimental, since these species can react with some of the intermediates like hydroxyl radical, responsible for the direct oxidaiton of the organic load (equation 4) precluding the extent of mineralization. The low COD and TOC removals may indicate that, although 2,6-dimethylaniline might be highly oxidizable, some of its derivatives and intermediates might not be as readily oxidized. From Table 4.13, it can be seen that the initial degradation rate followed the same trend as that of the 2,6-dimethylaniline removal efficiency.

Table 4.13. Effect of initial hydrogen peroxide concentration on 2,6-dimethylaniline removal efficiency, COD removal efficiency and 2,6-dimethylaniline initial degradation rate by photoelectro-Fenton; [2,6-dimethylaniline] = 1 mM, Fe2$^+$ = 1 mM, I = 1.43 A, UVA lamp = 12

[H_2O_2] (mM)	**2,6-dimethylaniline removal efficiency*** (%)	**COD removal efficiency** (%)	**Initial degradation rate**** ($mMmin^{-1}$)
5	88	35	0.0478
10	90	40	0.0572
20	100	57	0.0625
40	100	67	0.0652
100	86	65	0.0472

* After 60 minute of reaction ** After 10 minutes of reaction

The initial degradation rate increased from 0.0478, 0.0572, 0.0625 to 0.0652 $mMmin^{-1}$ as the H_2O_2 concentration was increased from 5 mM, 10 mM, 20 mM to 40 mM but decreased to 0.0472 $mMmin^{-1}$ when H_2O_2 concentration was further increased to 100 mM. This increase in initial degradation rate was due to the presence of higher concentration of H_2O_2 forming non-hydroxyl radicals and hydroxyl radicals when reacted with Fe^{2+}. Higher $OH^{\bullet}$ concentration increases the degradation rate since there are more available $OH^{\bullet}$ to react with the organics in the solution. The high H_2O_2 concentration could affect the removal efficiency and initial degradation rate as the unreacted H_2O_2 might favor the side reactions that scavenged the $OH^{\bullet}$ to form hydroperoxyl radicals ($OH^{\bullet}_2$) via reaction (4) with the rate constant about (1.2 – 4.5) x 10^7 $M^{-1}s^{-1}$ (Sun et al., 2007, Watts et al., 2005) and the recombination of hydroxyl radicals via equation (5). The H_2O_2 efficiency for 2,6-dimethylaniline and COD removal were also determined in the study and it shows in Table 4.14. The H_2O_2 efficiency for 2,6-dimethylaniline removal was calculated using the amount of H_2O_2 consumed for the amount of 2,6-dimethylaniline removed. From Table 4.14, it can be seen that increasing the H_2O_2 concentration had the effect of decreasing the H_2O_2 efficiency. As initial H_2O_2 concentration increased from 5 mM to 100 mM decreased H_2O_2 efficiency of 2,6-dimethylaniline removal from 71.28% to 3.56% where as the percent removal increased. Theoretically, the highest H_2O_2 efficiency of 100% for 2,6-dimethylaniline removal would mean that 1 mol of 2,6-dimethylaniline was removed by 1 mol of H_2O_2. The

H_2O_2 efficiency for 2,6-dimethylaniline removal at 5 mM of H_2O_2 was 71.28%. This means that not all of the H_2O_2 consumed were used to degrade 2,6-dimethylaniline only. The H_2O_2 consumed could be used for the degradation of intermediates of 2,6-dimethylaniline or by scavenging reactions.

Table 4.14. Comparison of the effect of H_2O_2 concentrations on 2,6-dimethylaniline removal and H_2O_2 efficiency using Fenton process

[H_2O_2] (mM)	**H_2O_2 efficiency** **2,6-dimethylaniline removal** (%)	**COD removal** (%)
5	71.28	228.49
10	35.64	128.53
20	17.82	95.36
40	8.91	55.27
100	3.56	25.20

The COD removal efficiency and the H_2O_2 efficiency for COD removal followed the same trend as that of the 2,6-dimethylaniline removal. The efficiency of hydrogen peroxide on COD removal can be define by the equation below,

$$\eta = \left[\frac{\Delta COD \ (mg/l)}{available \ O_2 (mg/l)} \right] x \ 100 \qquad (19)$$

where the available oxygen is the theoretical amount of reactive oxygen in the added hydrogen peroxide. The efficiency of hydrogen peroxide on the COD removal by Fenton process decreased when increasing hydrogen peroxide concentrations.

When increasing the initial hydrogen peroxide concentration from 5 mM to 100 mM, the H_2O_2 efficiency for COD removal decreased from 228.49% to 25.20% by using photoelectro-Fenton process. H_2O_2 efficiencies higher than 100% were possible in this study since COD removal was not only attributed to Fenton’s reaction. The COD removal was also due to the photolysis via irradiation of UVA, the electrolysis via electricity, and from other oxidant that might occurred during the photoelectro-Fenton process. COD could not be completely eliminated even though hydrogen peroxide concentration was higher than the theoretical dosage. The similar result also found when treated landfill leacheate by electro-Fenton process (Zhang et al., 2006). This was probably due to the intermediate from the change in this chemical structure such as from aromatic to aliphatic structure by the ring opening reactions. These intermediates may have more resistant to degradation.

4) Effect of applied electric current

Figure 4.40 illustrates the effect of applied electric current on the 2,6-dimethylaniline removal efficiency. Results showed that increasing the applied electric current will increased the removal efficiency. In this work, the removal efficiency was 87%, 97%, 100%, 100% and 100% for electric current of 0.50, 1.43, 2.00, 4.00 and 8.00 A, respectively, after 60 minutes of reaction.

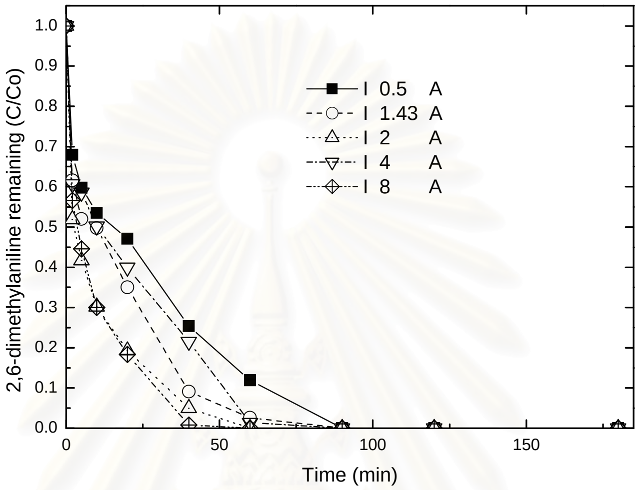

Figure 4.40. Effect of applied electric current on the 2,6-dimethylaniline degradation by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2, UVA lamp = 12.

Increasing the electric current increased the production rate of Fe^{2+} on the cathode. Therefore, the removal efficiency increased with increasing applied electric current. This observation was similar to the experiment on the removal of 4-nitrophenol by varied electric current from 0.5 to 1 A (Zhang et al., 2006). The results further indicate that the effect of the electric current on the removal efficiency was significant indicating that the production rate of Fe^{2+} was increased with increasing current.

The results further indicate that the effect of the electric current on the removal efficiency was significant indicating that the production rate of ferrous ion was increased with increasing current as shown in Figure 4.41. The results show that increased the applied electric current from 0.5, 1.43 to 4.00 A was able to increase the ferrous ion regeneration. This was due to the regeneration of Fe^{2+} induced at the cathode via reaction (12) which promotes hydroxyl radical production through reaction (1)

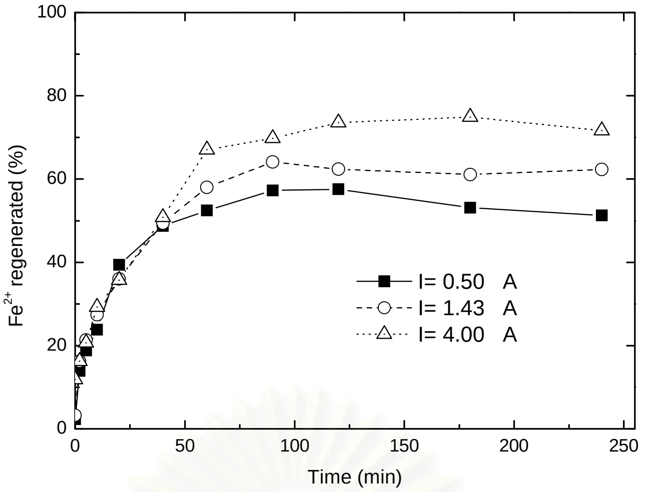

Figure 4.41. Effect of electric current on the regeneration of ferrous ion by photoelectro-Fenton.

It should be pointed that the optimal electric current also depends on the ferric ion concentration because ferric ion mass transfer also controls the ferric reduction efficiency (Chou et al., 1999). The COD removal also followed the same trend as 2,6-dimethylaniline removal as shown in Figure 4.42. COD removal increased when the applied current from 37%, 42%, 48%, 48% and 48% when applied electric current at 0.50, 1.43, 2.00, 4.00 and 8.00 A, respectively. Increasing the electric current increased the production rate of Fe^{2+} on the cathode (equation 12). Therefore, the hydroxyl radicals were more pronounced (equation 1) and further reacted with 2,6-dimethylaniline which will increased the COD removal efficiency.

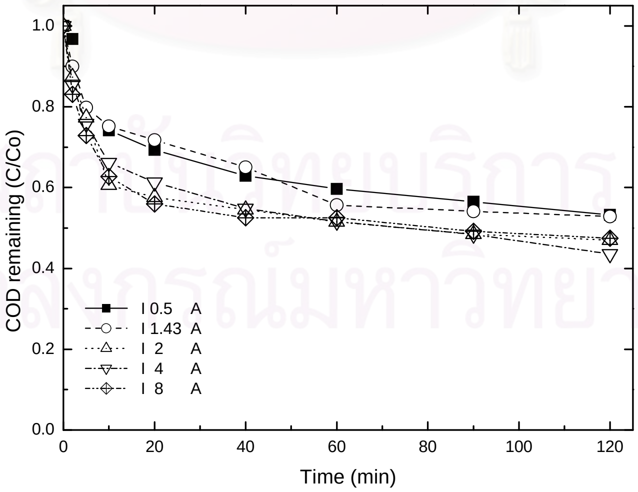

Figure 4.42. Effect of applied electric current on COD removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2, UVA lamp = 12.

The TOC removal efficiency by photoelectro-Fenton process was also determined in this part of experiment. TOC analysis was performed in order to know the amount of 2,6-dimethylaniline and other organic compounds that were depleted to carbon dioxide during the photoelectro-Fenton process. TOC removal was followed the same trend as 2,6-dimethylaniline removal and COD removal as shown in Figure 4.43. The TOC removal increased from 38%, 42%, 44%, 48% and 48% when increased applied electric current from 0.50, 1.43, 2.00, 4.00 and 8.00 A, respectively.

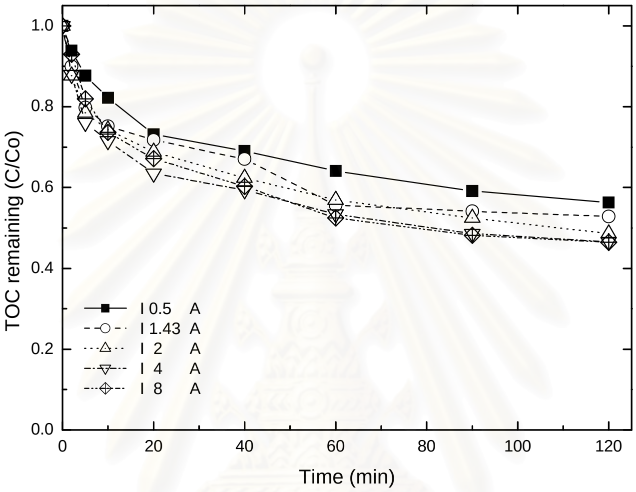

Figure 4.43. Effect of applied electric current on TOC removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2, UVA lamp = 12.

The highest TOC removal by photoelectro-Fenton process was 48% when the applied electric current was 2.00 A. The TOC removal efficiency can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton’s reaction, from electrochemically generated ferrous ion from ferric ion via equation (12) during electro-Fenton processes and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 14). The regenerated ferrous ions were then reacted with available hydrogen peroxide in the solution and thus produced hydroxyl radicals through equation (1).

Table 4.14. Effect of applied electric current on 2,6-dimethylaniline removal efficiency, COD removal efficiency, 2,6-dimethylaniline initial degradation rate and energy cost by photoelectro-Fenton; [2,6-dimethylaniline] = 1 mM, $Fe2^+$ = 1 mM, H_2O_2 = 20 mM, UVA lamp = 12

Electric current (A)	**2,6-dimethylaniline removal efficiency*** (%)	**COD removal efficiency** (%)	**Initial degradation rate**** ($mMmin^{-1}$)	**Energy cost** (kWh/m^3)
0.50	87	37	0.0397	0.77
1.43	97	42	0.0522	2.45
2.00	100	48	0.0584	3.56
4.00	100	48	0.0605	8.98
8.00	100	47	0.0610	26.57

* After 60 minute of reaction ** After 10 minutes of reaction

The effect of electric current on the initial degradation rate of 2,6-dimethylaniline degradation was also determined by varying the electric current from 0.5 to 8 A. The results are presented in Table 4.14. The 2,6-dimethylaniline initial degradation rate was increased from 0.0397, 0.0522, 0.0584, 0.0605 and 0.0610 $mMmin^{-1}$ when increased the applied electric current from 0.50, 1.43, 2.00, 4.00 and 8.00 A. The increase in 2,6-dimethylaniline removal, COD removal, TOC removal and initial degradation rate at increasing applied electric current was due to the increased regeneration of Fe^{2+} induced at the cathode via reaction (12) and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 14) thereby promoting hydroxyl radical production through reaction (1).

However, COD removal decreased to 47% when an electric current of 8 A was applied. At a higher electric current of 8 A, the competitive reactions such as the discharge of oxygen gas at the anode via reaction (20) and the evolution of hydrogen gas at the cathode via reaction (21) become more pronounced (Zhang et al., 2007).

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (20)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (21)$$

Hence, the initial degradation rate constant decreased and H_2O_2 was not efficiently used. The energy cost for photoelectro-Fenton process was also discussed and shown in Figure 4.44.

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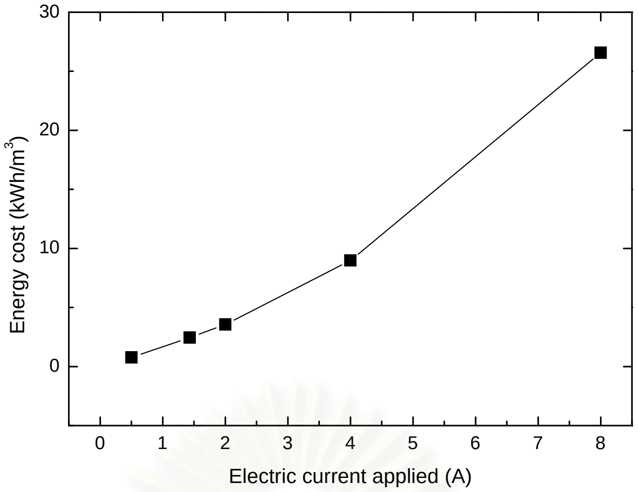

Figure 4.44. Effect of electric current on the energy cost.

The equation applied for calculate the energy cost is:

Energy cost : $$(kWh/m^3) = [\ V\ x\ I\ x\ t/volume\ ]\ x\ [COD_o/\Delta COD_{\exp.}] \qquad (22)$$

where V is the voltage applied until time t (Volt), I is the electric current (Ampere) used in the study, t is the given time (minute), volume is the amount of organic solution used in the experiment (liter), COD_o is the initial COD of the organic chemical and Δ COD_{exp} is the difference between the initial COD and the final COD after treatment. By using equation (22), the energy cost was increased when increasing the initial electric current and time applied. Consequently, the energy cost should be considered when applied photoelectro-Fenton process.

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5) Effect of number of UVA lamps

Our experimental results indicate that UVA lamp significantly affected the efficiency of 2,6-dimethylaniline degradation by photoelectro-Fenton process. In fact, applying UVA light induces the reduction of ferric ions, and photolysis of hydrogen peroxide to decompose 2,6-dimethylaniline. When UVA lamps were used, they simultaneously induced the reduction of ferric ion to ferrous ion by the following equation:

$$Fe^{3+} + H_2O + h\nu \quad \rightarrow \quad Fe^{2+} + OH^{\bullet} + H^{+} \qquad (23)$$

Moreover, the regenerated ferrous ion from equation 12 during electro-Fenton process will also occurred in the reactor. At the same time, the regenerated ferrous ion from both processes will reacted with hydrogen peroxide and produced hydroxyl radicals (equation 1). This will initiate the degradation of 2,6-dimethylaniline and lead to the mineralization of this chemical. Hence, the influence of UVA lamp on the degradation of 2,6-dimethylaniline has been investigated by varying the UVA lamp from 4,8 to 12 lamps. The results are shown in Figure 4.45.

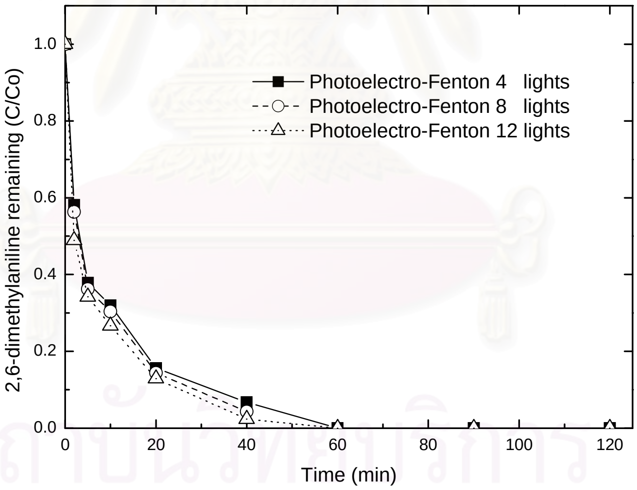

Figure 4.45. Effect of number of UVA lamps on 2,6-dimethylaniline removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2, I = 1.43 A

Increase of number of UVA lamps from 4, 8 to 12 lamps increases the degradation of 2,6-dimethylaniline from 92%, 95% to 97% at 40 minutes. This increase in degradation of 2,6-dimethylaniline is due to increased production of hydroxyl radical. However, the degradation of 2,6-dimethylaniline was the same at 60 minutes which is 100% removal. Hence, the number of UVA lamp at 4 lamps is sufficient for efficient 2,6-

dimethylaniline removal. The COD removal was followed the same trend as 2,6-dimethylaniline removal as shown in Figure 4.46. The COD removal increased from 50% to 54% when increased number of UVA lamp from 4 to 12 lamps. However, the difference of these COD removal were not significant. Hence, the 4 UVA lamps is enough for the COD removal of 2,6-dimethylaniline.

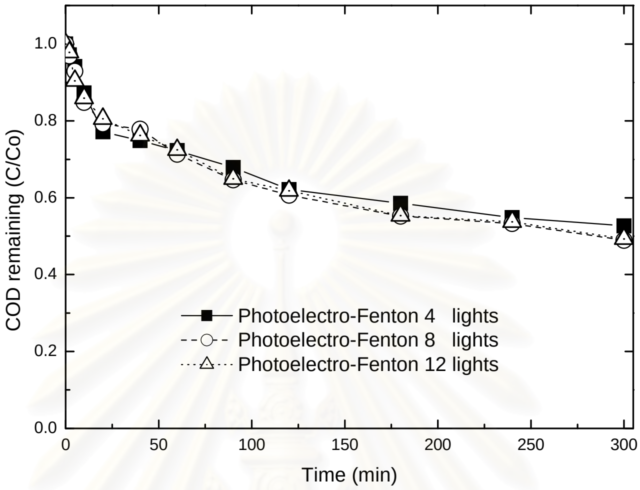

Figure 4.46. Effect of number of UVA lamps on COD removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2, I = 1.43 A

Under UVA irradiation, the degradation of 2,6-dimethylaniline is accelerated by reaction with hydroxyl radicals generated from equation (1) and the TOC removal is reduced from 35%, 37% to 40% when increased number of UVA lamp from 4, 8 to 12 lamps as shown in Figure 4.47.

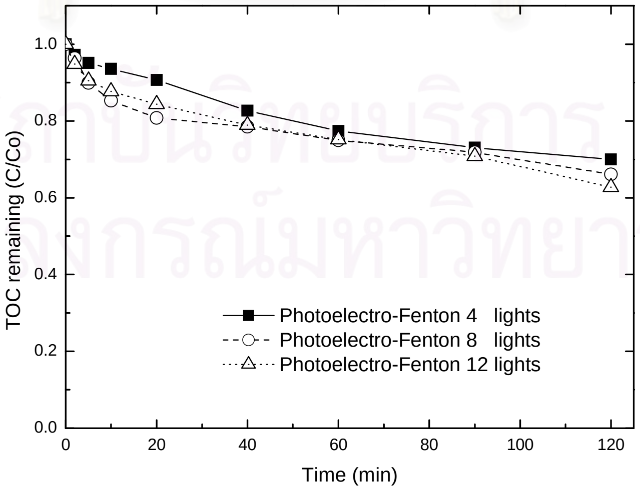

Figure 4.47. Effect of number of UVA lamps on TOC removal by photoelectro-Fenton. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2, I = 1.43 A

Photoreduction is expected to play an important role in enhancing mineralization of 2,6-dimethylaniline in photoelectro-Fenton process and coupling UV irradiation to the electro-Fenton application increases the rate of degradation of organic substrates and this should be due to the enhancement in hydroxyl radical formation.

From the overall study of photoelectro-Fenton process, it can be seen that initial pH, initial ferrous ion concentration, initial hydrogen peroxide concentration, applied electric current and number of UVA lamp are the important parameters in order to achieve the highest removal efficiency of 2,6-dimethylaniline, COD and TOC.

It is obvious that, with assisting of UVA lamps, the ferrous ion dose and reaction time can be reduced substantially. In fact, the ferric hydroxide sludge precipitating can also reduce significantly. This clearly shows the advantage of photoelectro-Fenton over convention Fenton process and electro-Fenton process. Photoelectro-Fenton process at its optimum conditions can completely remove 2,6-dimethylaniline at a much lower ferrous ion concentration than conventional Fenton process and electro-Fenton process.

4.1.1.4. Comparison between Fenton, Electro-Fenton and Photoelectro-Fenton processes

In this step, the degradation of 2,6-dimethylaniline was examined by various kind of processes. Electrolysis, Photolysis, UV + hydrogen peroxide, Fenton, electro-Fenton, photo-Fenton and photoelectro-Fenton experiments were conducted to investigate the synergistic effect of Fenton’s reagent combined photo and electrochemical methods. As shown in Figure 4.48, the results show that electrolysis can remove 18% of 2,6-dimethylaniline in 3 hr. In the electrolysis method, 2,6-dimethylaniline would be destroyed by reaction with adsorbed hydroxyl radical generated at the surface of a high oxygen-overvoltage anode from water oxidation. The same tendency can be found in the research of Brillas et al (Brillas et al., 1998). Photolysis has higher degradation efficiency compared to electrolysis. The removal efficiency by photolysis was 20% when using UVA lamps (12 lamps) at pH 2. 2,6-Dimethylaniline was not well degraded by electrolysis and photolysis. However, when UVA was combined with hydrogen peroxide, the degradation of 2,6-dimethylaniline increased significantly compared to that when using direct photolysis and electrolysis.

The degradation of 2,6-dimethylaniline was 38% when using UV+hydrogen peroxide. It is obvious that the UV+hydrogen peroxide system enhanced the photooxidation of 2,6-dimethylaniline. The hydroxyl radical which is a strong oxidant that can degrade 2,6-dimethylaniline occurs by the following equation:

$$H_2O_2 + UV \rightarrow OH^{\bullet} + OH^{\bullet} \qquad (1)$$

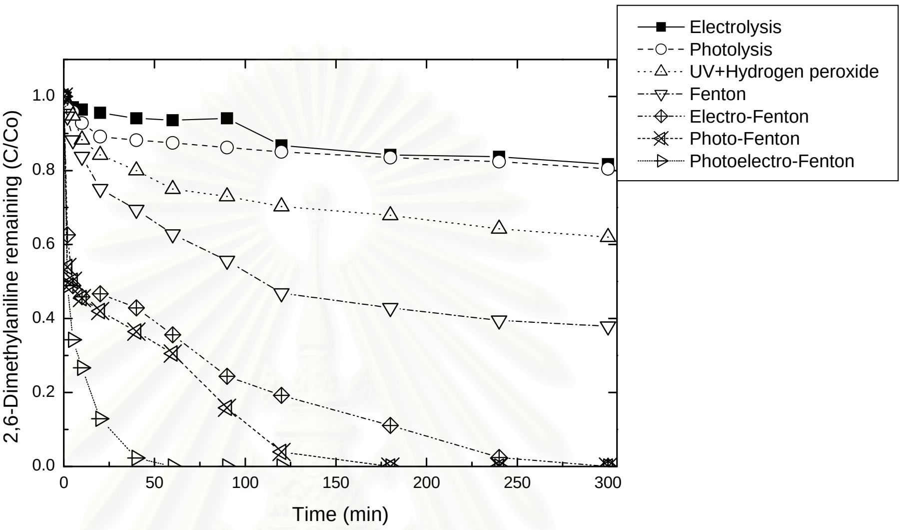

Figure 4.48. Effect of different processes on 2,6-dimethylaniline removal efficiency. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2; I = 1.43 A, UVA lamps = 12.

For Fenton process, the degradation of 2,6-dimethylaniline was 60%. This is due to the fast reaction of ferrous ion and hydrogen peroxide producing hydroxyl radicals (equation 2).

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \qquad (2)$$

The 100% removal efficiency achieved by the electro-Fenton process was nearly 40% higher than that of the Fenton process. The reason that electro-Fenton process can remove 2,6-dimethylaniline more than the Fenton process is due to the regeneration of ferrous ion from equation (3) on the cathode side:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad (3)$$

and the ability of electricity that can produced hydroxyl radicals from water oxidation as described in equation (4)

$$H_2O \rightarrow OH^{\bullet} + H^{+} + e^{-} \qquad (4)$$

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In photo-Fenton process 100% of 2,6-dimethylaniline degradation was observed at 180 min. Hence, photo-Fenton process is more efficient than Fenton process and electro-Fenton process. Degradation of 2,6-dimethylaniline is mainly due to hydroxyl radical generated by photochemical reaction. In photo-Fenton process in addition to the above reaction the formation of hydroxyl radical (equation 2) also occurs by equation (1) and (5)

$$Fe^{3+} + H_2O + h\nu \quad \rightarrow \quad Fe^{2+} + OH^{\bullet} + H^{+} \qquad (5)$$

Meanwhile, the utmost removal efficiency was found when applied photoelectro-Fenton process, 2,6-dimethylaniline was removed completely during the first 60 minutes. This indicates that the photoelectro-Fenton method had a synergistic effect for 2,6-dimethylaniline degradation. The degradation of 2,6-dimethylaniline was due to the formation of hydroxyl radical from Fenton's reaction (equation 2) and the ferric ion would be reduced to ferrous ion from photoreduction (equation 5) and the cathode (equation 3). This would induce Fenton chain reaction efficiently.

The relative efficiencies of the above processes are in the following order: Photoelectro-Fenton > Photo-Fenton > Electro-Fenton > Fenton > UV + hydrogen peroxide > Photolysis > Electrolysis.

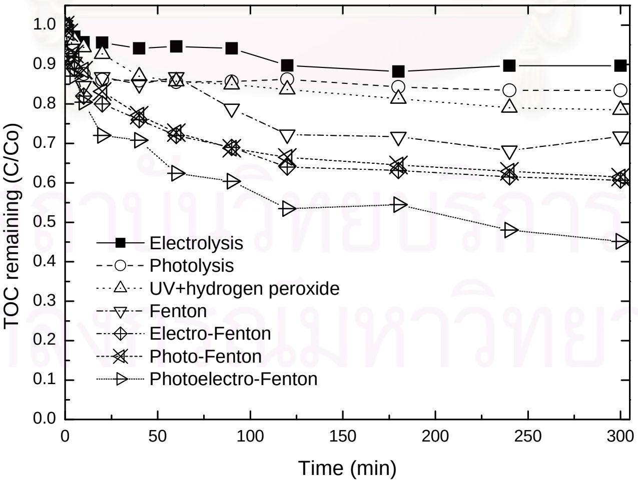

Figure 4.49. Effect of different processes on TOC removal efficiency. 2,6-dimethylaniline = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH = 2; I = 1.43 A, UVA lamps = 12.

The degradation of 2,6-dimethylaniline was monitored by measuring the total organic carbon (TOC) reduction. For TOC removal, by electrolysis, photolysis, UV+hydrogen peroxide, Fenton, electro-Fenton, photo-Fenton and photoelectro-Fenton processes, the same trend was found for 2,6-dimethylaniline degradation. The results reveal that electrolysis can remove TOC only 11%, while photolysis was able to remove about 13% as shown in Figure 4.49. When UVA was combined with hydrogen peroxide, the TOC removal increased to 20%. For Fenton process, the TOC removal was 30% which is higher than using direct photolysis, electrolysis and UV+hydrogen peroxide .This is due to the fast reaction of ferrous ion and hydrogen peroxide producing hydroxyl radicals (equation 2).

The TOC removal efficiency of 2,6-dimethylaniline by the electro-Fenton process and photo-Fenton process were nearly 40%. The reason was due to the formation of hydroxyl radical from Fenton's reaction (equation 2) and the ferric ion would be reduced to ferrous ion from photoreduction (equation 5) in photo-Fenton process and the regeneration of ferrous ion on the cathode (equation 3) in electro-Fenton process. The highest TOC removal was found when applied photoelectro-Fenton. It was about 55% and TOC removal by photoelectro-Fenton process was 15% higher than electro-Fenton and photo-Fenton at the same experimental condition. The decrease of TOC can be attributed to the mineralization of 2,6-dimethylaniline by the hydroxyl radicals from Fenton's reaction, from the electrochemically generated Fenton's reagent during electro-Fenton and photoelectro-Fenton processes and the production of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$ in photoelectro-Fenton process.

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4.1.2. Kinetics study of 2,6-dimethylaniline degradation by various Fenton processes

The kinetics of 2,6-dimethylaniline (2,6-DMA) degradation by Fenton process, electro-Fenton process and photoelectroc-Fenton process has been investigated. In this study, the kinetic comparison between Fenton, electro-Fenton and photoelectro-Fenton methods were performed by using an initial rate techniques (at the first 10 minute of the reaction) in order to eliminate the interferences from intermediate that might occurred during the study period.

The test range of each parameter was chosen according to the reality of Fenton, electro-Fenton and photoelectro-Fenton processes application and the needs of kinetic studies in this experiment. The effects of initial 2,6-dimethylaniline concentrations, initial concentrations of ferrous ion and hydrogen peroxide on the kinetic study of 2,6-dimethylaniline degradation will be separately discussed in the following sections.

1) Effect of initial 2,6-dimethylaniline concentration

The pollutant concentration is one of the important factors in Fenton, electro-Fenton and photoelectro-Fenton methods. The effect of initial 2,6-dimethylaniline concentration on the removal efficiency of 2,6-dimethylaniline by Fenton, electro-Fenton and photoelectro-Fenton processes shows in Figure 4.50 (a),(b) and (c). The figures clearly reveal that the increase in 2,6-dimethylaniline concentration in all processes decreases the removal efficiency of 2,6-dimethylaniline. When increasing 2,6-dimethylaniline concentration from 0.5 to 5 mM decrease the degradation of 2,6-dimethylaniline from 91% to 57.13% for Fenton process and from 100% to 80% for electro-Fenton process and 100% to 82% for photoelectro-Fenton process. The same results were found in the experiments of Muruganandham et al. on the decolourisation of dye by Fenton and photo-Fenton processes. They found that the increase in dye concentration decrease the removal efficiency and also removal rate (Muruganandham et al., 2004). The main reason for this phenomenon is hydroxyl radical. The increase in 2,6-dimethylaniline concentration increases the number of 2,6-dimethylaniline molecules, however, not the hydroxyl radical concentration and so the removal efficiency decreases.

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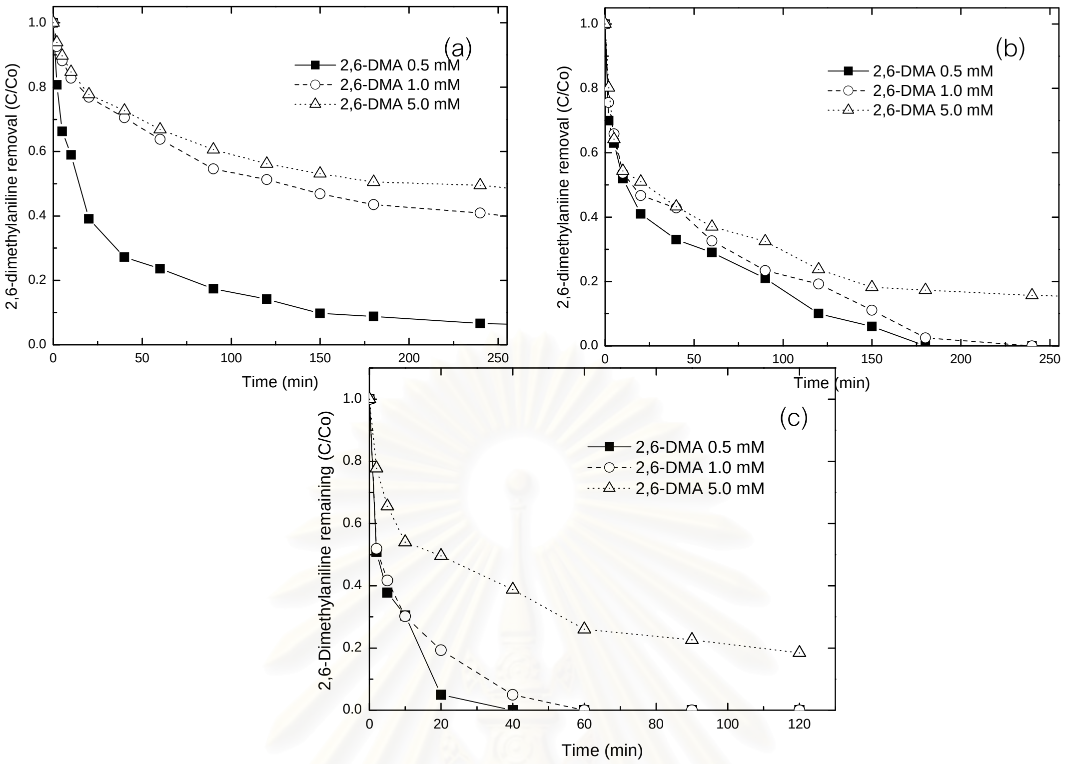

Figure 4.50. Effect of initial 2,6-dimethylaniline concentration on the removal efficiency of 2,6-dimethylaniline (a) Fenton process, (b) Electro-Fenton and (c) Photoelectro-Fenton process . Fenton process: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM , pH = 2; Electro-Fenton: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM, I = 1.43 A, pH = 2; Photoelectro-Fenton: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM, I = 1.43 A, pH = 2, UVA lamp = 12

Effect of initial 2,6-dimethylaniline concentration on the kinetic was studied by varying the initial concentration from 0.5 to 5 mM and at the experiment condition of 1 mM of ferrous ion, 20 mM of hydrogen peroxide, pH 2 and electric current 1.43 ampere for electro-Fenton method and combined UVA 12 lamps in photoelectro-Fenton process. The study showed that the 2,6-dimethylaniline degradation kinetics at the given test condition was different between conventional Fenton process, electro-Fenton process and photoelectro-Fenton process. The second-order behavior appealed to fit the degradation of 2,6-dimethylaniline by Fenton processes. The degradation kinetic for Fenton, electro-Fenton and photoelectro-Fenton processes when plot the relationship between 2,6-dimethylaniline degradation and initial 2,6-dimethylaniline concentration was in a good linear (R> 0.96) when using second-order kinetic model.

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The results from Table 4.15 showed that as 2,6-dimethylaniline concentration increased from 0.5 to 5 mM, the initial degradation rates were increased. The high initial degradation rate at high concentration of 2,6-dimethylaniline was probably due to the excess amount of 2,6-dimethylaniline to react with hydroxyl radical that produced from hydrogen peroxide and ferrous ion that will destroy 2,6-dimethylaniline.

Table 4.15. Initial rate of 2,6-dimethylaniline degradation by varying initial concentration of 2,6-dimethylaniline using Fenton, electro-Fenton and photoelectro-Fenton processes.

[2,6-Dimethylaniline]	**Initial degradation rate**		
($x10^{-3}$) M	**Fenton** (mMs^{-1})	**EF** (mMs^{-1})	**PEF** (mMs^{-1})
0.5	3×10^{-4}	4.5×10^{-4}	5×10^{-4}
1	3×10^{-4}	8×10^{-4}	10×10^{-4}
5	10×10^{-4}	20×10^{-4}	25×10^{-4}

* EF = Electro-Fenton process , PEF = Photoelectro-Fenton process

These results were also similar to the study of *p*-nitroaniline degradation by Fenton oxidation process by Sun et al., they found that the removal of PNA will decrease with the increase of initial PNA concentration but the initial degradation rate increased with the increasing PNA concentration (Sun et al., 2007) and the removal of nitroaromatic explosives with Fenton's reagent (Liou and Lu, 2007)

For the effect of initial 2,6-dimethylaniline on the degradation, the results showed that increasing initial concentration of 2,6-dimethylaniline will increased the removal efficiency for Fenton, electro-Fenton and photoelectro-Fenton processes as can be seen in Table 4.15. The plot between the initial rate and 2,6-dimethylaniline concentration on a log-log scale showed a straight line with the slopes of 0.56 for Fenton process, 0.63 for electro-Fenton process and 0.68 for photoelectro-Fenton process. Therefore, the reaction rate equations became:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{Fenton} = r_{F,2,6-DMA}\ [2,6-DMA]^{0.56} \qquad (1)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{electro-Fenton} = r_{EF,2.6-DMA}\ [2,6-DMA]^{\ 0.63} \qquad (2)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{photoelectro-Fenton} = r_{PEF,2.6-DMA}\ [2,6-DMA]^{\ 0.68} \qquad (3)$$

where 2,6-DMA is 2,6-dimethylaniline, $r_{F,2,6\text{-}DMA}$, $r_{EF,2,6\text{-}DMA}$ and $r_{PEF,2,6\text{-}DMA}$ are rate constants for Fenton and electro-Fenton processes with respect to 2,6-dimethylaniline, respectively.

2) Effect of ferrous ion concentration

The concentration of catalyst is another important parameter for the Fenton processes. Ferrous ion plays as catalyst’s role in this Fenton’s reaction. Normally, the rate of degradation increases with an increase in the concentration of ferrous ions (Fe^{2+}). The effect of ferrous ion concentration on the kinetic study for 2,6-dimethylaniline degradation was studied by varying ferrous ion concentration from 0.25 to 2 mM and at the experiment condition of initial 2,6-dimethylaniline 1 mM, 20 mM of hydrogen peroxide, pH 3 and electrical current 1.43 ampere for electro-Fenton process and UVA 12 lamps when using photoelectro-Fenton process. From the result, it showed that the removal efficiency by both Fenton, electro-Fenton and photoelectro-Fenton methods were promoted as the ferrous ion concentration increased from 0.25 to 2 mM as shown in Figure 4.51 (a), (b) and (c) (Gogate and Pandit, 2004). For Fenton process, the removal efficiency was increased from 24.54 to 89.63 % as the ferrous ion concentration increased. The same trend was found for the removal of electro-Fenton process. The removal efficiency increased from 86.71 to 100 %. For photoelectro-Fenton process, the removal efficiency was 100% in every initial ferrous ion concentration after 2 hour. However, at 60 minute, the removal efficiency increased from 88% to 100% when increased initial ferrous ion concentration.

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Table 4.16. Initial rate of 2,6-dimethylaniline degradation by varying initial concentration of ferrous ion using Fenton, electro-Fenton and photoelectro-Fenton processes.

[Fe^{2+}]	**Initial derate**		
	Fenton	**EF**	**PEF**
($x10^{-3}$) M	(mMs^{-1})	(mMs^{-1})	(mMs^{-1})
0.25	2×10^{-4}	7×10^{-4}	9×10^{-4}
1	3×10^{-4}	8×10^{-4}	10×10^{-4}
2	5×10^{-4}	11×10^{-4}	13×10^{-4}

For initial degradation rate of 2,6-dimethylaniline, the initial rate was increased when increasing initial ferrous ion concentration from 2×10^{-4} to 5×10^{-4} mMs^{-1} by Fenton process, 7×10^{-4} to 11×10^{-4} mMs^{-1} by electro-Fenton process and 9×10^{-4} to 13×10^{-4} by photoelectro-Fenton process as listed in Table 4.16. The ratio between ferrous ion concentration and hydrogen peroxide in this study was still less than one, hence, there might have some scavenging reaction occurred in this reaction (equation 6).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (4)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \quad (5)$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (6)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (7)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^\bullet + H^+ \quad (8)$$

Usually, when increasing initial ferrous ion concentration, it will increase the generation rate of hydroxyl radical due to equation (4). Moreover, the ferric ion from equation (4) can reduce to ferrous ion via equation (7) in electro-Fenton process and equation (8) via photoelectro-Fenton process. Consequently, this will enhanced the degradation rate of 2,6-dimethylaniline. For that reason, the results were underwent similar direction. An improvement in removal efficiency by ferrous ion should also considered the supplement of hydrogen peroxide through out the experiment which might led to more regeneration of ferrous ion from ferric as described in equation (7) and (8). Therefore, the total regenerated hydroxyl radicals and removal efficiency will be increased as the ferrous ion concentration increased

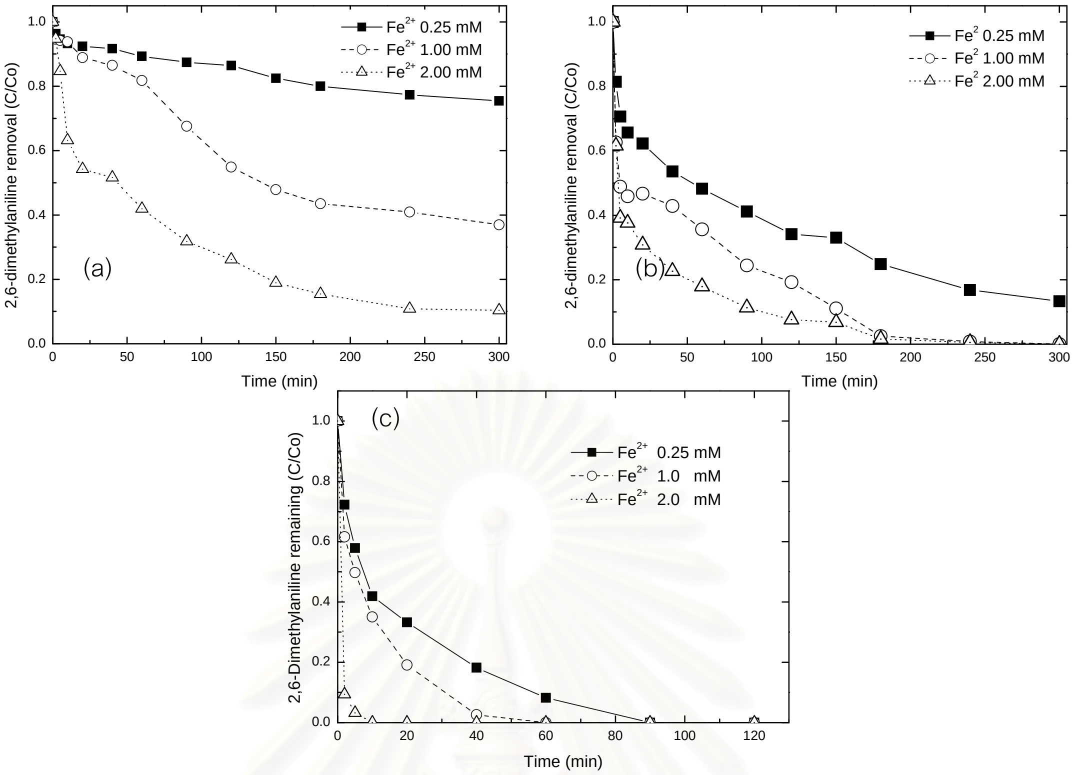

Figure 4.51. The effect of initial ferrous ion concentration on the removal efficiency of 2,6-dimethylaniline (a) Fenton process, (b) Electro-Fenton and (c) Photoelectro-Fenton processes. Fenton process: [2,6-DMA] = 1 mM, [H_2O_2] = 20 mM, pH = 2; Electro-Fenton: [2,6-DMA] = 1 mM, [H_2O_2] = 20 mM, I = 1.43 A, pH = 2. Electro-Fenton: [2,6-DMA] = 1 mM, [H_2O_2] = 20 mM, I = 1.43 A, pH = 2, UVA lamp = 12.

For electro-Fenton process, the initial rate and removal efficiency of 2,6-dimethylaniline were followed the same trend as Fenton process. In electro-Fenton process, the supplied electrons from electrical current could regenerate ferrous ion rapidly and thus can react with hydrogen peroxide as long as hydrogen peroxide still available in the reactor (Anotai et al., 2006). For that reason, the degradation of 2,6-dimethylaniline was continuously proceed without the inadequacy of ferrous ion in the solution and then it will increased the efficiency of hydroxyl radical production. For photoelectro-Fenton process, the initial degradation rate and removal efficiency of 2,6-dimethylaniline was followed the same trend as Fenton and electro-Fenton process.

In photoelectro-Fenton process, the advantage of Fenton's reaction on the formation of hydroxyl radical, the reduction of ferric ion to ferrous ion via cathode on electro-Fenton system and the photoreduction of ferric ion to ferrous ion via photoelectro-Fenton system were combined together. Those reasons made the photoelectro-Fenton had higher efficiency than Fenton process and electro-Fenton process.

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The 2,6-dimethylaniline degradation kinetics at the given test conditions were the same between conventional Fenton process and electro-Fenton process. The second–order behavior can also fitted the 2,6-dimethylaniline initial rate constant at the given test condition using Fenton and electro-Fenton processes as evidenced by the regression coefficient (>0.95). It was seen from the results that the rate of 2,6-dimethylaniline degradation was increased with the increasing of ferrous ions concentration.

The relationship between the initial rate and ferrous ion concentration for Fenton, electro-Fenton and photoelectro-Fenton processes were determined. From the calculation, it showed that the initial rate are linear-proportional to the added ferrous ion with the slopes of 0.42, 0.21 and 0.16 on a log-log scale for Fenton, electro-Fenton and photoelectro-Fenton processes, respectively. Thus, the kinetic for 2,6-dimethylaniline degradation on the effect of ferrous ion concentration can be described by following equations:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{Fenton} = r_{F,Fe^{2+}}\ [Fe^{2+}]^{0.42} \qquad (9)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{electro-Fenton} = r_{EF,Fe^{2+}}\ [Fe^{2+}]^{0.21} \qquad (10)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{photoelectro-Fenton} = r_{PEF,Fe^{2+}}\ [Fe^{2+}]^{0.16} \qquad (11)$$

where $r_{F,Fe2+}$, $r_{EF,Fe2+}$ and $r_{PEF,Fe2+}$ are the rate constants for Fenton, electro-Fenton and photoelectro-Fenton processes with respect to ferrous ion, respectively.

From the results, it indicated that ferrous ion plays an important role in degradation of 2,6-dimethylaniline by react with hydrogen peroxide to generate hydroxyl radical. However, higher ferrous ion concentration supplementation by using Fenton, electro-Fenton and photoelectro-Fenton processes are not recommended due to the large amount of ferric hydroxide sludge, which needed further separation and disposal, that could occurred and not appropriate in economical aspect.

3) Effect of hydrogen peroxide concentration

Hydrogen peroxide is an oxidizing agent in the Fenton reaction. It has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide (Pignatello, 1992). The effect of initial hydrogen peroxide concentration on the removal efficiency and kinetic rate of 2,6-dimethylaniline degradation was investigated by varying the initial hydrogen peroxide concentration from 5 to 100 mM under the experiment condition of initial 2,6-dimethylaniline concentration 1 mM, ferrous ion 1 mM, pH 2 and electrical current 1.43 A for electro-Fenton method and UVA 12 lamps when using photoelectro-Fenton process. It can be seen from the results that the removal efficiency of both Fenton, electro-Fenton and photoelectro-Fenton processes were increased when increasing the initial concentration of hydrogen peroxide as shown in Figure 4.52 (a), (b) and (c). (Lin et al., 1999). The removal efficiency was increased from 48.56 % to 76.65 % as the hydrogen peroxide concentration increased from 5 to 100 mM for Fenton process as can be seen in Figure 4.52 (a). For electro-Fenton process, the same trend was found, the removal efficiency increased from 88.9 to 100% as shown in Figure 4.52(b). For photoelectro-Fenton, 100% removal of 2,6-dimethylaniline was found after 2 hour of reaction time. However, at 60 min, the removal of 2,6-dimethylaniline increased from 90%, 100% to 88% when 5, 20 and 100 mM of hydrogen peroxide was applied. This was due to the fact that the production of hydroxyl radical produced during the experiment by the reaction of ferrous ion and hydrogen peroxide in the solution.

Table 4.17. Efficiency and initial rate of 2,6-dimethylaniline degradation by varying initial concentration of hydrogen peroxide using Fenton and electro-Fenton methods.

$[H_2O_2]$	**Initial rate**		
($x10^{-3}$) M	**Fenton** (mMs^{-1})	**EF** (mMs^{-1})	**PEF** (mMs^{-1})
5	1×10^{-4}	5×10^{-4}	9×10^{-4}
20	3×10^{-4}	8×10^{-4}	10×10^{-4}
100	3×10^{-4}	7×10^{-4}	8×10^{-4}

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It can be observed from Table 4.17. that the initial rate of 2,6-dimethylaniline degradation increased with the increasing of hydrogen peroxide concentration from 5 to 20 mM. The initial rate increased from 1 x 10^{-4} to 3 x 10^{-4} mMs^{-1} by Fenton process. This increasing in initial rate was due to the availability of hydrogen peroxide to react with ferrous ion in the solution. For electro-Fenton and photoelectro-Fenton methods, the initial rate increased from 5 x 10^{-4} to 8 x 10^{-4} mMs^{-1} and 9 x 10^{-4} to 10 x 10^{-4} mMs^{-1} as the hydrogen peroxide increased from 5 to 20 mM. However, with continuous increase initial hydrogen peroxide to 100 mM, the increasing of hydrogen peroxide leads to the decline of initial rate.

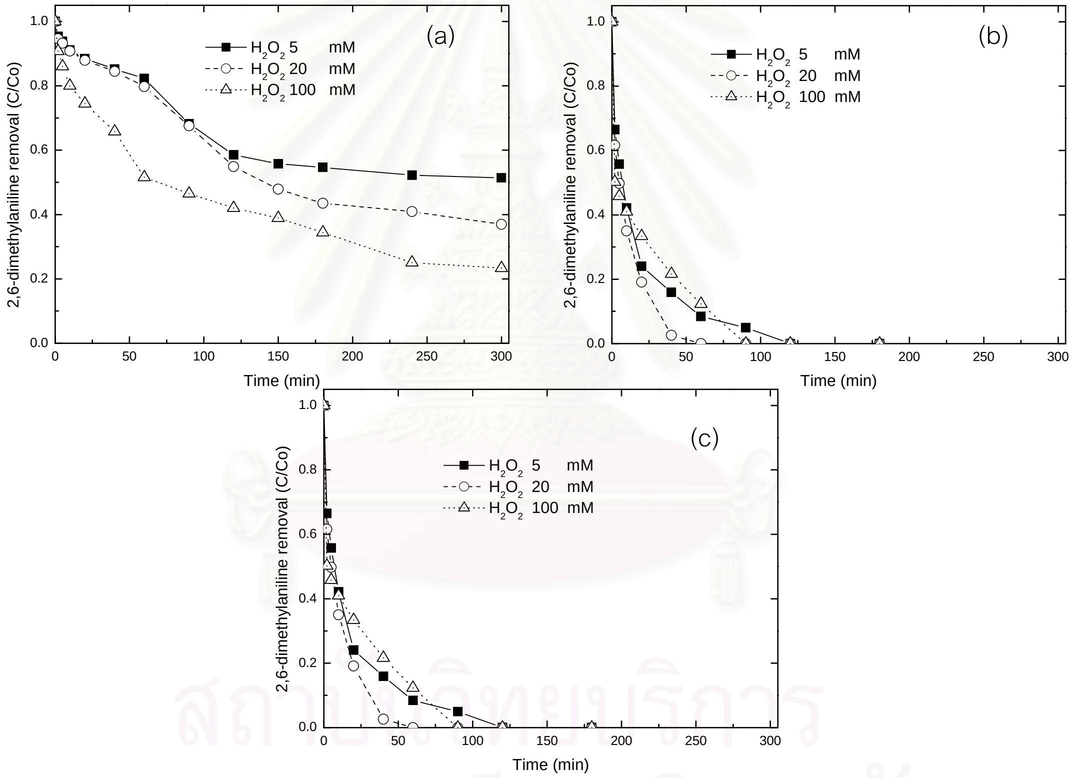

Figure 4.52. The effect of initial hydrogen peroxide concentration on the removal efficiency of 2,6-dimethylaniline (a) Fenton process, (b) Electro-Fenton and (c) Photoelectro-Fenton processes. Fenton process: [2,6-DMA] = 1 mM, [Fe^{2+}] = 1 mM , pH = 2; Electro-Fenton: [2,6-DMA] = 1 mM, [Fe^{2+}] = 1 mM, I = 1.43 A, pH = 2; Photoelectro-Fenton: [2,6-DMA] = 1 mM, [Fe^{2+}] = 1 mM, I = 1.43 A, pH = 2, UVA lamp = 12.

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The initial rate decreased from 8 x 10^{-4} to 7 x 10^{-4} mMs^{-1} and 10 x 10^{-4} to 8 x 10^{-4} mMs^{-1} when using electro-Fenton and photoelectro-Fenton processes, respectively. In Fenton process, the initial rate was stable. This phenomenon probably due to the scavenging of hydroxyl radicals by hydroxyl radical as described via equation (6) (Lu et al., 1999). The accumulation of hydroperoxyl radicals also consumed hydroxyl radicals (Sun et al., 2007, Kang et al., 2002). Hydrogen peroxide might have been consumed by the scavenging reaction and some intermediate (Pignatello, 1992).

It was found that the second-order kinetic model is applicable to the 2,6-dimethylaniline degradation quite well under Fenton process and electro-Fenton process with R> 0.98. The relationship of initial rate and hydrogen peroxide are linear on a log-log scale and the slopes are 0.36, 0.11 and -0.04 for Fenton, electro-Fenton and photoelectro-Fenton processes, respectively; therefore

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{Fenton} = r_{F,H_2O_2}\ [H_2O_2]^{0.36} \tag{12}$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{electro-Fenton} = r_{EF,H_2O_2}\ [H_2O_2]^{0.11} \tag{13}$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{photoelectro-Fenton} = r_{PEF,H_2O_2}\ [H_2O_2]^{-0.04} \tag{14}$$

where r_{F,H_2O_2} , r_{EF,H_2O_2} and r_{PEF,H_2O_2} are rate constant for Fenton, electro-Fenton and photoelectro-Fenton processes with respect to hydrogen peroxide, respectively.

4) The overall reaction rate equation for 2,6-dimethylaniline degradation

From previous sections, the reaction rate equation of 2,6-dimethylaniline degradation was proposed varied with the respect to 2,6-dimethylaniline, ferrous ion and hydrogen peroxide concentrations in Fenton, electro-Fenton and photoelectro-Fenton processes. The overall degradation kinetic for 2,6-dimethylaniline by three methods can be summarized as shown below:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{Fenton} = r_F\,[2,6-DMA]^{0.56}\ [Fe^{2+}]^{0.42}\ [H_2O_2]^{0.36} \qquad (15)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{electro-Fenton} = r_{EF}\,[2,6-DMA]^{0.63}\ [Fe^{2+}]^{0.21}\ [H_2O_2]^{0.11} \qquad (16)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{photoelectro-Fenton} = r_{PEF}\,[2,6-DMA]^{0.68}\ [Fe^{2+}]^{0.16}\ [H_2O_2]^{-0.04} \qquad (17)$$

where r_F, r_{EF} and r_{PEF} are the overall rate constants for Fenton, electro-Fenton and photoelectro-Fenton processes, respectively. From the equation (15 and 16), it can be seen that the degradation rate of 2,6-dimethylaniline by Fenton process and electro-Fenton process was depended on Fenton’s reagent both ferrous ion and hydrogen peroxide. However, from equation (17), the reaction shown that the 2,6-dimethylaniline degradation ,when applied electrical current and UVA, the degradation rate was almost independent from hydrogen peroxide. Nevertheless, the ferrous ion was still be the important species for the degradation of this chemical so the Fenton’s reagent still be the major key for this process. The r_F, r_{EF} and r_{PEF}, from equation (15), (16) and (17), could be calculated by using a non-linear least squares method which minimizing the sum of error squares between the observed initial rates attained from the study and from the calculated initial rates. Accordingly, the r_F, r_{EF} and r_{PEF} could be proposed by calculated using concentration of 2,6-dimethylaniline, ferrous ion and hydrogen peroxide in millimolar (mM) units. From the calculation, the r_F, r_{EF} and r_{PEF} were 3.41, 1.60 and 1.04, respectively. Therefore, the final reaction rate equations can be described as:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{Fenton} = 3.41\ [2,6-DMA]^{0.56}\ [Fe^{2+}]^{0.42}\ [H_2O_2]^{0.36} \qquad (18)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{electro-Fenton} = 1.60\ [2,6-DMA]^{0.63}\ [Fe^{2+}]^{0.21}\ [H_2O_2]^{0.11} \qquad (19)$$

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{photoelectro-Fenton} = 1.04\ [2,6-DMA]^{0.68}\ [Fe^{2+}]^{0.16}\ [H_2O_2]^{-0.04} \qquad (20)$$

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Therefore, from the kinetic study, it can be seen that the presence of Fenton’s reagent, electricity and UVA lamp can improve both 2,6-dimethylaniline removal efficiency and rate of degradation. Within the range of Fenton’s reagent applied in this study, the initial ferrous ion concentration seems to be the most important parameter affecting on the removal efficiency and initial degradation rate. Thus using electro-Fenton and photoelectro-Fenton to accelerate the regeneration of ferrous ion from ferric ion as described in equation (7) and (8) could significantly improve both removal efficiency and initial degradation rate of 2,6-dimethylaniline.

From the results, the overall rate equations for 2,6-dimethylaniline degradation by Fenton, electro-Fenton and photoelectro-Fenton processes as shown in equation (18 - 20), they indicated that the series of complex reactions occurred during the degradation of 2,6-dimethylaniline by hydroxyl radicals.

4.1.3. The mechanism degradation pathways for 2,6-dimethylaniline degradation and intermediate detection

The GC/MS and IC were applied to identify the intermediates that might have occurred from the degradation of 2,6-dimethylaniline by the electro-Fenton process. Several stable intermediates, such as 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid were detected during the degradation of 1 mM 2,6-dimethylaniline solution by the electro-Fenton method when an electric current of 1.43 A was applied. GC-MS (Agilent 6890) with DB-5MS capillary column showed the presence of 2,6-dimethylaniline absorption peak at 9.36 min. Moreover, the four additional peaks were found. The intermediates are 2,6-dimethylphenol at 8.68 min, 2,6-dimethylbenzoquinone at 8.77 min, 2,6-dimethylnitrobenzene at 9.59 min, and 3-hexanone at 4.18 min. The anions were examined by an Ion Chromatograph (Dionex DX-120). The anions included lactic acid at 1.15 min, acetic acid at 2.9 min, maleic acid at 9.79 min, formic acid at 3.58 min and oxalic acid at 10.64 min. The formic acid was found after 2 minutes of the reaction time and its concentration increased with the increasing of time after 60 minutes the concentration of formic acid decreased. Oxalic acid was also found after 2 minutes. The concentration of oxalic acid increased as the time increased. It is shown in Figure 4.53.

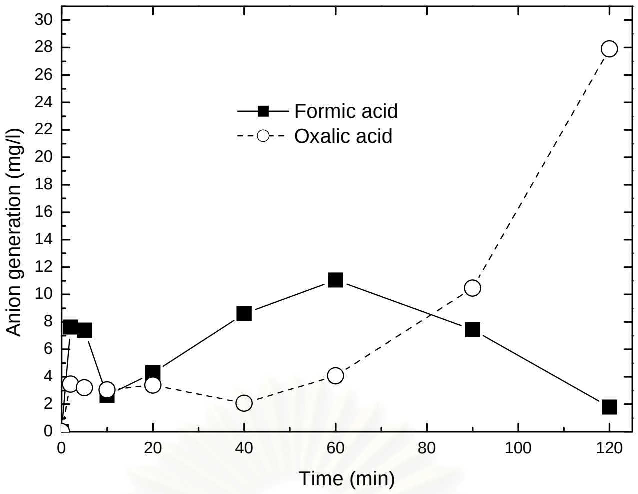

Figure 4.53. The profile of anions generation.

Nitrate ions were also detected in the electrolyzed solutions. However, no nitrite ions were found in the solution. The nitrate ion generation profile is presented in Figure 4.54. The nitrate ions were found due to the degradation of 2,6-dimethylaniline into other intermediates such as 2,6-dimethylphenol. Evolution of these species under electro-Fenton condition is presented in Figure 4.55. 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, formic acid, acetic acid and maleic acid are practically eliminated in the experiment after 4 hours of the reaction.

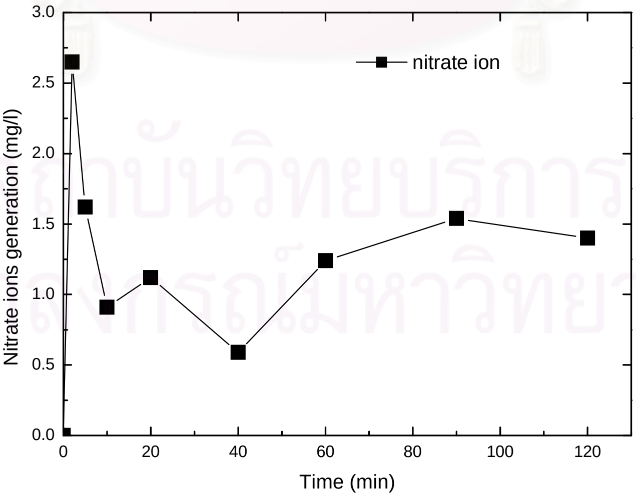

Figure 4.54. The nitrate ion generation profile.

Based on these finding, a general pathway for degradation of 2,6-dimethylaniline at pH 2 with the electro-Fenton process was proposed. The proposed pathway is shown in Figure 4.55. In electro-Fenton oxidation, the main oxidizing species is the hydroxyl radical. It is known that OH• radicals are nonselective and strong electrophilic oxidizing species (Pérez et al., 2005).

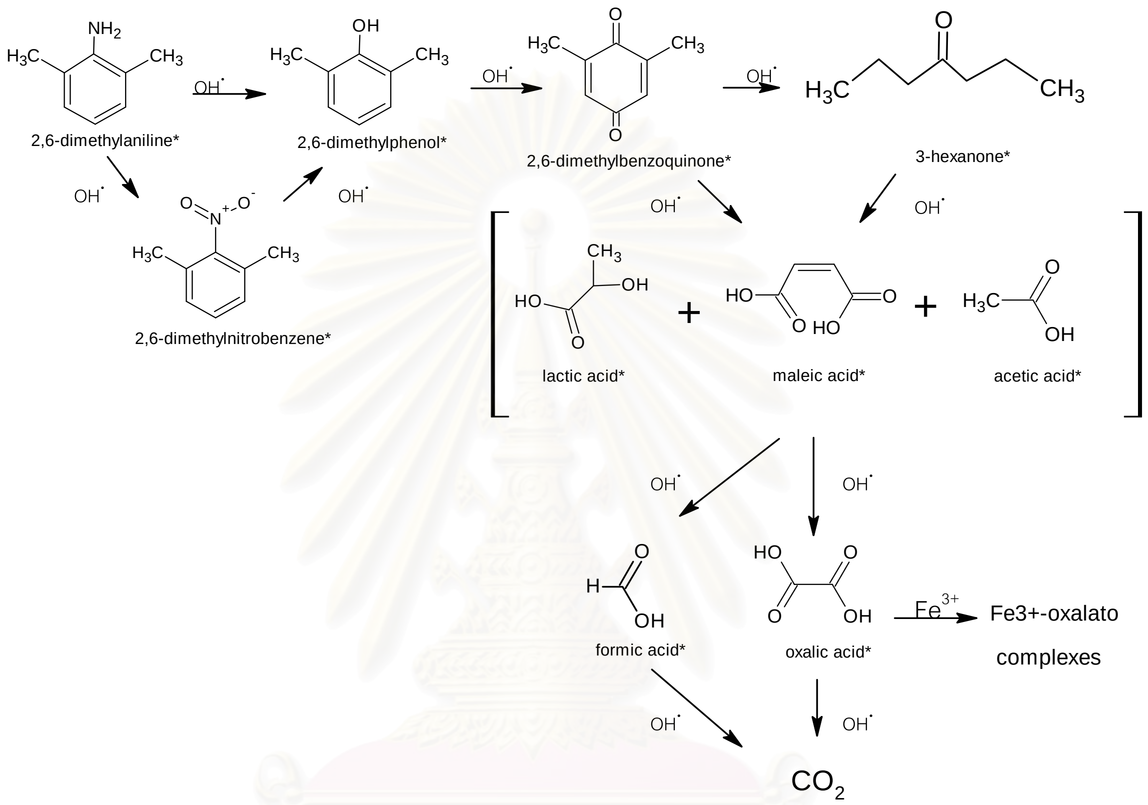

Figure 4.55. Proposed reaction pathways for mineralization of 2,6-dimethylaniline at pH 2 by electro-Fenton process. (* detected by GC-MS and IC)

The degradation process can be initiated either by the attack of $OH^{\bullet}$ on 2,6-dimethylaniline that yields 2,6-dimethylnitrobenzene or by the direct hydroxylation of 2,6-dimethylaniline's N-position to give 2,6-dimethylphenol. 2,6-dimethylbenzoquinone is also formed from $OH^{\bullet}$ attack on 2,6-dimethylphenol which further breaks into 3-hexanone. In Fenton reactions, $OH^{\bullet}$ addition to the aromatic substrates to give mono- or multihydroxyl intermediates or products (hydroquinone/quinone analogues) has been firmly established (Chen and Pignatello, 1997). The further degradation of 2,6-benzoquinone and 3-hexanone leads to a mixture of lactic acid, maleic acid and acetic acid. The three acids are transformed into formic acid and oxalic acid. The formic acid is directly mineralized to carbon dioxide. The ultimate carboxylic acid, oxalic acid, is very slowly converted into CO_2 by $OH^{\bullet}$ since it forms very stable Fe^{3+}-oxalato complexes under the electro-Fenton process.It can be easily established that 2,6-dimethylaniline is degraded to 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone and probably other nitrogen-free organic derivatives. As far as we know, the proposed degradation pathways of 2,6-dimethylaniline using the electro-Fenton process at pH 2 has not yet been reported in the literature.

4.2. Aniline degradation by Fenton processes

The degradation of aniline was studied by using three main processes including Fenton, electro-Fenton and photoelectro-Fenton processes in order to compare the efficiency of each process on the oxidation of aniline. In this section, the detailed explanation on each factor such as pH, ferrous ion, hydrogen peroxide, electric current and number of UV lights will be shown.

4.2.1. Effect of initial condition on the decomposition of aniline by various processes

4.2.1.1. Fenton process

In this experimental part, the Fenton process which uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade toxic pollutants (Lu et al., 1997). The Fenton's reactions on the degradation of organic compounds are shown in equations (1-8).

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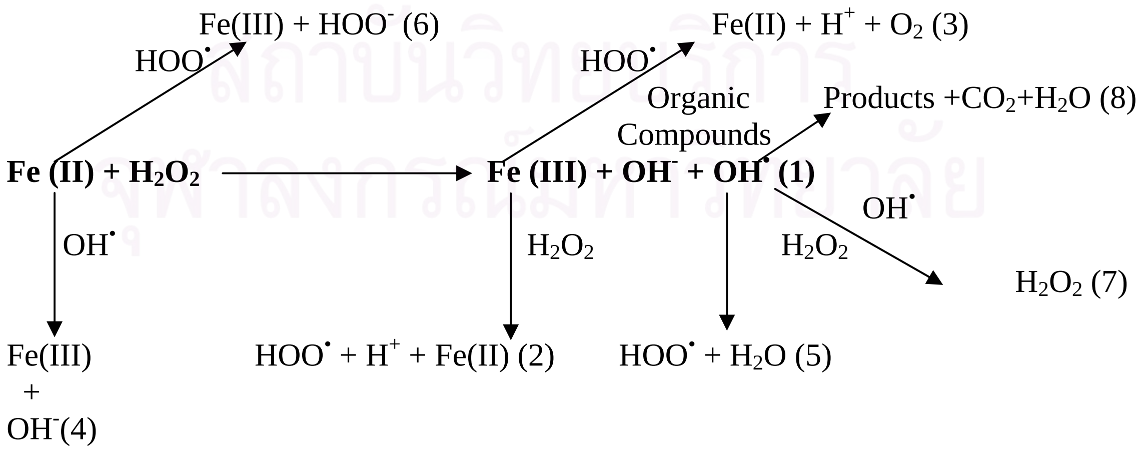


Figure 4.56. Fate of Fenton's reaction on the degradation of organic compounds.

In this study, the Fenton's condition was adapted from the study of Parichat Chewpreecha (2006). She found that ferrous ion 0.5 mM, hydrogen peroxide 20 mM at pH 3 was needed in order to remove 100% of aniline 1 mM. From my study, the result showed thatwhen using ferrous ion 0.5 mM, hydrogen peroxide 20 mM at pH 3 aniline can be removed 100% in 2 hour as shown in Figure 4.57.

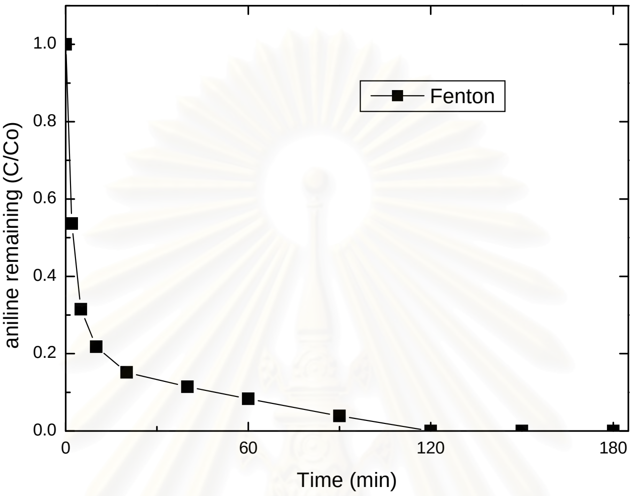


Figure 4.57. The degradation of aniline by Fenton process. Aniline = 1mM, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, pH = 3

The COD removal was also determined in this study. The COD removal was 47% and showed in Figure 4.58.

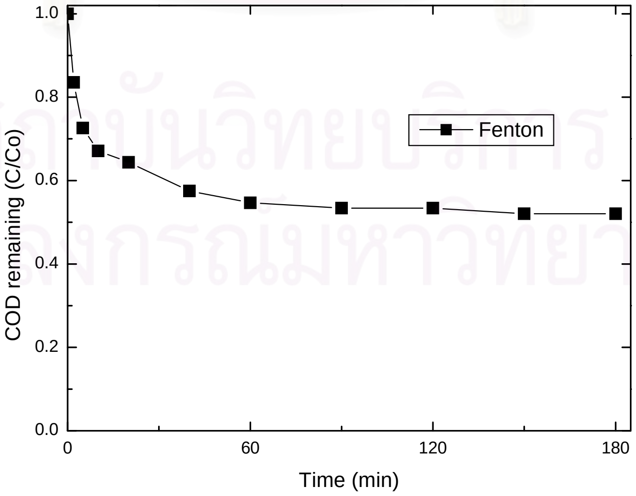


Figure 4.58. The COD removal of aniline by Fenton process. Aniline = 1mM, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, pH = 3

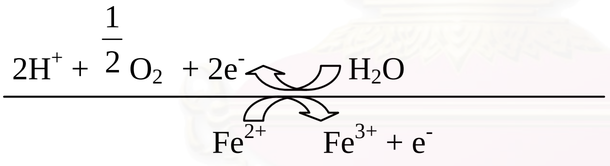
The increase in the aniline removal and COD removal can explain by the formation of hydroxyl radical in equation (1) enhanced the 2,6-dimethylaniline removal and COD removal via reaction (8). It can be seen in the Figure 4.57. that aniline degradation in this system underwent a two-stage reaction.

The degradation was fast during the initial 10 minutes of the reaction then slowed down until the end of the reaction time. The first stage or first 10 minutes, the degradation rate of aniline was high, it is probably due to the reaction between ferrous ion and hydrogen peroxide. The second stage is the reaction that took place after 10 minutes. The degradation rate of aniline in this reaction stage was slowed; it is possibly a reaction of ferric ion and hydrogen peroxide.

4.2.1.2. Electro-Fenton process

Electro-Fenton process uses the electrical current to induce the reduction of ferric hydroxide sludge to form ferrous ions. Hence, it reduces the sludge disposal cost which is one of the major drawbacks of conventional Fenton process (Anotai et al., 2006, Gnann et al., 1993).The proposed reactions in the electrolytic system are as follows:

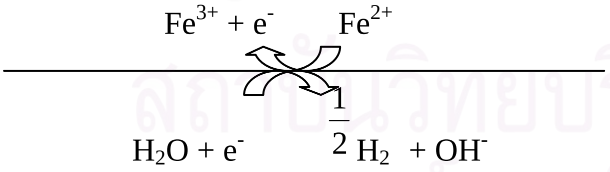
On the anode side:



$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O \qquad (9)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad (10)$$

On the cathode side:



$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (11)$$

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \qquad (12)$$

From the reactions above, it can be seen that the ferric ion can be transformed to ferrous ion by the reaction to an electron produced on the cathode side (equation 11). The regenerated ferrous ion will then react with hydrogen peroxide and produced more hydroxyl radicals that can destroy the target compounds. This reaction will not only minimize the ferric sludge, which is the major disadvantage of the Fenton process, but it will also enhance the degradation rate of target compounds. Therefore, it is interesting to determine whether aniline can also be effectively oxidized by the electro-Fenton process. In this part, the same condition as Fenton process was used. When applied ferrous ion 0.5 mM, hydrogen peroxide 20 mM at pH 3 and applied 1 A of electric current, the aniline removal was 100% at 90 min as shown in Figure 4.59 .

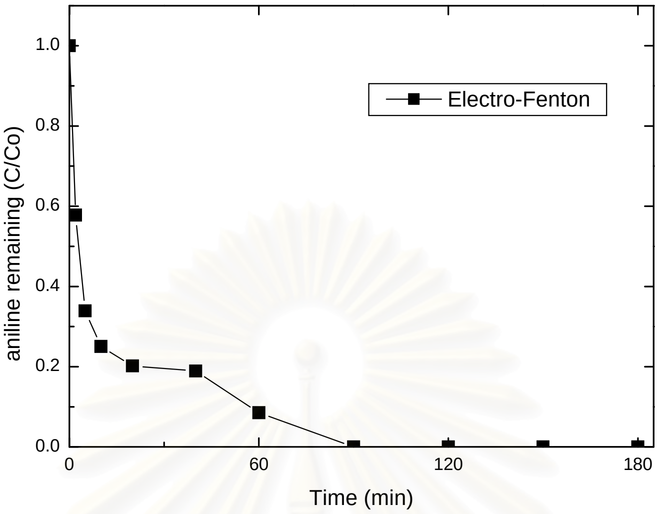


Figure 4.59. The degradation of aniline by electro-Fenton process. Aniline = 1mM, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, pH = 3, I = 1 A

The COD removal was also determined in this study. The COD removal was 58% and showed in Figure 4.60.

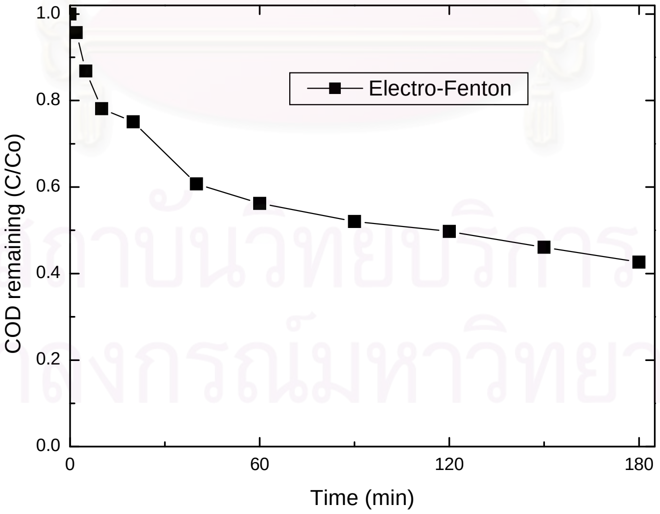


Figure 4.60. The COD removal of aniline by electro-Fenton process. Aniline = 1mM, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, pH = 3, I = 1 A

The increase in the aniline removal and COD removal can explain by the production of hydroxyl radical in equation (1) enhanced the 2,6-dimethylaniline removal and COD removal via reaction (8). And the ferric ion (from equation 1) can be transformed to ferrous ion by the reaction to an electron produced on the cathode side (equation 11). The regenerated ferrous ion will then react with hydrogen peroxide and produced more hydroxyl radicals that can destroy the target compounds.

4.2.1.3. Photoelectro-Fenton process

From the previous experiments on aniline degradation by Fenton process and electro-Fenton process, it can be seen that the formation of ferric oxyhydroxide sludge is still a problem here. In principle, the ferric ion could reduce to ferrous ion at the cathode in electro-Fenton process. However, the ferrous ion regeneration is slow even at optimum electric current applied. Therefore, the new method which can promote the ferrous ion regeneration was focused in this part of experiment.

The photoelectro-Fenton process involves the additional irradiation of the solution with UVA light. UVA light can favor (1) the regeneration of ferrous ion with production of more amount of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$, which is the predominant ferric ion species in acid medium (Sun and Pignatello, 1993) and (2) the photodecomposition of complexes of ferric ion with generated carboxylic acids (Flox et al., 2006) Moreover, under UVA irradiation, the overall efficiency of the process increases due mainly to the regeneration of ferrous ions and formation of additional hydroxyl radical. The action of this irradiation is complex and can be described by:

(1) the production of greater amount of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$, the predominant Fe^{3+} species in acid medium. Under light irradiation, Fe(III) is continuously reduced to Fe(II):

$$FeOH^{2+} + h\nu \rightarrow Fe(II) + OH^{\bullet} \tag{13}$$

(2) the photolysis of complexes of Fe(III) with generated carboxylic acids (Pignatello et al., 2006; Exposito et al., 2007).

$$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe(II) + CO_2 + R^{\bullet} \tag{14}$$

The maximum adsorption wavelength of $Fe(OH)^{2+}$ species is less than 360 nm, visible irradiation may not drive the reaction of equation (1). An interesting and potentially useful modification of the photoreduction reaction takes advantage of the photo-lability of Fe(Ⅲ)-oxalate complexes, which is efficiency up to 500 nm (Pignatello et al., 2006). Under these conditions, it is also feasible to used sunlight as an alternative inexpensive source of UVA light using the solar photoelectro-Fenton process (Flox et al., 2007).

1) Control experiment

Photolysis, UV + hydrogen peroxide, Fenton, Electro-Fenton, Photo-Fenton and Photoelectro-Fenton experiments were conducted to investigate the effect of UVA lamp, Fenton’s reagent and electrochemical methods. Figure 4.61 showed that photolysis could remove 10% of aniline in 2 hr. In the UV + hydrogen peroxide method, 2,6-dimethylaniline would be destroyed 15%. When using Fenton process, the removal was 100% after 2 hour. These was due to the production of hydroxyl radical during the Fenton’s reaction as described in equation 1. For electro-Fenton process, the removal efficiency of aniline degradation was faster than Fenton process. The 100% removal of aniline was found after 90 minutes of reaction. This is due to the regenerated ferrous ion form equation (11) that will reacted with hydrogen peroxide again in equation 1 making the formation of hydroxyl radicals more than Fenton process and thus the degradation of aniline by electro-Fenton was higher than Fenton.

When applied UVA combined with Fenton’s reagent, 100% removal was found in 40 min. This was due to the formation of additional hydroxyl radical from the Fenton’s reaction and the regeneration of ferric ion to ferrous ion (equation 13). The utmost removal efficiency was found when applied photoelectro-Fenton process, 2,6-dimethylaniline was removed completely during the first 20 minutes as shown in Figure 4.61.

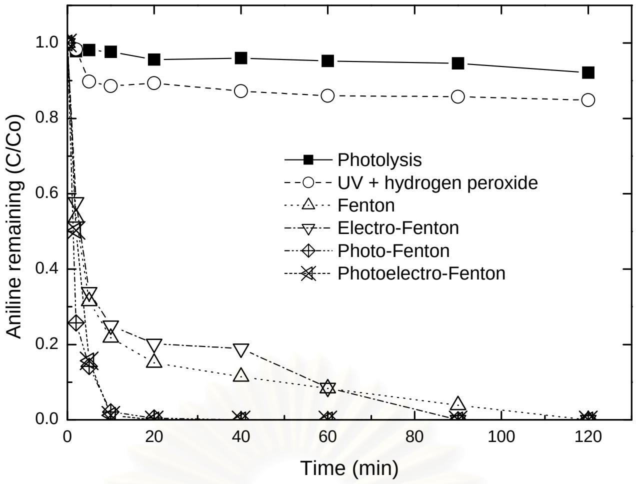


Figure 4.61. Effect of different processes on aniline removal efficiency. Aniline = 1 mM; [Fe^{2+}] = 0.5 mM; [H_2O_2] = 20 mM; pH = 3; I = 1A, UVA lamp = 12.

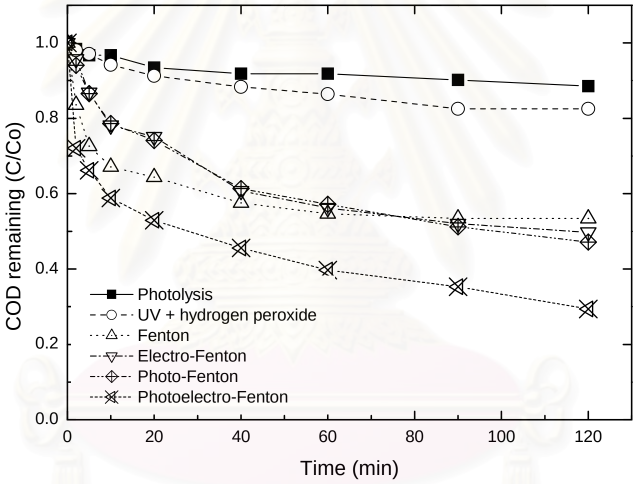


Figure 4.62. Effect of different processes on COD removal efficiency. Aniline = 1 mM; [Fe^{2+}] = 0.5 mM; [H_2O_2] = 20 mM; pH = 3; I = 1A, UVA lamp = 12.

Figure 4.62 shows the COD removal of a 1 mM aniline solution at pH 3. The results followed the same trend as aniline removal. It can be seen from Figure 4.62. that photolysis can remove COD only 11%, while UV + hydrogen peroxide method was able to remove about 17% and 47 % for Fenton process after 2 hours. The COD removal by electro-Fenton process is 53%. When combined UVA with Fenton process (Photo-Fenton process), the COD removal was almost the same as electro-Fenton process which is about 55%. The highest COD removal obtained by photoelectro-Fenton process was about 76% at the same experimental conditions. This indicates that photoelectro-Fenton had higher COD removal efficiency than other processes.

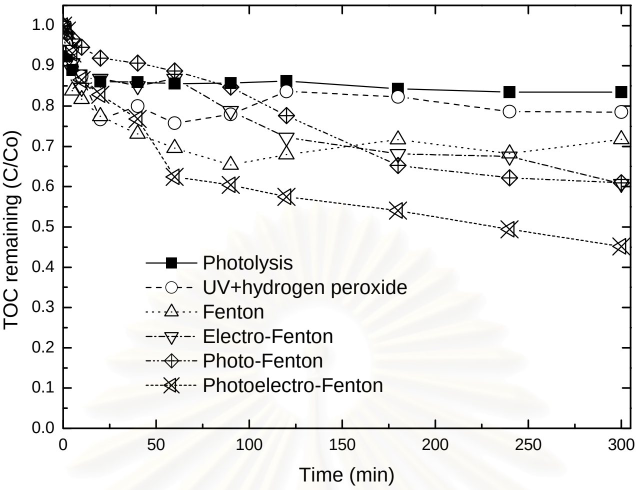


Figure 4.63. Effect of different processes on TOC removal. Aniline = 1 mM; [Fe^{2+}] = 0.5 mM; [H_2O_2] = 20 mM; pH = 3; I = 1 A, UVA lamp = 12.

The TOC removal was also determined in this study. The TOC removal was followed the same trend as COD removal as shown in Figure 4.63. The results showed that photolysis can remove TOC about 13%, while UV + hydrogen peroxide method was able to remove about 15% and 30% for Fenton process after 2 hours. The TOC removal by electro-Fenton process is 40%. When using photo-Fenton process, the TOC removal was 40% which is almost the same as electro-Fenton process. The highest TOC removal was 59% when photoelectro-Fenton process was applied.

The results showed that during the first 10 minutes, the removal of COD and TOC was rapidly decreased. Afterwards, the rate for COD and TOC removal was slowly decreased, which can be attributed to the depletion of ferrous ion in the solution. Hydroxyl radical formed from Fenton’s reaction, electricity and UVA lamp destroys more rapidly aromatic products, making photoelectro-Fenton processes much more efficient than others.

2) Effect of initial pH on aniline degradation

It wan known that the high efficiency of Fenton’s reaction took place at pH 2-4, and the optimum value is 2.8 proposed by Pignatello et al. (1992). The pH of the solution controls the production of the hydroxyl radical and the concentration of ferrous ions (Pignatello et al., 2006, Sun et al., 2007). The effect of pH on the degradation of aniline is shown in Figure 4.64.

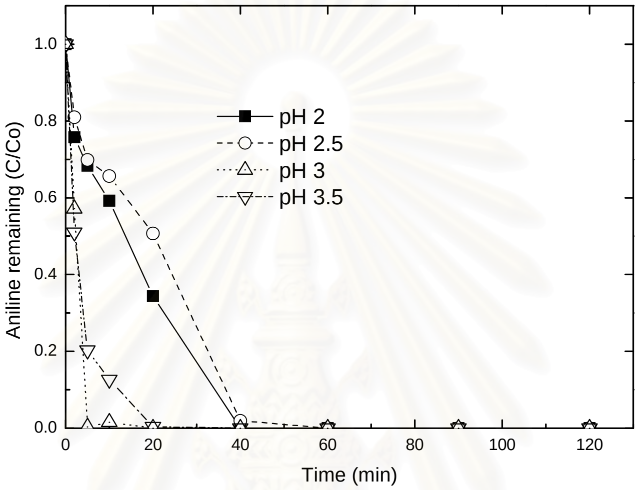


Figure 4.64. Effect of pH_i on the aniline degradation by photoelectro-Fenton. Aniline = 1 mM; $[Fe^{2+}]$ = 0.5 mM; $[H_2O_2]$ = 20 mM; I = 1 A, UVA lamp = 12.

Increasing the pH from 2, 2.5 to 3 increased the removal from 50%, 68% to 100%, respectively, in 20 min. A further increase of pH from 3 to 3.5 was not significant. It was reported earlier that at higher pH (>4), Fe^{3+} started to be precipitated in the form of amorphous $Fe(OH)_3$. The formation of $Fe(OH)_3$ not only decreased the dissolved Fe^{3+} concentration, but also inhibited Fe^{2+} regeneration by partially coating the electrode surface. However, from this study, the optimum pH was found to be about 3. It is in good agreement with early reports (Lu et al., 2003, Chou et al., 1999, Qiang et al., 2003).

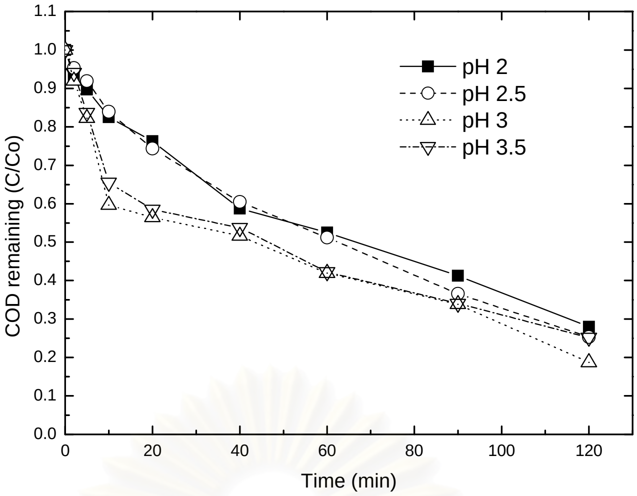


Figure 4.65. Effect of pH$_i$ on the COD removal by photoelectro-Fenton. Aniline = 1 mM; [Fe^{2+}] = 0.5 mM; [H$_2$O$_2$] = 20 mM; I = 1 A, UVA lamp = 12.

COD removal efficiency followed the same trend as aniline removal. Figure 4.65 shows that COD removal increased from 72%, 76% to 82% as pH increased from 2, 2.5 to 3, respectively. However, the COD removal decreased to 76% when increased pH to 3.5. The highest COD removal about 82% was achieved at pH 3. When pH was further increased, COD removal decreased.

The TOC removal was also examined in this study. TOC analysis was performed in order to know the amount of organic compounds that were depleted to carbon dioxide during the chemical oxidation. The TOC removal was followed the same trend as COD removal as shown in Figure 4.66.

At pH 2, the TOC removal was 46%. TOC removal increased from 50% to 57% when increased pH from 2.5 to 3. The highest TOC removal by photoelectro-Fenton process was 57% when the pH was 3. However, the TOC removal decreased from 57% to 54% when increased pH from 3 to 3.5. The TOC removal efficiency can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton's reaction, from electrochemically generated ferrous ion from ferric ion via equation (11) during electro-Fenton processes and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 13). The regenerated ferrous ions were then reacted with available hydrogen peroxide in the solution and thus produced hydroxyl radicals through equation (1).

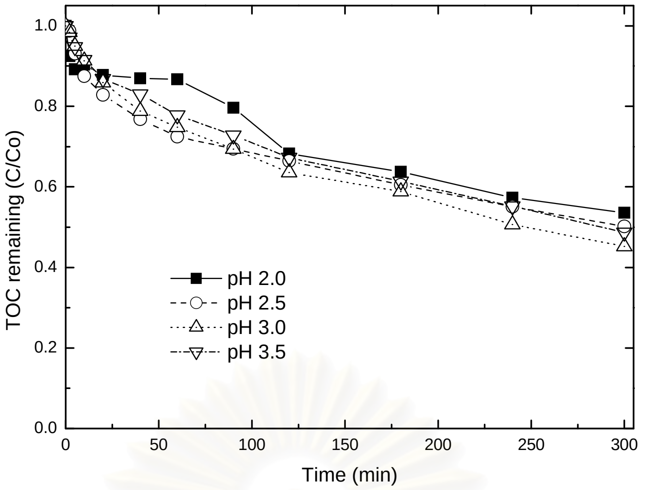


Figure 4.66. Effect of pH_i on the TOC removal by photoelectro-Fenton. Aniline = 1 mM; $[Fe^{2+}]$ = 0.5 mM; $[H_2O_2]$ = 20 mM; I = 1 A, UVA lamp = 12.

To further compare the aniline degradation, all experimental data were analyzed using initial degradation rate, which presented in Table 4.18.

Table 4.18. Effect of initial pH on aniline removal efficiency, COD removal efficiency and aniline initial degradation rate at the different initial pH by photoelectro-Fenton; [Aniline] = 1 mM, $[H_2O_2]$ = 20 mM, $Fe2^+$ = 0.5 mM, I = 1 A, UVA lamp = 12

pH initial	pH final	Aniline removal efficiency* (%)	COD removal efficiency (%)	Initial degradation rate** ($mMmin^{-1}$)
2.0	1.88	50	72	0.0312
2.5	2.22	68	76	0.0359
3.0	2.73	100	82	0.0960
3.5	2.70	100	76	0.0796

* After 20 minute of reaction ** After 10 minutes of reaction

The results in Table 4.18 show that the initial degradation rate of aniline degradation was significantly influenced by the pH value and that the optimal pH was observed at pH 3.0. The initial degradation rate was followed the same trend as aniline removal, COD removal and TOC removal. The value of initial degradation rate increased from 0.0312, 0.0359 to 0.0960 $mMmin^{-1}$ when the pH increased from 2, 2.5 to 3, suddenly decrease to 0.0796 $mMmin^{-1}$ when the pH is raised 3.5. The low activity detected for high pH values can be explained by the formation and precipitation of $Fe(OH)_3$, which has a low activity and will not react with hydrogen peroxide, a process that hamper the development of photoelectro-Fenton reaction. Ferrous ions are unstable at a pH > 4.0

and they easily form ferric ions, which have a tendency to produce ferric hydroxo complexes or ferric oxyhydroxides (Wang S., 2007).

On the contrary, the decrease of activity detected for pH values below the optimum is understandable taking into account that Fe(III) forms different complex species ($Fe(OH)^+$) in solution. It is formed at low pH and its activity is higher than Fe^{2+} in Fenton oxidation. The $Fe(OH)^+$ reacts more slowly with hydrogen peroxide and produces less hydroxyl radicals. This reduces the degradation efficiency. Moreover, the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant at a very low pH and also the reaction of Fe^{3+} with hydrogen peroxide is inhibited. (Pignatello J.J., 1992, Wang S., 2007). As a result, the initial degradation rate of aniline at different initial pH showed that at the optimum pH is pH 3.

2) Effect of initial ferrous ion concentration on aniline degradation

Amount of ferrous ion is one of the main parameters to influence the photoelectro-Fenton process. Ferrous ion can catalyze hydrogen peroxide to produce hydroxyl radical with powerful oxidizing abilities to degrade certain toxic contaminants (Spacek et al., 1995). Usually, the rate of degradation increases with an increase in the concentration of ferrous ions (Gogate P.R., 2004). Figure 4.67 illustrates the effect of initial Fe^{2+} concentration on the aniline removal efficiency.

From the results, it can be seen that the removal of aniline was very fast in the first 10 minutes and then the reaction was relatively slow until the end of reaction time. The results show that increasing the initial Fe^{2+} concentration from 0.1 to 2.5 mM enhanced the aniline removal. The removal of aniline increased from 68% to 100% when applied ferrous ion from 0.1 to 2.5 mM. One hundred percent of aniline degradation was achieved after 40 minutes when an initial Fe^{2+} concentration of 0.25 and 0.5 mM was applied. Moreover, the degradation of aniline was faster when increased initial ferrous ion concentration. 100% removal of aniline was achieved when applied 1 and 2.5 mM of ferrous ion in 20 minutes. However, the reaction was too fast for observed the effect of ferrous ion and using too much ferrous ion. For that reason, the optimum ferrous ion concentration for aniline removal was 0.25 mM, due to the high efficiency on the aniline removal (100% removal in 40 minutes) and the concentration was not high, so it is good on economic aspect.

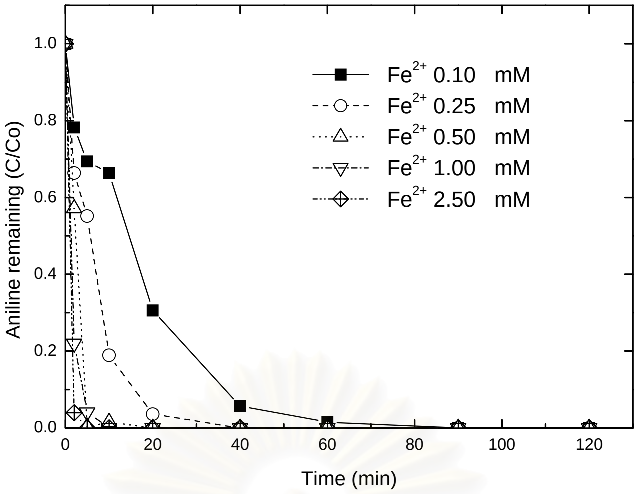


Figure 4.67. Effect of initial Fe^{2+} concentration on the aniline degradation by photoelectro-Fenton. [Aniline] = 1 mM; [H$_2$O$_2$] = 20 mM; pH = 3; I = 1 A, UVA lamp = 12.

It was found that the improvement of the degradation efficiency can be enhanced by UVA lamp. UVA lamp produces additional hydroxyl radicals as described in equation 13. This result is agreed with the result reported by Casero et al. (1997). COD removal efficiency followed the same trend as aniline removal. Figure 4.68 shows that COD removal increased from 75, 83, 84, 63 and 62% as ferrous ion concentration increased from 0.10, 0.25, 0.50, 1.00 and 2.50 mM. The highest COD removal about 84% were achieved when using 0.50 mM of ferrous ion. However, the different of removal efficiency of ferrous ion from 0.25 mM to 0.5 mM was not significant, so the optimum initial ferrous ion concentration was 0.25 mM.

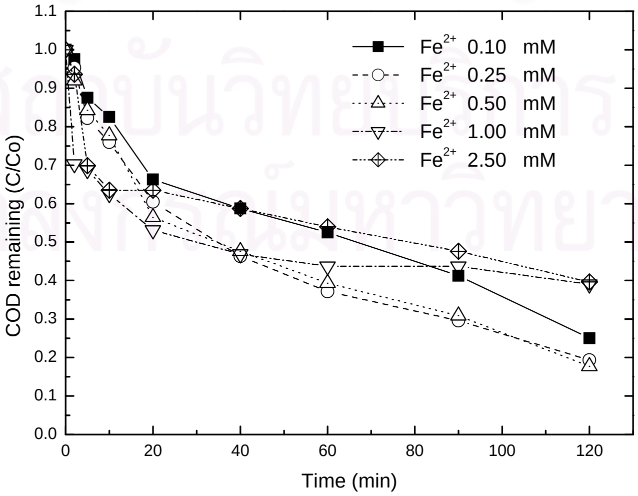


Figure 4.68. Effect of initial Fe^{2+} concentration on the COD removal by photoelectro-Fenton. [Aniline] = 1 mM; [H$_2$O$_2$] = 20 mM; pH = 3; I = 1 A, UVA lamp = 12.

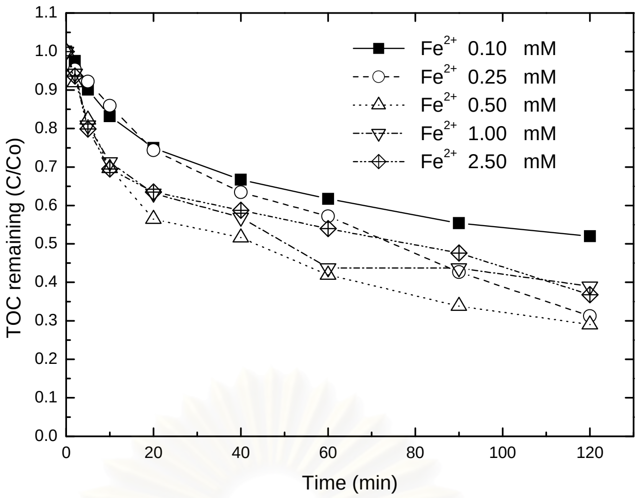


Figure 4.69. Effect of initial Fe^{2+} concentration on the TOC removal by photoelectro-Fenton. [Aniline] = 1 mM; [H_2O_2] = 20 mM; pH = 3; I = 1 A, UVA lamp = 12.

The degradation of 2,6-dimethylaniline can also be monitored by measuring the total organic carbon (TOC) reduction during photoelectro-Fenton process. Figure 4.69 shows that TOC removal increased from 48, 69, 71, 61 and 63% as ferrous ion concentration increased from 0.10, 0.25, 0.50, 1.00 and 2.50 mM. The COD and TOC removal efficiency can be attributed to the mineralization of aniline by hydroxyl radicals from Fenton’s reaction, from electrochemically generated ferrous ion from ferric ion via equation (11) during electro-Fenton processes and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 13).

Table 4.19. Effect of initial ferrous ion on aniline removal efficiency, COD removal efficiency and aniline initial degradation rate by photoelectro-Fenton; [Aniline] = 1 mM, pH =3, [H_2O_2] = 20 mM, I = 1 A, UVA lamp = 12

[Fe^{2+}]	**Aniline removal efficiency***	**COD removal efficiency**	**Initial degradation rate****
(mM)	(%)	(%)	($mMmin^{-1}$)
0.10	68	75	0.0295
0.25	93	83	0.0747
0.50	100	84	0.0960
1.00	100	63	0.0831
2.50	100	62	0.0764

* After 20 minute of reaction ** After 10 minutes of reaction

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The effect of Fe^{2+} concentration on the initial degradation rate for aniline degradation was also studied by varying ferrous ion from 0.1 to 2.5 mM. The results are presented in Table 4.19. It can be seen that the initial degradation rate of aniline increased from 0.0295 $mMmin^{-1}$ to 0.0960 $mMmin^{-1}$ when increasing Fe^{2+} concentration from 0.10 to 1 mM. Accordingly, increasing in the initial Fe^{2+} concentration promoted the hydroxyl radicals formation through reaction (1) and enhanced the aniline removal. Moreover, this is also due to the fact that ferrous ion plays a very important role in initiating the decomposition of hydrogen peroxide to generate the hydroxyl radical in the Fenton process. When the concentrations of Fe^{2+} and $OH^{\bullet}$ are high, Fe^{2+} can react with the $OH^{\bullet}$ according to equation (2). However, it is not a good idea to use over high concentration of Fe^{2+}. By reason of a large quantity of ferric oxide sludge will be generated, resulting in much more requirement of separation and disposal of the sludge. As shown in Table 4.19. , the initial degradation decreased from 0.0831 to 0.0764 $mMmin^{-1}$ when increased initial ferrous ion concentration from 1 to 2.5 mM.

It can be concluded from the study that increasing the relative concentration of Fe^{2+} with respect to the organic compound increases the rate of formation of hydroxyl radicals, which in turn enhances the degradation rate, but this takes place at the expense of consuming more electrical charge due to the enhancement of some competing reactions during electrolysis. Increasing of Fe^{2+} concentration led less H_2O_2 accumulation in the reaction medium and efficient formation of hydroxyl radicals by reaction with H_2O_2 according to Fenton reaction. However, an increase in the Fe^{2+} concentration inhibits the degradation rate of organic substrates because of competitive reaction as shown in equation 2. It is evident from our results that increasing ferrous ion do not cause that inhibition effect in these experimental conditions since $[Fe^{2+}]$ used was not excess.

3) Effect of initial hydrogen peroxide concentration

Initial concentration of hydrogen peroxide plays an important role in photoelectro-Fenton process. It is the precursor in generating the hydroxyl radical in combination with ferrous ion (equation 1). It has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide (Lin et al., 1999).

Figure 4.70 shows the effect of the initial H_2O_2 concentration on the aniline removal efficiency. The results show that increasing in the initial H_2O_2 concentration could promoted the aniline removal.

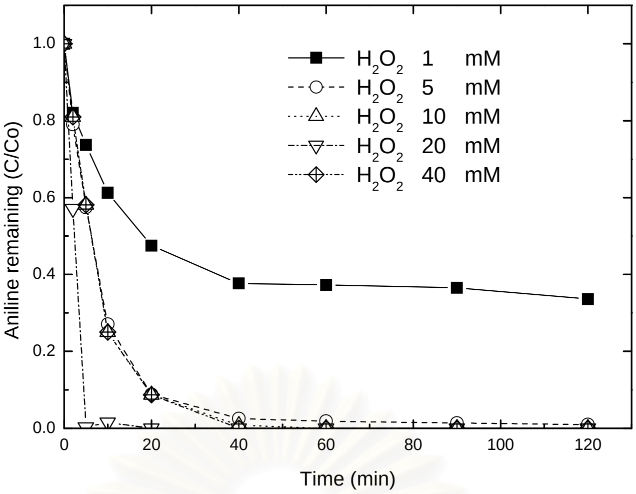

Figure 4.70. Effect of initial hydrogen peroxide concentration on the aniline degradation by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.25 mM; pH = 3; I = 1 A, UVA lamp = 12.

After 40 minutes, the removal efficiency of aniline was 64%, 99%, 100%, 100% and 100% with 1 mM, 5 mM, 10 mM, 20 mM and 40 mM of initial hydrogen peroxide concentration, respectively. This phenomenon was due to an increase in initial H_2O_2 concentration can increase the productions of hydroxyl radicals that could react with the organics in the solution. The results agreed with the experiment by Lu, 1999. The decomposition rate of organic contaminants increased with the increasing of hydrogen peroxide concentration. From the results, the optimum hydrogen peroxide concentration for removal 100% of aniline was 10 mM.

COD removal efficiency followed the same trend as aniline removal. Figure 4.71 shows that COD removal increased from 23, 45, 77, 79 and 80% as hydrogen peroxide concentration increased from 1, 5, 10, 20 and 40 mM. The highest COD removal about 80% was achieved when using 40 mM of initial hydrogen peroxide concentration. However, the removal efficiency of 10 mM, 20 mM and 40 mM of hydrogen peroxide concentration were not significant, in this case, the optimum hydrogen peroxide needed for COD removal was 10 mM. The increasing of initial H_2O_2 concentration also increased the COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize 2,6-dimethylaniline and its intermediates.

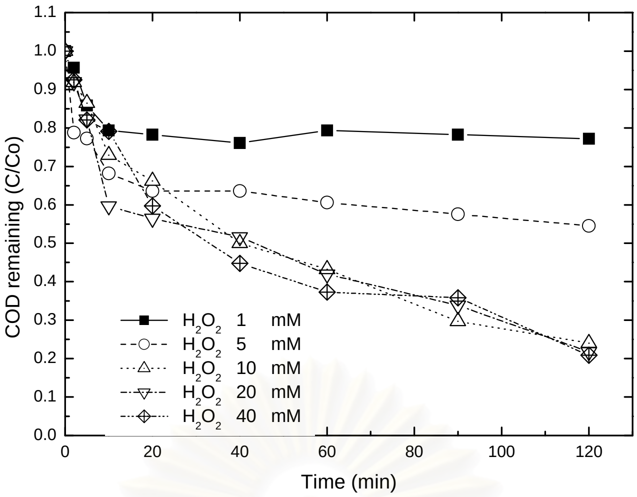

Figure 4.71. Effect of initial hydrogen peroxide concentration on the COD removal by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.25 mM; pH = 3; I = 1 A, UVA lamp = 12.

At higher H_2O_2 concentrations, the produced $OH^{\bullet}$ might have followed other reaction pathways instead of equation (8) after aniline was degraded. Higher H_2O_2 concentrations might have favored the side reactions that scavenged the hydroxyl radical to form hydroperoxyl radicals ($OH^{\bullet}_2$). The TOC removal followed the same trend as COD removal. TOC removal of aniline at different initial hydrogen peroxide was shown in Figure 4.72 It was clearly showed that Fenton's reagent assisted electric current under irradiation of UVA can improve TOC removal. Figure 4.72 shows that TOC removal increased when increasing the initial hydrogen peroxide concentration.

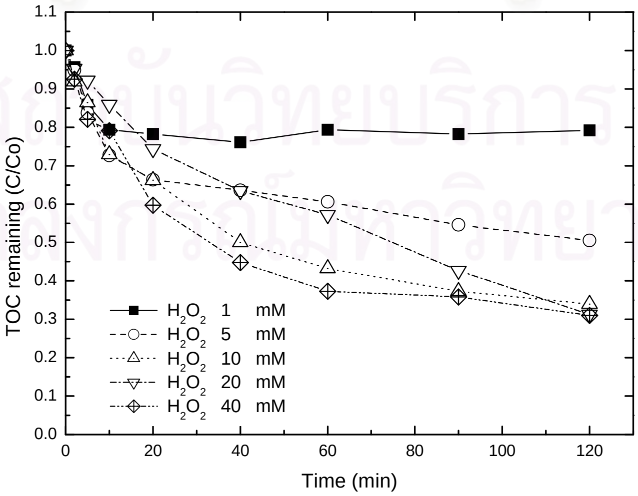

Figure 4.72. Effect of initial hydrogen peroxide concentration on the TOC removal by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.25 mM; pH = 3; I = 1 A, UVA lamp = 12.

TOC removal efficiency increased from 21, 40, 66, 68 and 69% as initial hydrogen peroxide concentration increased from 1, 5, 10, 20 and 40 mM. It is obvious that increasing amounts of hydrogen peroxide lead to larger TOC removal. However, excess of hydrogen peroxide might be negative, since these species can react with some of the intermediates like hydroxyl radical, then decreased the mineralization. The low COD and TOC removals may indicate that, although aniline might be highly oxidizable but some of its derivatives and intermediates might not be as readily oxidized.

Table 4.20. Effect of initial hydrogen peroxide concentration on aniline removal efficiency, COD removal efficiency and aniline initial degradation rate by photoelectro-Fenton; [Aniline] = 1 mM, Fe2$^+$ = 0.25 mM, I = 1 A, UVA lamp = 12

[H_2O_2] (mM)	**Aniline removal efficiency*** (%)	**COD removal efficiency** (%)	**Initial degradation rate**** (mMmin^{-1})
1	64	23	0.0356
5	99	45	0.0712
10	100	77	0.0739
20	100	79	0.0902
40	100	80	0.0739

* After 40 minute of reaction ** After 10 minutes of reaction

The initial degradation rate increased from 0.0356, 0.0712, 0.0739 to 0.0902 mMmin^{-1} as the H_2O_2 concentration was increased from 1, 5, 10 to 20 mM but decreased to 0.0739 mMmin^{-1} when H_2O_2 concentration was further increased to 40 mM as listed in Table 4.20. This increase in initial degradation rate was due to the presence of higher concentration of H_2O_2 forming non-hydroxyl radicals and hydroxyl radicals when reacted with Fe^{2+}. Higher $OH^\bullet$ concentration increases the degradation rate since there are more available $OH^\bullet$ to react with the organics in the solution. The high H_2O_2 concentration could affect the removal efficiency and initial degradation rate as the unreacted H_2O_2 might favor the side reactions that scavenged the $OH^\bullet$ to form hydroperoxyl radicals ($OH^\bullet_2$) (Sun et al., 2007, Watts et al., 2005) and the recombination of hydroxyl radicals.

4) Effect of applied electric current

Figure 4.73 illustrates the effect of applied electric current on the aniline removal efficiency. Results showed that increasing the applied electric current will increased the removal efficiency. In this work, the removal efficiency was 85%, 93%, 94%, 94% and 93% for electric current of 0.5, 1, 2, 4 and 8 A, respectively, after 20 minutes of reaction.

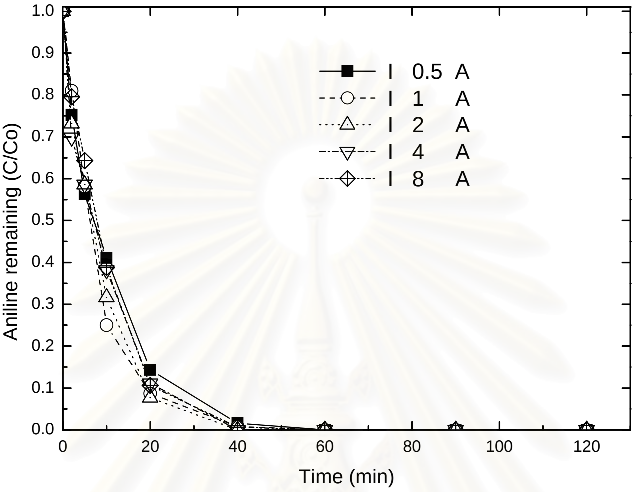

Figure 4.73. Effect of applied electric current on the aniline degradation by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.25 mM; [H_2O_2] = 10 mM; pH = 3, UVA lamp = 12.

Increasing the electric current increased the production rate of Fe^{2+} on the cathode. Therefore, the removal efficiency increased with increasing applied electric current. This observation was similar to the experiment on the removal of 4-nitrophenol by varied electric current from 0.5 to 1 A (Zhang et al., 2006). The results further indicate that the effect of the electric current on the removal efficiency was significant indicating that the production rate of Fe^{2+} was increased with increasing current. This was due to the regeneration of Fe^{2+} induced at the cathode via reaction (11) which promotes hydroxyl radical production through reaction (1)

The COD removal also followed the same trend as aniline removal as shown in Figure 4.74. COD removal increased when the applied current from 67%, 73%, 84%, 82% and 83% when applied electric current at 0.5, 1.00, 2.00, 4.00 and 8.00 A, respectively. Increasing the electric current increased the production rate of Fe^{2+} on the cathode (equation 11). Therefore, the hydroxyl radicals were more pronounced (equation 1) and further reacted with aniline which will increased the COD removal efficiency.

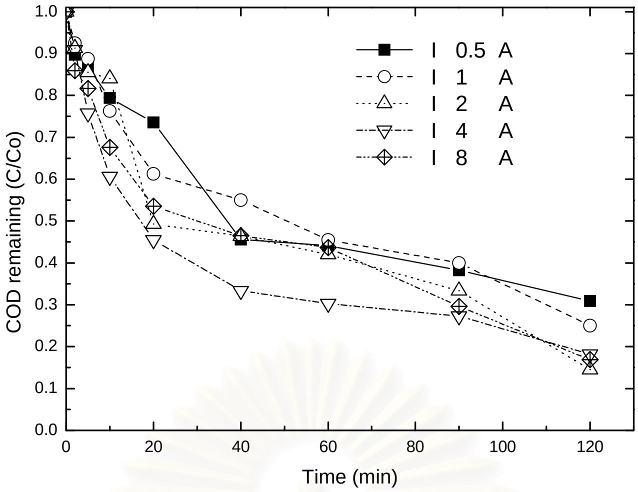

Figure 4.74. Effect of applied electric current on COD removal by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.25 mM; [H_2O_2] = 10 mM; pH = 3, UVA lamp = 12.

The TOC removal efficiency by photoelectro-Fenton process was also determined in this part of experiment. TOC removal was followed the same trend as aniline removal and COD removal as shown in Figure 4.75. The TOC removal increased from 51%, 66%, 69%, 69% and 66% when increased applied electric current from 0.50, 1.00, 2.00, 4.00 and 8.00 A, respectively.

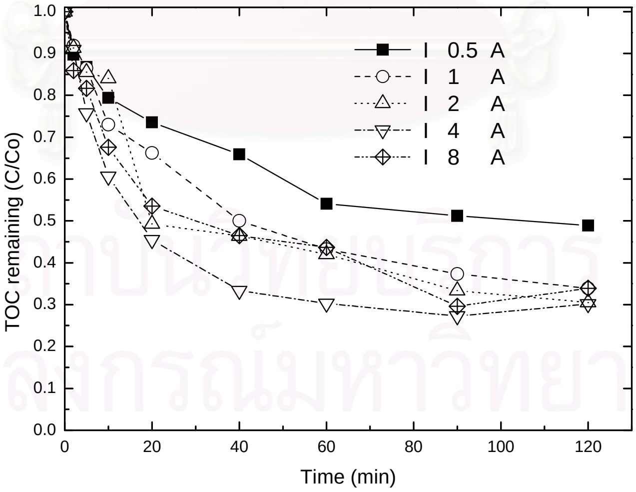

Figure 4.75. Effect of applied electric current on TOC removal by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.25 mM; [H_2O_2] = 10 mM; pH = 3, UVA lamp = 12.

The highest TOC removal by photoelectro-Fenton process was 69% when the applied electric current was 2.00 A. The TOC removal efficiency can be attributed to the mineralization of aniline by hydroxyl radicals from Fenton's reaction, from electrochemically generated ferrous ion from ferric ion via equation (11) during electro-Fenton processes and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 13). The regenerated ferrous ions were then reacted with available hydrogen peroxide in the solution and thus produced hydroxyl radicals through equation (1).

Table 4.21. Effect of applied electric current on aniline removal efficiency, COD removal efficiency, aniline initial degradation rate and energy cost by photoelectro-Fenton; [Aniline] = 1 mM, $Fe2^+$ = 0.25 mM, H_2O_2 = 10 mM, pH = 3, UVA lamp = 12

Electric current (A)	**Aniline removal efficiency*** (%)	**COD removal efficiency** (%)	**Initial degradation rate**** ($mMmin^{-1}$)	**Energy cost** (kWh/m^3)
0.50	85	67	0.0557	0.77
1.00	93	73	0.0641	2.45
2.00	94	84	0.0739	3.56
4.00	94	82	0.0732	8.98
8.00	93	83	0.0586	26.57

* After 20 minute of reaction ** After 10 minutes of reaction

The effect of electric current on the initial degradation rate of aniline degradation was also determined by varying the electric current from 0.5 to 8 A. The results are presented in Table 4.21. The aniline initial degradation rate was increased from 0.0557, 0.0641, 0.0739, 0.0732 and 0.0586 $mMmin^{-1}$ when increased the applied electric current from 0.50, 1.00, 2.00, 4.00 and 8.00 A, respectively. The increase in aniline removal, COD removal, TOC removal and initial degradation rate at increasing applied electric current was due to the increased regeneration of Fe^{2+} induced at the cathode via reaction (11) and from the regeneration of ferrous ion from UVA lamp by photoreduction (equation 13) thereby promoting hydroxyl radical production through reaction (1).

However, TOC removal and initial degradation rate decreased to 66% and 0.0586 $mMmin^{-1}$, respectively, when an electric current of 8 A was applied. At a higher electric current of 8 A, the competitive reactions such as the discharge of oxygen gas at the anode via reaction (15) and the evolution of hydrogen gas at the cathode via reaction (16) become more pronounced (Zhang et al., 2007).

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (15)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (16)$$

Hence, the initial degradation rate constant decreased and H_2O_2 was not efficiently used. The energy cost for photoelectro-Fenton process was also discussed and shown in Figure 4.76.

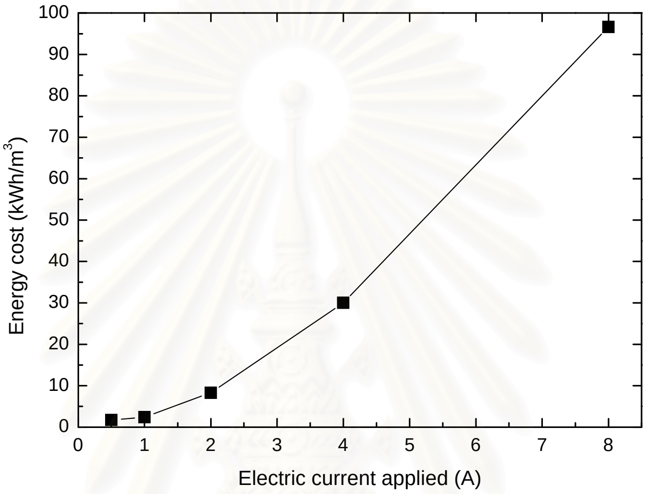

Figure 4.76. Effect of electric current on the energy cost.

The equation applied for calculate the energy cost is:

$$\text{Energy cost}: (kWh/m^3) = [\ V\ x\ I\ x\ t/volume\ ]\ x\ [COD_o / \Delta COD_{\text{exp.}}] \qquad (17)$$

where V is the voltage applied until time t (Volt), I is the electric current (Ampere) used in the study, t is the given time (minute), volume is the amount of organic solution used in the experiment (liter), COD_o is the initial COD of the organic chemical and $\Delta\ COD_{exp}$ is the difference between the initial COD and the final COD after treatment. By using equation (17), the energy cost was increased when increasing the initial electric current and time applied. Consequently, the energy cost should be considered when applied photoelectro-Fenton process.

5) Effect of number of UVA lamps

The results showed that UVA lamp significantly affected the efficiency of aniline degradation by photoelectro-Fenton process. Applying UVA light induces the reduction of ferric ions, and photolysis of hydrogen peroxide to decompose aniline. When UVA lamps were used, they simultaneously induced the reduction of ferric ion to ferrous ion by the following equation:

$$Fe^{3+} + H_2O + h\nu \quad \rightarrow \quad Fe^{2+} + OH^{\bullet} + H^{+} \qquad (18)$$

Moreover, the regenerated ferrous ion from equation 11 during electro-Fenton process will also occurred in the reactor. At the same time, the regenerated ferrous ion from both processes will reacted with hydrogen peroxide and produced hydroxyl radicals (equation 1). This will initiate the degradation of aniline and lead to the mineralization. Thus, the influence of UVA lamp on the degradation of aniline was investigated by varying the UVA lamp from 4,8 to 12 lamps. The results are shown in Figure 4.77.

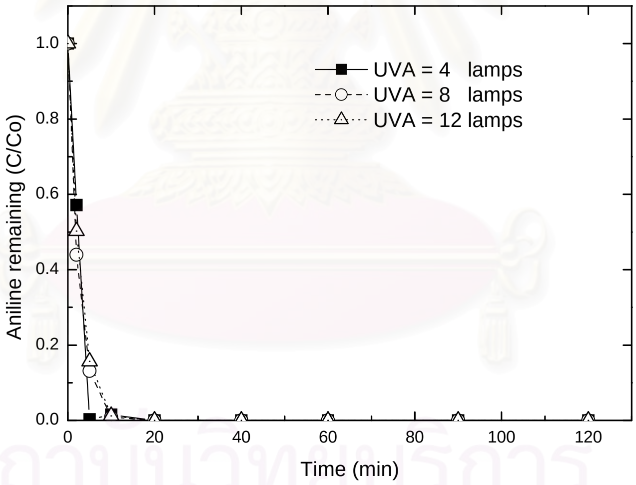

Figure 4.77. Effect of number of UVA lamps on aniline removal by photoelectro-Fenton. [Aniline] = 1 mM; $[Fe^{2+}]$ = 0.5mM; $[H_2O_2]$ = 20 mM; pH = 3, I = 1 A

Increase of number of UVA lamps from 4, 8 to 12 lamps can completely removed aniline in 20 minutes. This was due to increased production of hydroxyl radical. However, the degradation of aniline was the same at 20 minutes which is 100% removal. Hence, the number of UVA lamp at 4 lamps is sufficient for efficient laniline removal. The COD removal was followed the same trend as 2,6-dimethylaniline removal as shown in Figure 4.78.

The COD removal increased from 81%, 84% to 82% when increased number of UVA lamp from 4, 8 to 12 lamps. However, the difference of these COD removal was not significant. Hence, the 4 UVA lamps is enough for the COD removal of aniline.

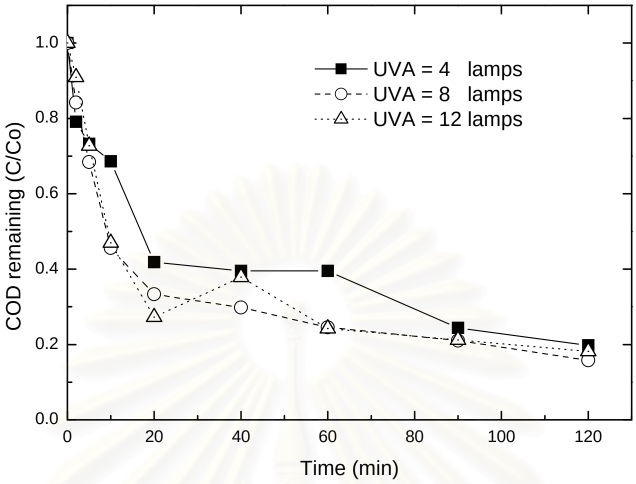

Figure 4.78. Effect of number of UVA lamps on COD removal by photoelectro-Fenton. [Aniline] = 1 mM; [Fe^{2+}] = 0.5 mM; [H_2O_2] = 20 mM; pH = 3, I = 1 A

Photoreduction is expected to play an important role in enhancing mineralization of aniline in photoelectro-Fenton process and coupling UV irradiation to the electro-Fenton application increases the rate of degradation of organic substrates and this should be due to the enhancement in hydroxyl radical formation. From the overall study of photoelectro-Fenton process, it can be seen that initial pH, initial ferrous ion concentration, initial hydrogen peroxide concentration, applied electric current and number of UVA lamp are the important parameters in order to achieve the highest removal efficiency of aniline, COD and TOC.

It is obvious that, with assisting of UVA lamps, the ferrous ion dose and hydrogen peroxide concentration can be reduced substantially. This clearly shows the advantage of photoelectro-Fenton over convention Fenton process and electro-Fenton process. Photoelectro-Fenton process at its optimum conditions can completely remove aniline at a much lower ferrous ion concentration than conventional Fenton process and electro-Fenton process.

4.2.1.4. Comparison between Fenton, Electro-Fenton and Photoelectro-Fenton processes

In this step, the degradation of aniline was examined by various processes. Electrolysis, Photolysis, UV + hydrogen peroxide, Fenton, electro-Fenton, photo-Fenton and photoelectro-Fenton experiments were conducted to investigate the synergistic effect of Fenton's reagent combined photo and electrochemical methods. As shown in Figure 4.79, the results show that electrolysis can remove 10% of 2,6-dimethylaniline in 1 hr. In the electrolysis method, aniline would be destroyed by reaction with adsorbed hydroxyl radical generated at the surface of a high oxygen-overvoltage anode from water oxidation. The same tendency can be found in the research of Brillas et al (Brillas et al., 1998).

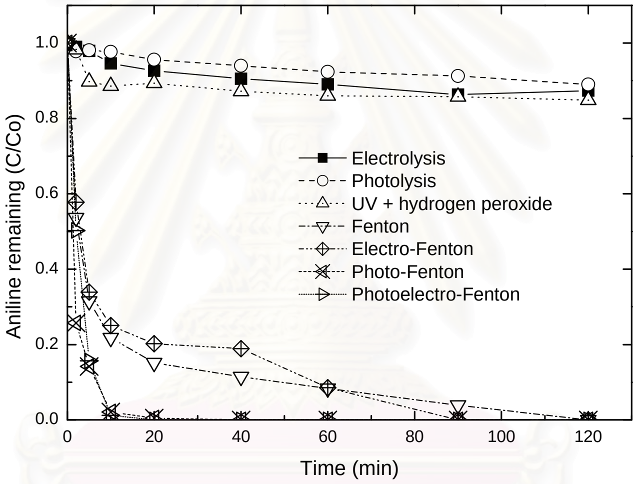

Figure 4.79. Effect of different processes on aniline removal efficiency. [Aniline] = 1 mM; $[Fe^{2+}]$ = 0.5 mM; $[H_2O_2]$ = 20 mM; pH = 3; I = 1 A, UVA lamps = 12.

Photolysis has lower degradation efficiency compared to electrolysis. The removal efficiency by photolysis was only 8% when using UVA lamps (12 lamps) at pH 3. The degradation of aniline was 12% when using UV+hydrogen peroxide after 60 minutes. Aniline was not well degraded by electrolysis, photolysis and UV+hydrogen peroxide. When using Fenton process, the degradation of aniline increased significantly compared to that when using direct photolysis, electrolysis and UV+hydrogen peroxide. For Fenton process, the degradation of aniline was 88% in 1 hr. This is due to the fast reaction of ferrous ion and hydrogen peroxide producing hydroxyl radicals (equation 1).

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \qquad (1)$$

The 90% removal efficiency was achieved by the electro-Fenton process. The reason that electro-Fenton process can remove aniline more than the Fenton process is due to the regeneration of ferrous ion from equation (2) on the cathode side:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad (2)$$

and the ability of electricity that can produced hydroxyl radicals from water oxidation as described in equation (3).

$$H_2O \rightarrow OH^{\bullet} + H^{+} + e^{-} \qquad (3)$$

In photo-Fenton process 100% of aniline degradation was observed at 60 min. Hence, photo-Fenton process is more efficient than Fenton process and electro-Fenton process. It is obvious that the photo-Fenton system enhanced the photooxidation of aniline. The hydroxyl radical which is a strong oxidant that can degrade aniline occurs by the following equation:

$$H_2O_2 + UV \rightarrow OH^{\bullet} + OH^{\bullet} \qquad (4)$$

Degradation of aniline is mainly due to hydroxyl radical generated by photochemical reaction. In photo-Fenton process in addition to the above reaction the formation of hydroxyl radical (equation 1) also occurs by equation (4) and (5)

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \qquad (5)$$

Meanwhile, the utmost removal efficiency was found when applied photoelectro-Fenton process, aniline was removed completely during the first 20 minutes. The degradation of aniline was due to the formation of hydroxyl radical from Fenton’s reaction (equation 1) and the ferric ion would be reduced to ferrous ion from photoreduction (equation 5) and the cathode (equation 2). This would induce the formation of hydroxyl radicals efficiently.

The relative efficiencies of the above processes are in the following order: Photoelectro-Fenton > Photo-Fenton > Electro-Fenton > Fenton > UV + hydrogen peroxide > Electrolysis $\geq$ Photolysis.

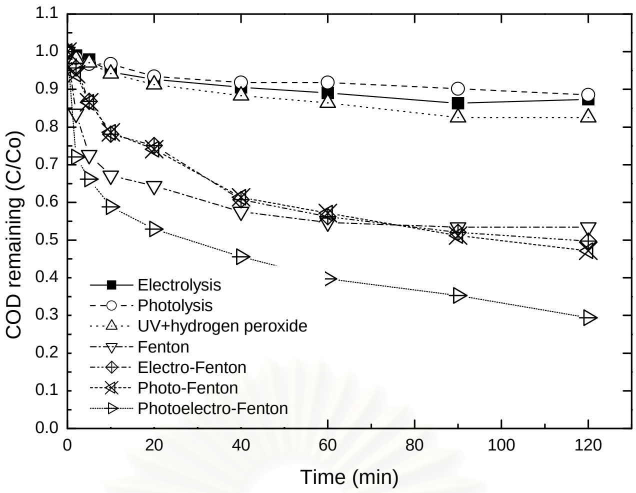

Figure 4.80. Effect of different processes on COD removal efficiency. [Aniline] = 1 mM; [Fe^{2+}] = 0.5 mM; [H_2O_2] = 20 mM; pH = 3; I = 1 A, UVA lamps = 12.

The degradation of aniline was monitored by measuring the COD removal. For COD removal, by electrolysis, photolysis, UV+hydrogen peroxide, Fenton, electro-Fenton, photo-Fenton and photoelectro-Fenton processes, it was followed the same trend as aniline degradation. The results revealed that electrolysis can remove COD only 9%, while photolysis was able to remove about 8% as shown in Figure 4.80. When UVA was combined with hydrogen peroxide, the COD removal increased to 14%. For Fenton process, the COD removal was 43% which is higher than using direct photolysis, electrolysis and UV+hydrogen peroxide .This is due to the fast reaction of ferrous ion and hydrogen peroxide producing hydroxyl radicals (equation 1).

The COD removal efficiency of aniline by the electro-Fenton process and photo-Fenton process were 49% and 52%, respectively. The reason was due to the formation of hydroxyl radical from Fenton’s reaction (equation 1) and the ferric ion would be reduced to ferrous ion from photoreduction (equation 5) in photo-Fenton process and the regeneration of ferrous ion on the cathode (equation 2) in electro-Fenton process. The highest COD removal was found when applied photoelectro-Fenton. It was about 70%. The decrease of COD can be attributed to the mineralization of aniline by the hydroxyl radicals from Fenton’s reaction, from the electrochemically generated Fenton’s reagent during electro-Fenton and photoelectro-Fenton processes and the production of hydroxyl radical from photoreduction of $Fe(OH)^{2+}$ in photoelectro-Fenton process.

4.2.2. Kinetics study of aniline degradation by photoelectro-Fenton process

The kinetics of aniline degradation by the photoelectro-Fenton was investigated. In this study, the kinetic was performed using initial rate techniques (at the first 10 minute of the reaction) in order to eliminate the interferences from intermediates that might occur during the study period. The test range of each parameter was chosen according to the reality of photoelectro-Fenton process application and the needs of kinetic studies in this experiment. The effects of the initial concentration of aniline, initial concentration of ferrous ion and hydrogen peroxide on the kinetic study of aniline degradation will be separately discussed in the following sections.

1) Effect of initial aniline concentration

The pollutant concentration is one of the important factors in photoelectro-Fenton proces. The effect of initial aniline concentration on the removal efficiency of aniline by photoelectro-Fenton processes is shown in Figure 4.81. The figures clearly reveal that increasing the aniline concentration decreases the removal efficiency of aniline. When increasing the aniline concentration from 0.5 to 5 mM, the degradation of aniline decreases from 100%, 100% to 60%. The main reason for this phenomenon is the hydroxyl radical. Increasing in aniline concentration increases the number of aniline molecules, however, there is not enough hydroxyl radicals to degrade 2,6-aniline, then the removal efficiency decreases.

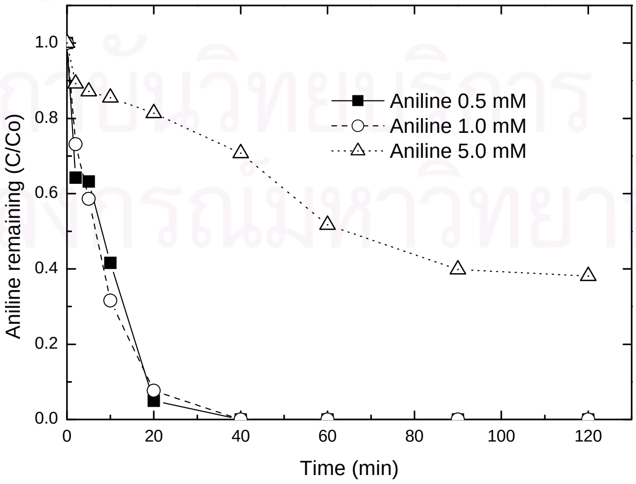

Figure 4.81. Effect of initial aniline concentration on the removal efficiency of aniline by Photoelectro-Fenton process . [Fe^{2+}] = 0.5 mM, [H_2O_2] = 20 mM, I = 1 A, pH = 3, UVA lamp = 12

The effect of the initial aniline concentration on the kinetic was studied by varying the initial concentration from 0.5 to 5 mM and at the experimental condition of 0.5 mM of ferrous ion, 20 mM of hydrogen peroxide, pH 3, an electric current of 1 amperes for and UVA 12 lamps. The study showed that the aniline degradation kinetics at the given test condition. The second-order behavior appeared to fit the degradation of aniline by the photoelectro-Fenton process when plot the relationship between aniline degradation and initial aniline concentration was in a good linear (R> 0.98).

Table 4.22. Initial rate of aniline degradation by varying initial concentration of aniline using photoelectro-Fenton processes.

[Aniline]	**Initial degradation rate**
	PEF
($\times 10^{-3}$) M	(mMs^{-1})
0.5	0.0006
1	0.0008
5	0.0010

* PEF = Photoelectro-Fenton process

The results on Table 4.22 showed that when the aniline concentration was increased from 0.5 to 5 mM, the initial degradation rates increased. The high initial degradation rate at a high concentration of aniline was probably due to the excess amount of aniline to reacting with hydroxyl radical which produced during the process that destroyed the aniline.

For that reason, the initial rate for the higher concentration of aniline increased. These results are similar to the study of *p*-nitroaniline degradation by Fenton oxidation process by Sun and others (Sun et al., 2007) and the results are also similar to the removal of nitroaromatic explosives with Fenton’s reagent (Liou and Lu, 2007)**.**

For the effect of initial aniline on the removal efficiency, the results showed that increasing the initial concentration of aniline will decrease the removal. The plot between the initial rate and aniline concentration showed a straight line with the slopes of 0.21 for the photoelectro-Fenton process. Therefore, the reaction rate equations became:

$$-\left(\frac{d[Aniline]}{dt}\right)_{photoelectro-Fenton} = r_{PEF,Aniline}\ [2,6-DMA]^{0.21} \qquad (6)$$

where $r_{PEF,Aniline}$ is rate constants for the photoelectro-Fenton processes with respect to aniline.

2) Effect of ferrous ion concentration

The concentration of the catalyst is another important parameter for Fenton processes. The ferrous ion plays the catalyst's role in this Fenton's reaction. Normally, the rate of degradation increases with an increase in the concentration of ferrous ions (Fe^{2+}). The effect of the ferrous ion concentration on the kinetic study of aniline degradation was studied by varying the ferrous ion concentration from 0.1 to 1 mM. The result showed that the removal efficiency of photoelectro-Fenton method was promoted when the ferrous ion concentration increased from 0.1 to 1 mM, as shown in Figure 4.82. The removal efficiency increased from 94% to 100 % in 40 minutes.

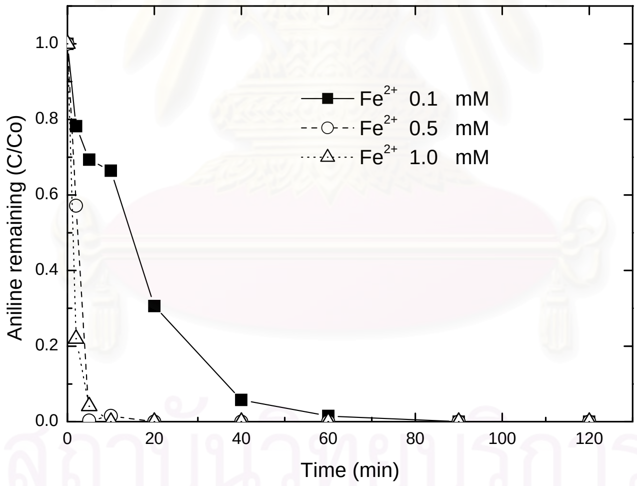

Figure 4.82. Effect of initial ferrous ion concentration on the removal efficiency of aniline by Photoelectro-Fenton process . [Aniline] = 1 mM, [H_2O_2] = 20 mM, I = 1 A, pH = 3, UVA lamp = 12

For the initial degradation rate of aniline, the initial rate increased when the initial ferrous ion concentration increased from 0.0005 to 0.0016 mMs^{-1} on the photoelectro-Fenton process as listed in Table 4.23. Usually, when increasing the initial ferrous ion concentration, it will increase the generation rate of hydroxyl radical due to equation (1).

Therefore, this will enhanced the degradation rate of aniline. Accordingly, the results underwent a similar direction. An improvement in removal efficiency by ferrous ion should also considered the supplement of hydrogen peroxide through out the experiment which might led to more regeneration of ferrous ion from ferric ion. Therefore, the total regenerated hydroxyl radicals and the removal efficiency will increase as the ferrous ion concentration increased.

Table 4.23. Initial rate of aniline degradation by varying initial concentration of ferrous ion using photoelectro-Fenton process.

[Fe^{2+}] (x10^{-3}) M	**Initial degradation rate** **PEF** (mMs^{-1})
0.1	0.0005
0.5	0.0014
1.0	0.0016

In photoelectro-Fenton process, the applied electricity and UVA lamps during experiment will enhanced the regeneration of ferrous ion from ferric ion via equation (3) and (5). The supplied electrons from electrical current could regenerate ferrous ions rapidly and, thus, can react with hydrogen peroxide as long as hydrogen peroxide was still available in the reactor (Anotai et al., 2006). For that reason, the degradation of aniline continuously proceeded without the inadequacy of ferrous ions in the solution which in turn increased the efficiency of hydroxyl radical production.

The aniline degradation kinetics at the given test conditions was second–order behavior. The degradation kinetic for the photoelectro-Fenton process when plot the relationship between aniline degradation and aniline concentration was in a good linear (R> 0.95) when using second-order kinetic model. It was seen from the results that the rate of aniline degradation increased with the increase of ferrous ions concentration. The relationship between the initial rate and the ferrous ion concentration on the photoelectro-Fenton process was determined. From the calculation, it showed that the slope of photoelectro-Fenton processes was 0.5289. Thus, the kinetics for aniline degradation on the effect of ferrous ion concentration can be described by following equation:

$$-\left(\frac{d[Aniline]}{dt}\right)_{photoelectro-Fenton} = r_{PEF,Fe^{2+}}\ [Fe^{2+}]^{0.5289} \qquad (7)$$

where $r_{PEF,Fe^{2+}}$ is the rate constants for photoelectro-Fenton process with respect to the ferrous ion. The results indicated that ferrous ions play an important role in degradation of aniline by reacting with hydrogen peroxide to generate hydroxyl radicals. However, higher ferrous ion concentration supplementation by using photoelectro-Fenton processes is not recommended due to the large amount of ferric hydroxide sludge that could occur.

3) Effect of hydrogen peroxide concentration

Initial concentration of hydrogen peroxide plays an important role in the photoelectro-Fenton process. It is an oxidizing agent in the Fenton reaction. It has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide (Pignatello 1992). The effect of initial hydrogen peroxide concentration on the removal efficiency and kinetic rate of aniline degradation was investigated by varying the initial hydrogen peroxide concentration from 1 to 40 mM under the experiment condition of initial aniline concentration 1 mM, ferrous ion 0.5 mM, pH 3, electrical current 1 A and UVA 12 lamps. It can be seen from the results that the removal efficiency of photoelectro-Fenton processes increased when increasing the initial concentration of hydrogen peroxide as shown in Figure 4.83. (Lin et al., 1999). The removal efficiency increased from 63 % to 100 % as the hydrogen peroxide concentration increased from 1 to 40 mM in 60 minutes. This was from the production of hydroxyl radicals produced during the experiment by the reaction of ferrous ion and hydrogen peroxide in the solution.

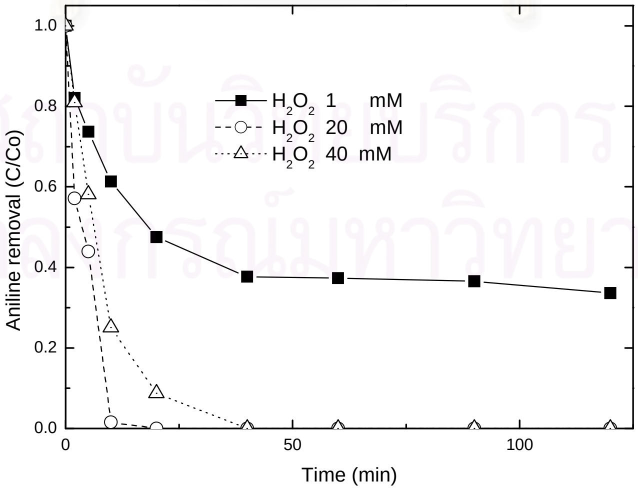

Figure 4.83. Effect of initial hydrogen peroxide concentration on the removal efficiency of aniline by Photoelectro-Fenton process . [Aniline] = 1 mM, $[Fe^{2+}]$ = 0.5 mM, I = 1 A, pH = 3, UVA lamp = 12

Table 4.24 shows that the initial rate of aniline degradation increased when the hydrogen peroxide concentration was increased from 1 to 20 mM. The initial rate increased from 0.0006 to 0.0015 mMs^{-1} by photoelectro-Fenton process. This increase in the initial rate was due to the availability of hydrogen peroxide to react with ferrous ions in the solution. However, with the continuous increase in the initial hydrogen peroxide concentration to 40 mM, the increase of hydrogen peroxide leads to the decline of the initial rate. This phenomenon was probably due to the scavenging of hydroxyl radicals by hydroxyl radical as described via equation (5) (Lu et al., 1999). The accumulation of hydroperoxyl radicals also consumed hydroxyl radicals (Sun et al., 2007; Kang et al., 2002).

Table 4.24. Initial rate of aniline degradation by varying initial concentration of hydrogen peroxide using photoelectro-Fenton process.

[H_2O_2]	**Initial degradation rate**
	PEF
($x10^{-3}$) M	(mMs^{-1})
1	0.0006
20	0.0015
40	0.0012

It was found that the second-order kinetic model is applicable to the aniline degradation quite well under photoelectro-Fenton process with R> 0.98. The relationship between the initial rate and hydrogen peroxide are linear and the slopes are 0.2232 for the photoelectro-Fenton processes, therefore:

$$-\left(\frac{d[Aniline]}{dt}\right)_{photoelectro-Fenton} = r_{PEF,H_2O_2}\ [H_2O_2]^{0.2232} \tag{8}$$

where r_{PEF,H_2O_2} is rate constants for the photoelectro-Fenton methods with respect to hydrogen peroxide.

4) The overall reaction rate equation for aniline degradation by photoelectro-Fenton

From the previous sections, the reaction rate equation of aniline degradation was proposed and it varied with the respect to aniline, ferrous ion and hydrogen peroxide concentrations in photoelectro-Fenton process. The overall degradation kinetic for aniline by the photoelectro-Fenton process can be summarized as shown below:

$$-\left(\frac{d[Aniline]}{dt}\right)_{photoelectro-Fenton} = r_{PEF}[Aniline]^{0.21}\ [Fe^{2+}]^{0.5289}\ \ [H_2O_2]^{0.2232} \qquad (9)$$

where r_{PEF} is the overall rate constant for the photoelectro-Fenton method. From the equation (9), it can be seen that the degradation rate of aniline by photoelectro-Fenton process depended on Fenton's reagent both ferrous ion and hydrogen peroxide. However, from equation (9), the reaction shown that the aniline degradation, when applied with an electrical current and UVA lamp, the degradation rate was almost independent from hydrogen peroxide. Nevertheless, the ferrous ion was still the important species for the degradation of this chemical so the Fenton's reagent still be the major key for this process.

The r_{PEF} , from equation (9) could be calculated by using a non-linear least squares method which minimizes the sum of the error squares between the observed initial rates attained from the study and from the calculated initial rates. Accordingly, the r_{PEF} could be proposed by calculated using concentration of aniline, ferrous ion and hydrogen peroxide in millimolar (mM) units. From the calculation, the r_{PEF} was 1.32. Therefore, the final reaction rate equations can be described as:

$$-\left(\frac{d[Aniline]}{dt}\right)_{photoelectro-Fenton} = 1.32[Aniline]^{0.21}\ \ [Fe^{2+}]^{0.5289}\ \ [H_2O_2]^{0.2232} \qquad (10)$$

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4.2.3. The Intermediates detection and possible mechanism pathway for aniline degradation by various Fenton processes

The IC was applied to identify the intermediates that might have occurred from the degradation of aniline by the photoelectro-Fenton process. Several stable intermediates, such as oxalic acid, acetic acid, maleic acid and formic acid were detected during the degradation of 1 mM aniline solution by the photoelectro-Fenton method when an electric current of 1A and UVA 12 lamps was applied.

The anions were examined by an Ion Chromatograph (Dionex DX-120). The anions included, acetic acid at 2.9 min, maleic acid at 9.79 min, formic acid at 3.58 min and oxalic acid at 10.64 min. The formic acid was found after 2 minutes of the reaction time and its concentration increased with the increasing of time after 40 minutes the concentration of formic acid decreased. Oxalic acid was also found after 2 minutes. The concentration of oxalic acid increased as the time increased. It is shown in Figure 4.84.

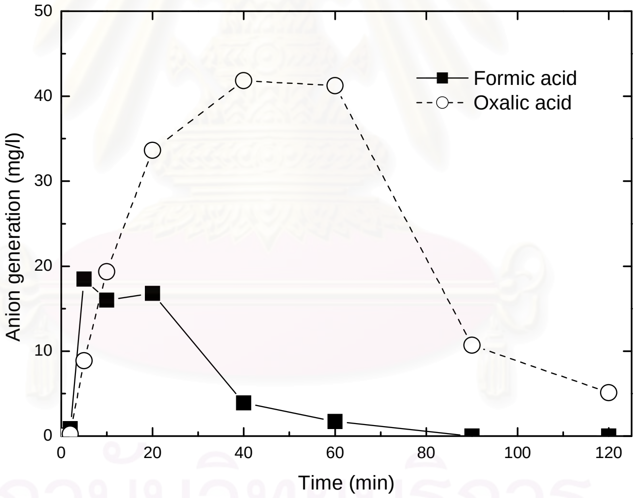

Figure 4.84. The profile of anions generation.

Formic acid is practically eliminated in the experiment after 2 hours of the photoelectro-Fenton reaction. The general pathway for degradation of aniline at pH 3 with the photoelectro-Fenton process was proposed. The proposed pathway is shown in Figure 4.85. In photoelectro-Fenton process, the main oxidizing species is the hydroxyl radical. It is known that OH• radicals are nonselective and strong electrophilic oxidizing species (Pèrez et al., 2005).

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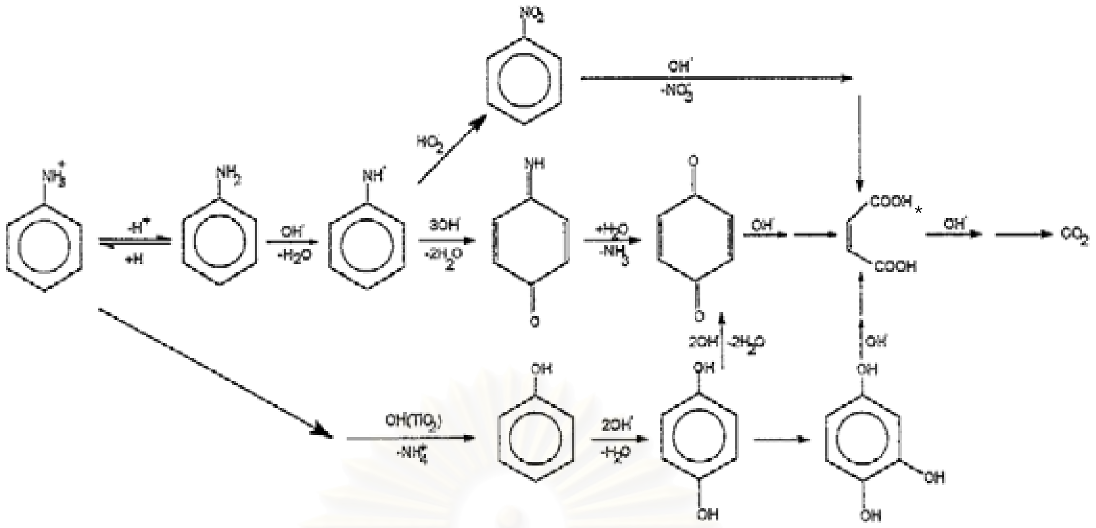

Figure 4.85. Proposed reaction pathways for mineralization of aniline at pH 3 by electro-Fenton process (Brillas et al., 1998). (* detected by IC)

The degradation process can be initiated either by the attack of $OH^•$ on aniline that yields nitrobenzene or by the direct hydroxylation of aniline's N-position to give phenol. Benzoquinonimine is also formed from $OH^•$ attack on phenol which further breaks into hydroquinone, through abstraction of two hydrogens (Brillas et al., 1998).

The further degradation of benzoquinonimine and hydroquinone leads to a mixture of lactic acid, maleic acid and acetic acid. The three acids are transformed into formic acid and oxalic acid. The formic acid is directly mineralized to carbon dioxide. The ultimate carboxylic acid, oxalic acid, is very slowly converted into CO_2 by $OH^•$ since it forms very stable Fe^{3+}-oxalato complexes under the photoelectro-Fenton process.

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4.3. Comparison of 2,6-dimethylaniline and aniline degradation

The comparison between 2,6-dimethylaniline and aniline degradation was also determined in this study. It is recognized that hydroxyl radicals can be obtained from different reaction pathways. In Fenton process, hydrogen peroxide can be formed by the reaction between ferrous ion and hydrogen peroxide. In electro-Fenton process, the hydroxyl radicals was produced in the same way as Fenton process, but the ferric ion, which is the disadvantage of Fenton process, will be transformed to ferrous ion via the electron transport. In photoelectro-Fenton process, hydroxyl radicals can be initiated by the combination of UV / hydrogen peroxide / ferrous ion/ electricity. The relative contribution to hydroxyl radical formation among reaction pathways is one of the principle issues to be investigated in this part of study. In order to evaluate the effect of UV light, electricity and Fenton's reagent on the degradation of 2,6-dimethylanilien and aniline, Fenton process, electro-Fenton process and photoelectro-Fenton process were compared as shown in Figure 4. 86 (a) and (b).

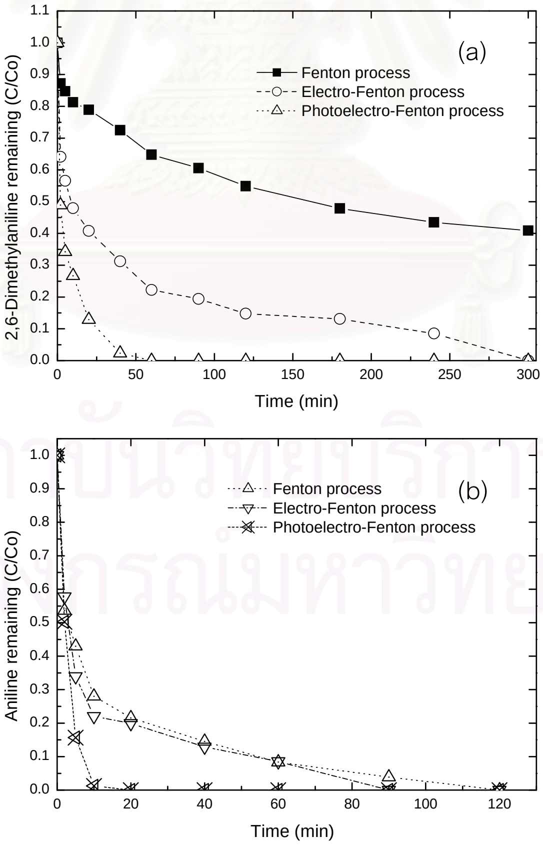

Figure 4.86. Comparison on the removal of 2,6-dimethylaniline (a) and aniline (b) in different processes (Fenton, electro-Fenton and photoelectro-Fenton processes).

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The removal efficiency of 2,6-dimethylaniline and aniline treated by photoelectro-Fenton process was higher than that by the Fenton and electro-Fenton process. Results indicated that the electricity and UVA lamps were important for the degradation of 2,6-dimethylaniline and aniline. The enhancing effects of electric current on the degradation of both chemicals can be observed from the experimental data obtained from the electro-Fenton process and the enhancing effect of UVA lamps on the degradation of 2,6-dimethylaniline and aniline can be observed from the photoelectro-Fenton process. Results indicated that electricity and UVA lamps can increased the removal efficiency by using photoelectro-Fenton process.

The enhancing effects of Fenton's reagent on the degradation of 2,6-dimethylaniline and aniline can be observed from Fenton process. The enhancing effects of electricity on the degradation of both chemicals can be observed from experimental data obtained from the electro-Fenton process and the enhancing effects of UVA lamps on the removal of 2,6-dimethylanilne and aniline can be observed from photoelectro-Fenton process as shown in Figure 4.86. According the change during 60 minutes of the irradiation and electricity application, the degradation rate of 2,6-dimethylaniline and aniline by photoelectro-Fenton process was faster than those by Fenton and electro-Fenton process. In Fenton process, the removal efficiency of 2,6-dimethylaniline and aniline at the first 60 minutes were 40% and 88% and at 120 minutes (2 hours) were 48% and 100%, respectively. When electric current was applied in the reaction or electro-Fenton process, the removal efficiency of 2,6-dimethylaniline and aniline were increased. As seen from the figure, the 2,6-dimethylaniline aniline at the first 60 minutes were 78% and 93% and at 120 minutes were 87% and 100%, respectively. By photoelectro-Fenton process, when applied UVA lamps combined with electric current and Fenton's reagent, the removal efficiency drastically increased. The 2,6-dimethylaniline and aniline removal efficiency at the first 60 minutes were the same which is 100% in both processes. These data indicate that UVA lamps play a crucial role in the photoelectro-Fenton. Basically, the hydroxyl radicals produced from the reaction of UVA lamps with Fenton's reagent can be shown in equation (1).

$$Fe^{3+} + UVA + H_2O \rightarrow Fe^{2+} + H^{+} + OH^{\bullet} \quad (1)$$

With the UVA irradiation, a regeneration of the ferrous ion by the reduction of ferric ions from the photoreduction is occurred. Moreover, the regeneration of ferrous ion

from ferric ion by electricity through the electron transport on the cathode side was also occurred in photoelectro-Fenton process as described in equation (2).
The regenerated ferrous ion then reacted with hydrogen peroxide and thus produced hydroxyl radicals (equation (3)).

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \quad (3)$$

By this way, the hydroxyl radicals produced more rapidly and making the photoelectro-Fenton process has higher removal efficiency than Fenton and electro-Fenton processes. From the above explanation, it indicated that the photoelectro-Fenton system has more efficient in 2,6-dimethylaniline and aniline removal than Fenton and electro-Fenton systems.

The experimental results obtained also show that the oxidation reactions of 2,6-dimethylaniline and aniline removal were very fast during the first 10 minutes, especially in photoelectro-Fenton process. Then they gradually slowed down until the end of reaction. It is a two stage reaction. In the first stage, 2,6-dimethylaniline and aniline were degraded swiftly; this is referred to as the ferrous ion/hydrogen peroxide (Fe^{2+}/H_2O_2) stage. In the second stage, the 2,6-dimethylaniline and aniline were slowly decreased, This declining phase was due to the ferric ion that played a role during this stage. This stage is called the ferric ion/hydrogen peroxide (Fe^{3+}/H_2O_2) stage (Lu et al., 1999). It is obvious that the degradation efficiency of the second stage was much slower than the first stage. Therefore, it can be obtained that the first stage is the most rapid stage compared the second stage, resulting in a higher rate of hydroxyl radicals formation in the first stage reaction than in the second stage.

4.3.1. Kinetics study of the degradation of 2,6-dimethylaniline and aniline

The rate constants of 2,6-dimehylaniline and aniline from Fenton process, electro-Fenton process and photoelectro-Fenton process were calculated as shown in Table 4.25. The initial degradation rate was obtained by use the first 10 minutes of the reaction time. Of all the applied processes, photoelectro-Fenton process was found to be the most effective method for 2,6-dimethylaniline and aniline degradations.

In the Fenton process, the initial degradation rate of 2,6-dimethylaniline and aniline were 0.0179 and 0.0699 $mMmin^{-1}$, respectively. In electro-Fenton process, the initial rate of 2,6-dimethylaniline and aniline were 0.0468 and 0.0776 $mMmin^{-1}$, respectively. For photoelectro-Fenton, the initial rate of 2,6-dimethylaniline and aniline were 0.0594 and 0.0795 mMmin-1, respectively.

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Table 4.25. 2,6-Dimethylaniline and aniline initial degradation rates and rate constants using Fenton, electro-Fenton and photoelectro-Fenton processes.

Process	**Initial rate ($mMmin^{-1}$)**		**Rate ($mM^{-1}min^{-1}$)**			
	2,6-DMA	**Aniline**	**2,6-DMA**	**r^2**	**Aniline**	**r^2**
Fenton	0.0179	0.0699	0.0124	0.9589	0.2741	0.9617
Electro-Fenton	0.0468	0.0776	0.0985	0.9512	0.3367	0.9692
Photoelectro-Fenton	0.0594	0.0795	0.1975	0.9841	0.9294	0.9776

* By using the optimum condition obtained from previous study; 2,6-dimethylaniline 1 mM; Fenton process: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM, pH = 2; Electro-Fenton process: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM, pH = 2, I = 2 A; Photoelectro-Fenton process: $[Fe^{2+}]$ = 1 mM, $[H_2O_2]$ = 20 mM, pH = 2, I = 2 A , UVA = 12 lamps; Aniline 1 mM; Fenton process: $[Fe^{2+}]$ = 0.5 mM, $[H_2O_2]$ = 20 mM, pH = 3; Electro-Fenton process: $[Fe^{2+}]$ = 0.5 mM, $[H_2O_2]$ = 20 mM, pH = 3, I = 1 A; Photoelectro-Fenton process: $[Fe^{2+}]$ = 0.5 mM, $[H_2O_2]$ = 20 mM, pH = 3, I = 1 A , UVA = 12 lamps.

The rate constants of both chemicals by Fenton, electro-Fenton and photoelectro-Fenton processes were followed the same trend as initial degradation rate. In the Fenton process, the rate constant of 2,6-dimethylaniline and aniline were 0.0124 and 0.2741 $mMmin^{-1}$, respectively. In electro-Fenton process, the rate constant of 2,6-dimethylaniline and aniline were 0.0985 and 0.3367 $mMmin^{-1}$, respectively. For photoelectro-Fenton, the rate constant of 2,6-dimethylaniline and aniline were 0.1975 and 0.9294 mMmin-1, respectively. From the experiments, it can be concluded that photoelectro-Fenton can significantly increase the efficiency of 2,6-dimethylaniline and aniline removal. However, the degradation rate of both chemicals changed slightly in the second stage of reaction. This was due to the slow rate of ferric ion/hydrogen peroxide reaction and almost complete disappearance of hydrogen peroxide in this stage. The experimental data were fitted by second- order kinetics. This phenomenon was also found in the study of Ghaly et al., (2002) on the dechlorination of p-chlorophenol by Fenton and photo-Fenton processes and Momani et al., (2004) on the oxidation of various AOPs such as UV, Fenton and photo-Fenton processes.

2) Degradation pathways for 2,6-dimethylaniline and aniline degradation

For the degradation pathway of 2,6-dimethylaniline, the GC/MS and IC were applied to identify the intermediates that might have occurred from the degradation of 2,6-dimethylaniline by the electro-Fenton process. Several stable intermediates, such as 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid were detected during the degradation of 1 mM 2,6-dimethylaniline solution by the electro-Fenton method when an electric current of 1.43 A was applied.

GC-MS (Agilent 6890) with DB-5MS capillary column showed the presence of 2,6-dimethylaniline absorption peak at 9.36 min. Moreover, the four additional peaks were found. The intermediates are 2,6-dimethylphenol at 8.68 min, 2,6-dimethylbenzoquinone at 8.77 min, 2,6-dimethylnitrobenzene at 9.59 min, and 3-hexanone at 4.18 min. The anions were examined by an Ion Chromatograph (Dionex DX-120). The anions included lactic acid at 1.15 min, acetic acid at 2.9 min, maleic acid at 9.79 min, formic acid at 3.58 min and oxalic acid at 10.64 min.

Based on these finding, a general pathway for degradation of 2,6-dimethylaniline at pH 2 with the electro-Fenton process was proposed. The proposed pathway is shown in Figure 4.87. In electro-Fenton oxidation, the main oxidizing species is the hydroxyl radical. It is known that OH• radicals are nonselective and strong electrophilic oxidizing species (Pérez et al., 2005).

The degradation process can be initiated either by the attack of $OH^{\bullet}$ on 2,6-dimethylaniline that yields 2,6-dimethylnitrobenzene or by the direct hydroxylation of 2,6-dimethylaniline’s N-position to give 2,6-dimethylphenol. 2,6-dimethylbenzoquinone is also formed from $OH^{\bullet}$ attack on 2,6-dimethylphenol which further breaks into 3-hexanone. In Fenton reactions, $OH^{\bullet}$ addition to the aromatic substrates to give mono- or multihydroxyl intermediates or products (hydroquinone/quinone analogues) has been firmly established (Chen and Pignatello, 1997).

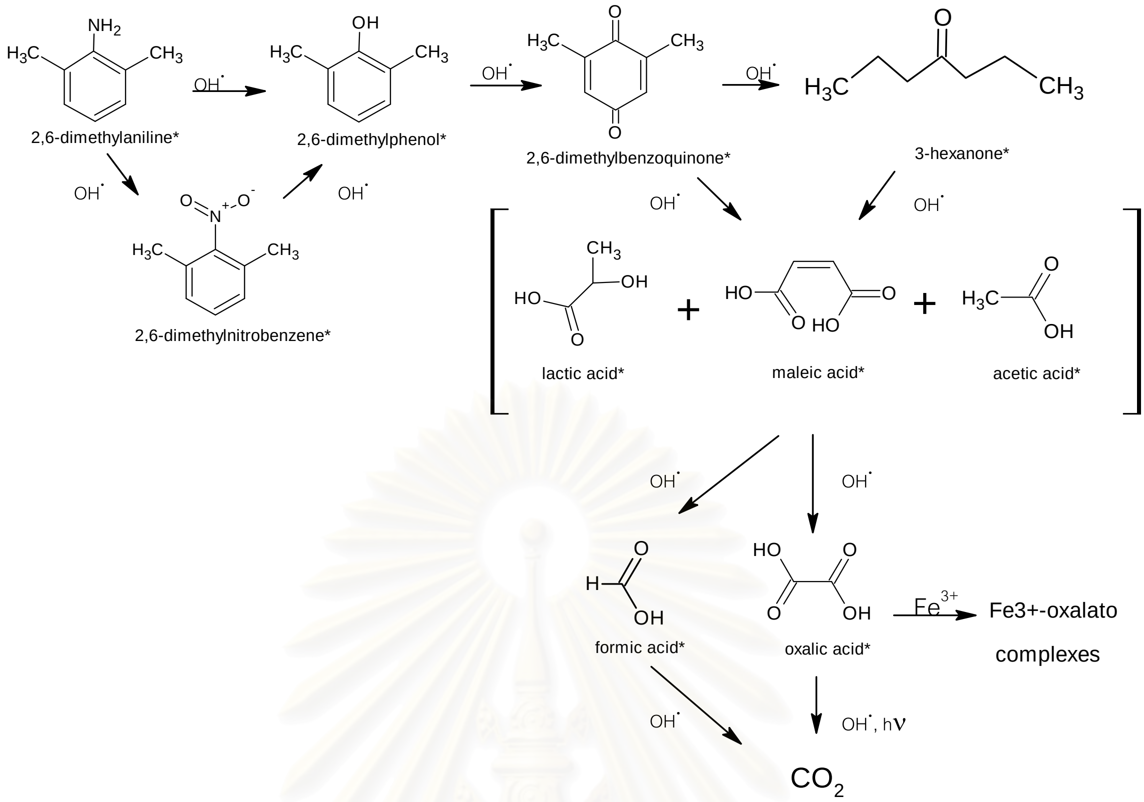

Figure 4.87. Proposed reaction pathways for mineralization of 2,6-dimethylaniline at pH 2 by Fenton, electro-Fenton and photoelectro-Fenton processes. (* detected by GC-MS and IC)

The further degradation of 2,6-benzoquinone and 3-hexanone leads to a mixture of lactic acid, maleic acid and acetic acid. The three acids are transformed into formic acid and oxalic acid. The formic acid is directly mineralized to carbon dioxide. The ultimate carboxylic acid, oxalic acid, is very slowly converted into CO_2 by $OH^{\bullet}$ since it forms very stable Fe^{3+}-oxalato complexes under the electro-Fenton process.It can be easily established that 2,6-dimethylaniline is degraded to 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone and probably other nitrogen-free organic derivatives. As far as we know, the proposed degradation pathways of 2,6-dimethylaniline using the electro-Fenton process at pH 2 has not yet been reported in the literature.

For the aniline degradation pathway, on the basis of some intermediates detected in this work and previous results reported in the literature such as Sauleda and Brillas (2001), Shen et al., (2007), Brillas et al.,(2007)., a general reaction parthway for aniline mineralization at pH 3 is proposed in Figure 4. 88.

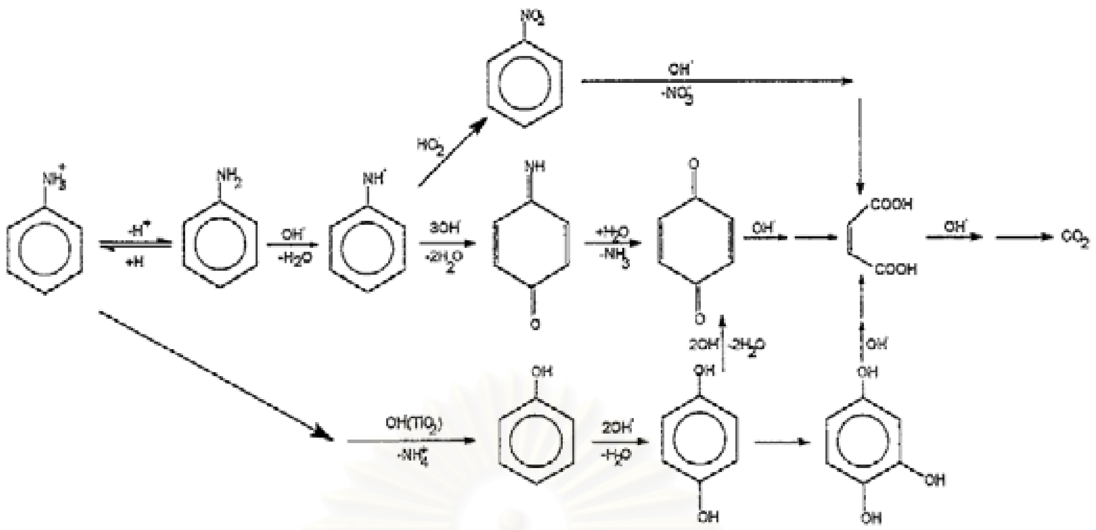

Figure 4.88. Proposed reaction pathway for aniline mineralization by Fenton, electro-Fenton and photoelectro-Fenton processes at pH 3.

The main oxidizing agent is hydroxyl radicals from Fenton, electro-Fenton and photoelectro-Fenton processes. This oxidant has degradation power on aniline mineralization. The process is then initiated by the attack of hydroxyl radical to form other intermediates such as benzoquinonimine, nitrobenzene, phenol, maleic acid, formic acid and oxalic acid. Oxalic and formic acids are further mineralized to CO_2 as ultimate carboxylic acid.

From the degradation pathways of both chemicals, they explained the reason why aniline was easier degraded than 2,6-dimethylaniline. This was due to the number of methyl groups on the structure of 2,6-dimethylaniline. The aniline structure included 1 benzene ring and 1 amine group, however, 2,6-dimethylaniline was consisted of 1 benzene ring, 1 amine group and 2 methyl groups. This reason made the 2,6-dimethylaniline degradation slower than aniline in all processes.

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CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1. Conclusions

○ It is obvious from the study that Fenton, electro-Fenton and photoelectro-Fenton processes were able to degrade wastewater containing 2,6-dimethylaniline and aniline.

○ Optimum initial pH, initial ferrous ion concentration, initial hydrogen peroxide concentration, applied electric current and UVA lamps are important factors on the degradation of both chemicals

○ On its own, none of the ferrous ion, hydrogen peroxide, electrical current and UVA lamps within the ranges and conditions used in this study has significant effect on 2,6-dimethylaniline and aniline degradation.

○ 2,6-Dimethylaniline and aniline were effectively degraded by Fenton processes. The oxidation reaction of 2,6-dimethylaniline and aniline was very fast at the first 10 minutes then gradually slowed down until the end of the reaction.

○ The removal efficiency of 2,6-dimethylaniline and aniline increased with increasing ferrous ion concentration. In this study, the oxidation of 2,6-dimethylaniline and aniline were not inhibited by increasing the concentration of ferrous ion.

○ It is evident that removal efficiency of 2,6-dimethylaniline and aniline increased with increasing hydrogen peroxide concentration. However, in this study, the oxidation of 2,6-dimethylaniline and aniline were inhibited by increasing in too much amount of hydrogen peroxide concentration.

○ Variation of initial pH in acidic condition exerted less effect in the oxidation reaction of 2,6-dimethylaniline and aniline. However, initial pH 2.0 provided the most significant effect on degradation for 2,6-dimethylaniline and pH 3.0 was the optimum pH for aniline removal.

○ The optimum condition for treating 1 mM 2,6-dimethylaniline by

1) Fenton process is 2 mM [Fe^{2+}] : 20 mM [H_2O_2] at pH 3, removal of 2,6-dimethylaniline 65% in 5 hours.

2) Electro-Fenton is 1 mM [Fe^{2+}]: 20 mM [H_2O_2]: 2 A of applied electric current at pH 3, 100% of 2,6- dimethylaniline removal in 4 hours.

3) Photoelectro-Fenton is 1 mM [Fe^{2+}]: 20 mM [H_2O_2]: 2 A of applied electric current: UVA 4 lamps at pH 3, 100% of 2,6- dimethylaniline removal in 1 hour.

○ The optimum condition for treating 1 mM aniline by

1) Fenton process is 0.5 mM [Fe^{2+}] : 20 mM [H_2O_2] at pH 2, 100% of aniline removal in 2 hours.

2) Electro-Fenton is 0.5 mM [Fe^{2+}]: 20 mM [H_2O_2]: 1 A of applied electric current at pH 2, 100% of aniline removal in 1 hour.

3) Photoelectro-Fenton is 0.25 mM [Fe^{2+}]: 10 mM [H_2O_2]: 2 A of applied electric current: UVA 4 lamps at pH 3, 100% of aniline removal in 20 minutes.

○ Under similar chemical dosages, photoelectro-Fenton process degraded 2,6-dimethylaniline and aniline and theirs oxidation products much more rapidly and effectively than electro-Fenton and Fenton processes.

○ Degradation kinetics for 2,6-dimethylaniline and aniline degradation by Fenton process, electro-Fenton process and photoelectro-Fenton process can be described by the following equations:

2,6-Dimethylaniline:

Fenton process:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{Fenton} = 3.41\ [2,6-DMA]^{0.56}\ [Fe^{2+}]^{0.42}\ [H_2O_2]^{0.36}$$

Electro-Fenton process:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{electro-Fenton} = 1.60\ [2,6-DMA]^{0.63}\ [Fe^{2+}]^{0.21}\ [H_2O_2]^{0.11}$$

Photoelectro-Fenton process:

$$-\left(\frac{d[2,6-DMA]}{dt}\right)_{photoelectro-Fenton} = 1.04\ [2,6-DMA]^{0.68}\ [Fe^{2+}]^{0.16}\ [H_2O_2]^{-0.04}$$

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Aniline:

$$-\left(\frac{d[Aniline]}{dt}\right)_{photoelectro-Fenton} = 1.32[Aniline]^{0.21}\ [Fe^{2+}]^{0.5289}\ [H_2O_2]^{0.2232}$$

○ The proposed degradation pathway of 2,6-dimethylaniline was proposed in this study. The intermediates produced after the degradation of 2,6-dimethylaniline were 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid. They were detected during the degradation of 1 mM 2,6-dimethylaniline solution by the electro-Fenton method when an electric current of 1.43 A was applied. For aniline degradation pathway, the intermediates were benzoquinonimine, nitrobenzene, phenol, maleic acid, formic acid and oxalic acid.

○ Aniline was easier to degrade than 2,6-dimethylaniline. This was due to the number of methyl groups on the structure of 2,6-dimethylaniline. The aniline structure included 1 benzene ring and 1 amine group, however, 2,6-dimethylaniline was consisted of 1 benzene ring, 1 amine group and 2 methyl groups. This reason made the 2,6-dimethylaniline degradation slower than aniline in all processes.

○ The advantages of Fenton processes, especially photoelectro-Fenton process, are economics, lest investment, less energy demand and harmless process products. Combination of an AOP with biological treatment is a promising alternative because one can take advantage of both methods and develop as result a potent wastewater purification method.

5.2. Suggestions for future work

1. Real wastewater should be applied to study other parameters in real wastewater which can affect the degradation behavior.
2. The other kind of UV light such as mercury lamp or UVC (245 nm) should be applied to examine the degradation efficiency of both chemicals.

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APPENDICES

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APPENDIX A

Analytical Method

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Chemical Oxygen Demand (COD) ANALYSIS

(Closed-reflux titrimetric method based on the Standard methods, APHA, 1992).

1. General Discussion

The chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. Older references may express the units as parts per million (ppm). The basis for the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions.

For many years, the strong oxidizing agent potassium permanganate ($KMnO_4$) was used for measuring chemical oxygen demand. Measurements were called oxygen consumed from permanganate, rather than the oxygen demand of organic substances. Potassium permanaganate's effectiveness at oxidizing organic compounds varied widely, and in many cases biochemical oxygen demand (BOD) measurements were often much greater than results from COD measurements. This indicated that potassium permanganate was not able to effectively oxidize all organic compounds in water, rendering it a relatively poor oxidizing agent for determining COD. Since then, other oxidizing agents such as ceric sulfate, potassium iodate, and potassium dichromate have been used to determine COD. Of these, potassium dichromate ($K_2Cr_2O_7$) has been shown to be the most effective: it is relatively cheap, easy to purify, and is able to nearly completely oxidize almost all organic compounds.

For all organic matter to be completely oxidized, an excess amount of potassium dichromate (or any oxidizing agent) must be present. Once oxidation is complete, the amount of excess potassium dichromate must be measured to ensure that the amount of Cr^{3+} can be determined with accuracy. To do so, the excess potassium dichromate is titrated with ferrous ammonium sulfate (FAS) until all of the excess oxidizing agent has been reduced to Cr^{3+}. Typically, the oxidation-reduction indicator Ferroin is added during this titration step as well. Once all the excess dichromate has been reduced, the Ferroin indicator changes from blue-green to reddish-brown. The amount of ferrous ammonium sulfate added is equivalent to the amount of excess potassium dichromate added to the original sample

2. Apparatus

The reagent uses in COD measurement are:

$K_2Cr_2O_7$ (0.1 N) : 167 ml H_2SO_4 add into 1000 ml volumetric flask and then add 200 ml of DI water. After that 4.913 gram of $K_2Cr_2O_7$ was added and then 33.3 ml of $HgSO_4$. Then DI water was adjusted up-to 1 liter.

H_2SO_4 solution : prepared by added 25.3 gram of Ag_2SO_4 into 2.5 liter of H_2SO_4

FAS (0.025 N) : 9.8 gram of $FeSO_4(NH_4)SO_4.6H_2O$ was put into 1 liter volumetric flask and then 20 ml of H_2SO_4 was added. Then the DI water was poured until 1 liter.

Ferroin Indicator : 1 drop

3. Procedure

The sample 2.5 ml was put into tube and then 1.5 ml of $K_2Cr_2O_7$ (0.1 N), 3.5 ml of H_2SO_4 reagent were added. After that the mixed chemical was incubate at 150°C for 2 hours. Then the chemical was put outside at room temperature to cool down the temperature. After that, 1 drop of Ferroin indicator was added and titrated by using FAS.

4. Calculation

The following formula is used to calculate COD:

$$\text{COD} = \frac{(\textit{blank} - \textit{sample}) * \text{FAS conc.} * 8000}{2.5}$$

$$\text{FAS conc.} = \frac{0.1 * 1.5}{V_{\text{FAS (normal)}}}$$

where blank is the volume of FAS used in the blank sample, *sample* is the volume of FAS in the original sample, and *FAS conc.* is the normality of FAS. If milliliters are used consistently for volume measurements, the result of the COD calculation is given in mg/L.

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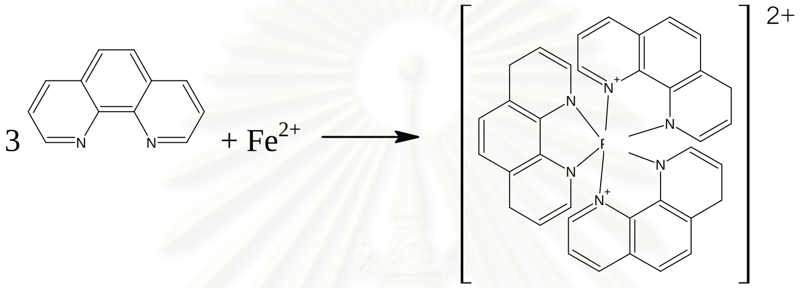
Analytical Method of Ferrous ion (Fe^{2+})

(Standard Method, 1995)

1. General Discussion

The phenanthroline method is the preferred standard procedure for the measurement of iron in water at the present time, except when color, turbidity, phosphate, or heavy metal interferences are present. The method depends upon the fact that 1,10-phenanthroline combine with ferrous to form a complex iron that is orange-red in color. Three molecules of 1,10-phenanthroline are required to sequester or form a complex ion with each ferrous ion. The reaction may be represented as shown in the following equation:



(A-1)

The 1,10-phenanthroline complex with iron (II) was first discovered by Blau. A spectrophotometric determination of iron dependent on the formation of the iron (II) - 1,10- phenanthroline complex was developed by Fortune Mellon. The iron (II) – 1,10-phenanthroline complex was reddish orange in color.

2. Apparatus

2.1 Colorimetric Equipment

2.1.1 Spectrophotometer (Shimadsu UV-1201): The absorbance used for ferrous (Fe^{2+}) analysis was 510 nm.

2.1.2 Acid-washed Glassware: All glass wares were washed with conc. HCl and rinsed with DI water to remove deposit of iron oxide.

2.1.3 Membrane Filter: a 0.45 µm membrane filter was used to filter the sample to remove precipitation particle on solution.

2.2 Reagent

All reagents were prepared by distilled water. Reagents were stored in glass bottles. The hydrochloric acid and ammonium acetate solutions were stable indefinitely if they were tightly closed the bottles. The standard ferrous ion (Fe^{2+}) solutions were not stable, it was prepared daily.

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2.2.1 Hydrochloric Acid, HCl: 20 ml of concentrated hydrochloric acid was diluted to 1000 ml with DI water.

2.2.2 Ammonium Acetate Buffer Solution: 500 g of $NH_4C_2H_3O_2$ was dissolved in 300 ml of DI water. Then, 1400 ml of concentrated acetic acid was filled up to the mark of 2000 ml.

2.2.3 Phenanthroline Solutions: 5 g of 1,10 – phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$, was dissolved and 1 ml of concentrated hydrochloric acid was added. Then, DI waster was used to make the mark of 1000 ml.

2.2.4 Stock Ferrous Ion Solution: 20 ml of concentrated H_2SO_4 was slowly added to 50 ml DI water and 0.25 g of ferrous sulfate ($FeSO_4.7H_2O$) was added. Then, DI water was used to make the mark of 1000 ml. The stock solution was 500 mg/l as Fe^{2+}.

2.2.5 Standard Solution: 1 ml of concentrated H_2SO_4 was slowly added to 25 ml DI water. Then 5 ml of stock ferrous ion solution was diluted to 50 ml with DI water. The standard solution was 50 mg/l as Fe^{2+}.

3. Procedure

3.1 Sample Preparation for Calibration Curves: The standard ferrous (Fe^{2+}) solutions were prepared in the range 0 to 10 mg/l as Fe^{2+}. 25 ml of HCl from stock solution was prepared in six 50 ml volumetric flasks. Then, 10 ml of phenanthroline solution and 5 ml of ammonium acetate solution were added with vigorous stirring. 1,2,3,4,5 and 10 ml of 50 mg/l as Fe^{2+} standard solution were pipetted, respectively. After that, the samples were diluted to 50 ml with DI water, mixed thoroughly.

3.2 Ferrous Ion Analysis: To determine ferrous ion, 25 ml of HCl from stock solution was prepared in 50 ml volumetric flask. Then, 10 ml of phenanthroline solution and 5 ml of ammonium acetate solution were added with vigorous stirring. 2 ml of sample was filled and diluted to 50 ml with DI water. After that, it had to stand for 10-30 min. Do not expose to sunlight. (Color development was rapid in the presence of excess phenanthroline)

4. Preparing for Calibration Curve

The standard ferrous solution were prepared in the range of 0 to 5 mg/l as Fe^{2+}

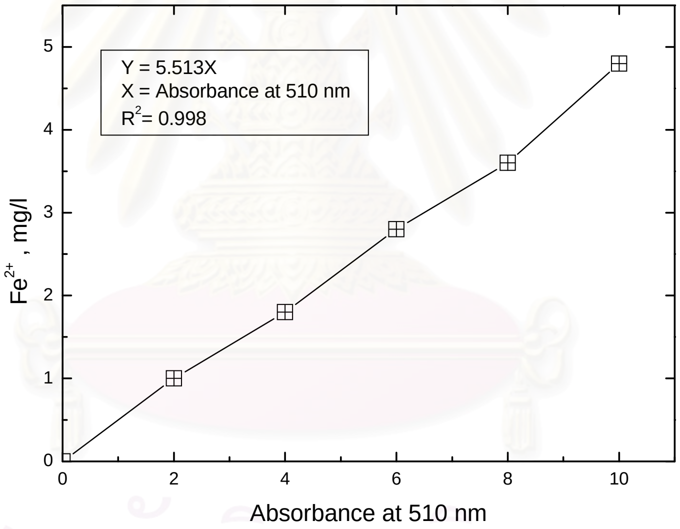
1. 25 ml of HCl from stock solution was prepared in five 50 ml volumetric flasks. Then, 10 ml of phenanthroline solution and 5 ml of ammonium acetate solution were added with vigorous stirring.
2. 1 ml of 0, 0.5, 1, 3, and 5 mg/l as Fe^{2+} standard solution were pipetted, respectively.
3. The samples were diluted to 50 ml with RO water, mixed thoroughly. After that, it had to stand for 10 min.
4. Measured samples by spectrophotometer at 510 nm.

5.Calculation

$Y = 5.513x$

Where $Y = Fe^{2+}$, mg/l

X = absorbance at 510 nm



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Analytical Method of Hydrogen Peroxide

(Iodometric titration with $Na_2S_2O_3$ method, Kolthof et al 1969)

1. Principle

Hydrogen peroxide oxidizes iodide to iodine in the presence of acid and molybdate catalyst. The iodine formed is titrated with thiosulfate solution, incorporating a starch indicator.

$$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

2. Interferences

Other oxidizing agents will also produce iodine, whereas reducing agents (and unsaturated organics) will react with the liberated iodine. The contribution from other oxidizing agents can be determined by omitting the acid and molybdate catalyst.

3. Safety Precautions

Concentrated sulfuric acid is a corrosive, hazardous material and should be handled and disposed of in accordance with the MSDS. Neoprene gloves and monogoggles are recommended, as is working under a vacuum hood.

Sample bottles containing H_2O_2 should not be stopper, but rather vented or covered loosely with aluminum foil or paraffin film.

4. Reagents

1). Potassium iodide solution (1% w/v). Dissolve 1.0 grams KI into 100 ml demineralized water. Store capped in cool place away from light. Yellow-orange tinted KI solution indicated some air oxidation to iodine, which can be removed by adding a 1-2 drops of dilute sodium thiosulfate solution.

2). Ammomium molybdate solution. Dissolve 9 grams ammonium molybdate in 10 ml 6N NH_4OH. ADD 24 grams NH_4NO_3 and dilute to 100 ml.

3). Sulfuric acid solution. Carefully add one part H_2SO_4 – 98% to four parts demineralized water.

4). Starch indicator. 2 g of starch and dilute to 100 ml by DI water.

5). Sodium thiosulfate solution (0.1N).

5. Apparatus

1). Analytical balance (+/- 0.1 mg/l)

2). Small weighing bottle (< 5ml)

3). 250 ml Erlenmeyer flask

4). 50 ml buret (Class A)

5). Medicine dropper

6. Procedure

1). Weigh to the nearest 0.1 mg an amount of hydrogen peroxide equivalent to a titer of 30 ml (0.06 grams) using 1 5 ml beaker and medicine dropper. Transfer sample to Erlenmeyer flask.

2). Add to Erlenmeyer flask 50 ml of demineralized water, 10 ml of sulfuric acid solution, 10-15 ml of potassium iodide solution, and 2 drops ammonium molybdate solution.

3). Titrate with 0.1 N sodium thiosulfate to faint yellow or straw color. Swirl or stir gently during titration to minimize iodine loss.

4). Add about 2 ml starch indicator, and continue titration until the blue color just disappears.

5). Repeat steps 2-4 on a blank sample of water (omitting the hydrogen peroxide).

7. Calculation

$$\text{Weight \% Hydrogen peroxide} = \frac{(A - B) \times (\text{Normality of } Na_2S_2O_3) \times 1.7}{\text{Sample weight in grams}}$$

where: A = ml $Na_2S_2O_3$ for sample

B = ml $Na_2S_2O_3$ for blank

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APPENDIX B

Experimental Figures

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Figure B.1.   Fenton reactor setup

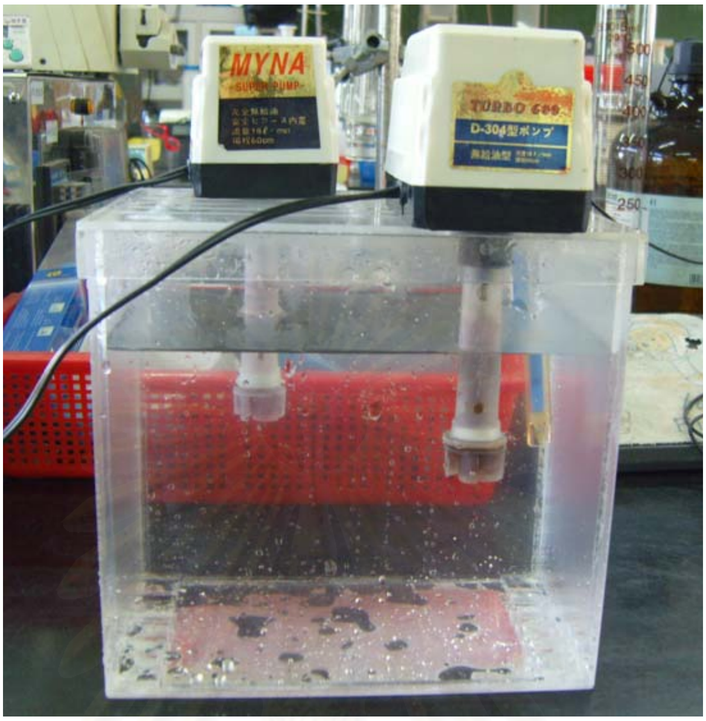


Figure B.2. Electro-Fenton reactor setup

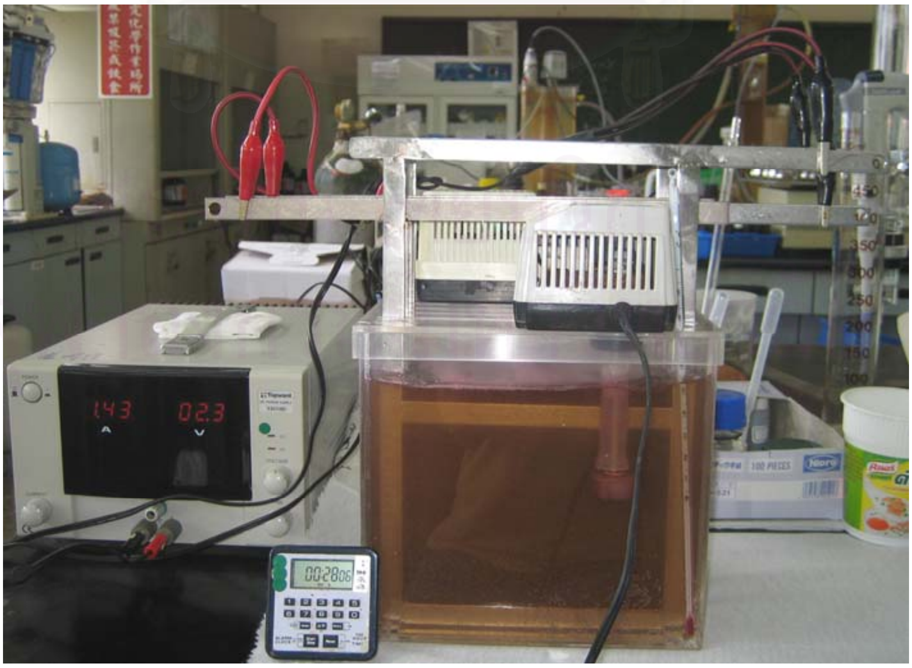


Figure B.3. Photo-Fenton reactor setup

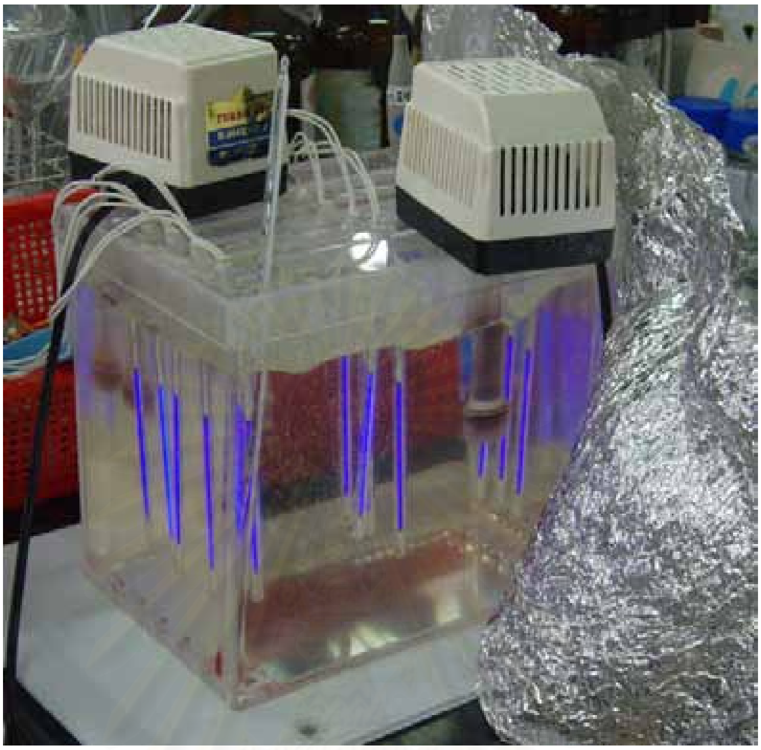


Figure B.4. Photoelectro-Fenton reactor setup

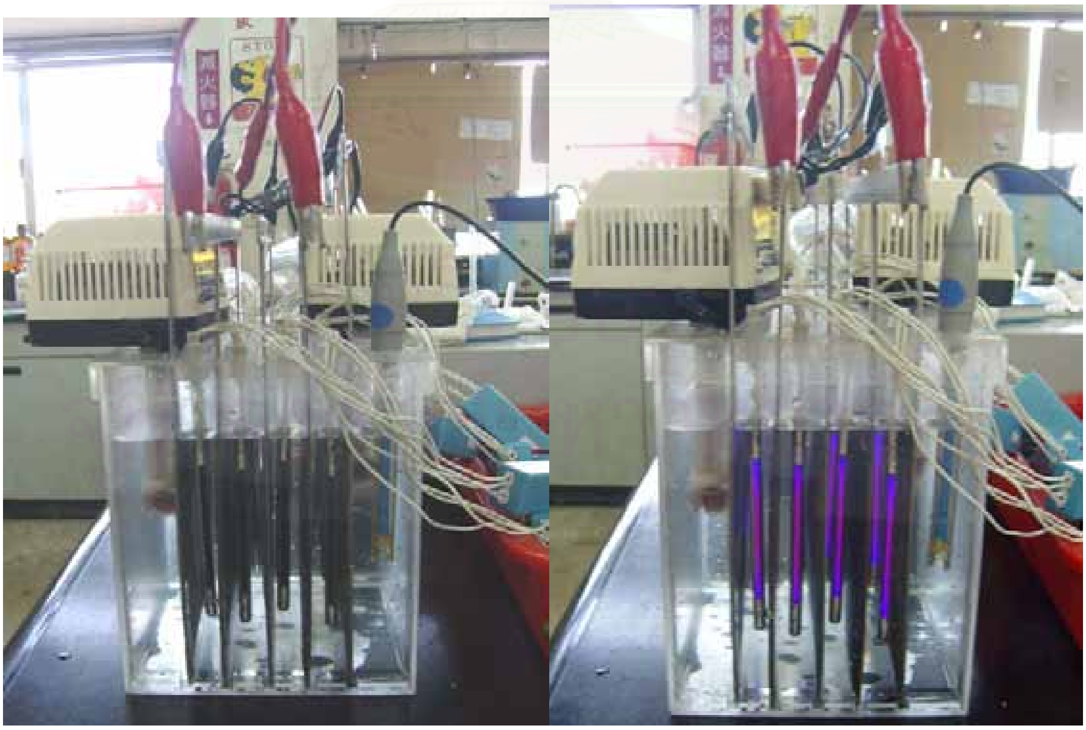
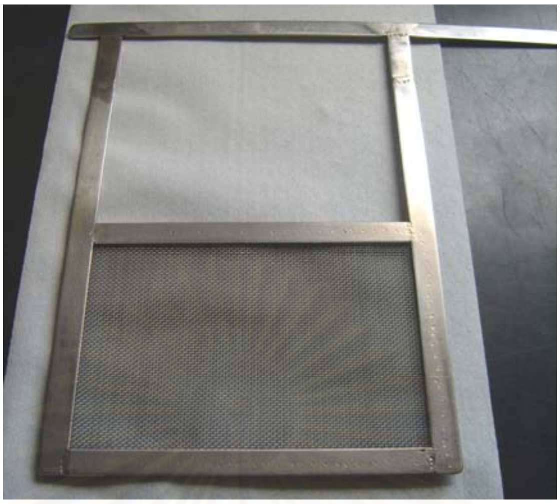


Figure B.5. Electrode

(a) Cathode



(b) Anode

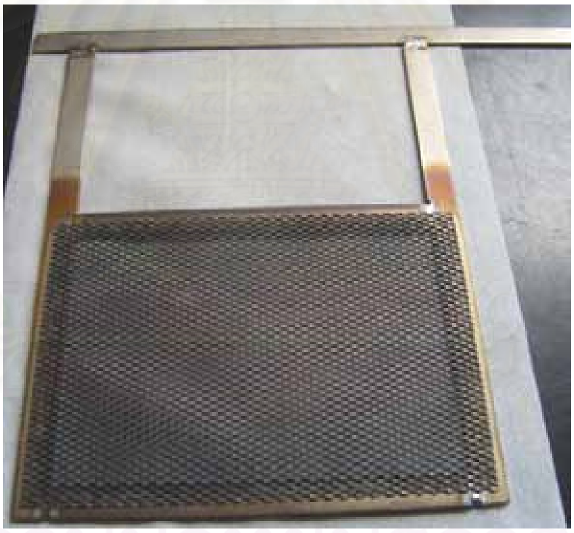


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Figure B.6. UV light

Figure B.7. Experimental instruments

HPLC

AAS

GC

TOC

IC

DI water

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pH meter

Filter set

APPENDIX C

Experimental Data

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2,6-Dimethylaniline degradation

Table C.1. 2,6-Dimethylaniline degradation by various processes

Time	Electrolysis	Photolysis	UV+H_2O_2	Fenton	EF	PF	PEF
(min)	(C/Co)						
0	1	1	1	1	1	1	1
2	0.9705	0.9622	0.9769	0.9462	0.6259	0.5393	0.4893
5	0.9705	0.9184	0.9480	0.8821	0.4888	0.5020	0.3423
10	0.9264	0.8482	0.8734	0.8377	0.4586	0.4552	0.2669
20	0.9558	0.80177	0.8285	0.7506	0.4666	0.4200	0.1289
40	0.9411	0.7820	0.7563	0.6949	0.4287	0.3647	0.0231
60	0.9558	0.7845	0.6321	0.6278	0.3560	0.3553	0
90	0.9411	0.7819	0.5435	0.5564	0.2438	0.1586	0
120	0.8676	0.7606	0.4832	0.4688	0.1922	0.0393	0

- EF = electro-Fenton process
- PF = photo-Fenton process
- PEF = photoelectro-Fenton process

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, H_2O_2 = 20 mM,
Electric current = 1.43 A, UVA light= 12 lamps

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Table C.2. TOC removal by various processes

Time (min)	Electrolysis	Photolysis	UV+H2O2	Fenton	EF	PF	PEF
	(C/Co)						
0	1	1	1	1	1	1	1
2	0.9705	0.9235	0.9707	0.9108	0.9287	0.9808	0.9277
5	0.9690	0.8896	0.9624	0.9071	0.8935	0.9270	0.8709
10	0.9564	0.8758	0.9437	0.8457	0.8212	0.8860	0.8047
20	0.9558	0.8612	0.9269	0.8682	0.8046	0.8319	0.7205
40	0.9511	0.8594	0.8702	0.8503	0.7695	0.7716	0.7081
60	0.9458	0.8557	0.8577	0.8682	0.7246	0.7275	0.6245
90	0.9411	0.8571	0.8494	0.7887	0.6961	0.6877	0.6042
120	0.8976	0.8625	0.8368	0.7224	0.6447	0.6647	0.5346

- EF = electro-Fenton process
- PF = photo-Fenton process
- PEF = photoelectro-Fenton process

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, H_2O_2 = 20 mM,
Electric current = 1.43 A, UVA light= 12 lamps

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Table C.3. Effect of initial pH on 2,6-dimethylaniline degradation by Fenton process

Time	pH1	pH1.5	pH2	pH2.5	pH3	pH3.5	pH 4
(min)	(C/Co)						
0	1	1	1	1	1	1	1
2	0.9568	0.8866	0.9462	0.9517	0.9107	0.9485	0.9295
5	0.9361	0.8565	0.9021	0.8838	0.8426	0.9174	0.9168
10	0.7697	0.8089	0.8637	0.8417	0.7426	0.8349	0.8157
20	0.7615	0.7830	0.84972	0.7606	0.6436	0.8108	0.8017
40	0.7502	0.7542	0.7649	0.7255	0.6458	0.7835	0.7840
60	0.7429	0.7228	0.6778	0.6255	0.5723	0.7595	0.7776
90	0.7354	0.6914	0.6156	0.5772	0.5686	0.7386	0.7667
120	0.7251	0.6678	0.5488	0.4411	0.4871	0.6712	0.7572

Note: 2,6-Dimethylaniline = 1 mM, Fe^{2+} = 1 mM, H_2O_2 = 20 mM.

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Table C.4. Effect of initial ferrous ion concentration on 2,6-dimethylaniline degradation by Fenton process

Time (min)	**Fe^{2+} (mM)**					
	0.25	**0.5**	**1**	**1.5**	**2**	**2.5**
	(C/Co)					
0	1	1	1	1	1	1
2	0.9630	0.8768	0.9462	0.9076	0.9371	0.9249
5	0.9464	0.8121	0.9021	0.8551	0.8466	0.8631
10	0.9327	0.7293	0.8677	0.8186	0.6917	0.7369
20	0.9239	0.7085	0.8890	0.7298	0.5426	0.6844
40	0.9167	0.6830	0.8649	0.6878	0.5167	0.6366
60	0.8933	0.6447	0.8178	0.6328	0.4194	0.5393
90	0.8743	0.6170	0.6756	0.5447	0.3176	0.4633
120	0.8641	0.5961	0.5488	0.4851	0.2617	0.3849

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, H_2O_2 = 20 mM.

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Table C.5. Effect of initial hydrogen peroxide concentration on 2,6-dimethylaniline degradation by Fenton process

Time (min)	H_2O_2 (mM)								
	5	10	20	30	40	60	100	120	150
	(C/Co)								
0	1	1	1	1	1	1	1	1	1
2	0.8932	0.8825	0.9462	0.8940	0.8007	0.9127	0.9073	0.9014	0.9374
5	0.7694	0.8105	0.9421	0.8242	0.6305	0.8412	0.8602	0.7927	0.7886
10	0.7584	0.6483	0.9377	0.7543	0.4456	0.8206	0.8002	0.7423	0.7727
20	0.7145	0.6292	0.8890	0.7359	0.4083	0.7887	0.7444	0.6683	0.7347
40	0.6421	0.5695	0.8649	0.6925	0.4899	0.7073	0.6577	0.5753	0.6223
60	0.6224	0.5572	0.8178	0.6677	0.4331	0.6012	0.5157	0.5112	0.5073
90	0.5919	0.5270	0.6756	0.6218	0.3648	0.5043	0.4653	0.4148	0.3773
120	0.5855	0.5006	0.5488	0.4783	0.3447	0.3421	0.4202	0.3678	0.3628

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM.

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Table C.6. Effect of initial pH on 2,6-dimethylaniline degradation by electro-Fenton process

Time	pH1	pH1.5	pH2	pH2.5	pH3	pH3.5	pH 4
(min)				(C/Co)			
0	1	1	1	1	1	1	1
2	0.9507	0.8905	0.6259	0.8795	0.9679	0.7997	0.9340
5	0.8663	0.6817	0.4888	0.5670	0.8469	0.6877	0.7449
10	0.8615	0.6183	0.4586	0.5371	0.7570	0.6348	0.7067
20	0.8202	0.5833	0.4666	0.4936	0.6833	0.6014	0.7042
40	0.7647	0.5230	0.4287	0.4883	0.6615	0.5657	0.6899
60	0.7388	0.5080	0.3560	0.4773	0.6085	0.5484	0.5948
90	0.7050	0.4798	0.2438	0.4437	0.5817	0.5294	0.5354
120	0.6459	0.4185	0.1922	0.4197	0.5746	0.5394	0.5207

Note: 2,6-Dimethylaniline = 1 mM, Fe^{2+} = 1 mM, H_2O_2 = 20 mM, I = 1.43 A

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Table C.7. Effect of initial ferrous ion concentration on 2,6-dimethylaniline degradation by electro-Fenton process

Time (min)	Fe^{2+} (mM)					
	0.25	**0.5**	**1**	**1.5**	**2**	**2.5**
	(C/Co)					
0	1	1	1	1	1	1
2	0.8142	0.9545	0.6259	0.7718	0.7980	0.8009
5	0.7348	0.7781	0.4888	0.7333	0.6152	0.7320
10	0.7305	0.5328	0.4586	0.6842	0.3915	0.7191
20	0.7062	0.4782	0.4666	0.6300	0.3759	0.6015
40	0.6566	0.4430	0.4287	0.4155	0.3084	0.5339
60	0.6131	0.4339	0.3560	0.3559	0.1761	0.4502
90	0.6053	0.3633	0.2438	0.3234	0.1786	0.4084
120	0.5809	0.2587	0.1922	0.2983	0.1132	0.3906

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, H_2O_2 = 20 mM, I = 1.43 A

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Table C.8. Effect of initial hydrogen peroxide concentration on 2,6-dimethylaniline degradation by electro-Fenton process

Time (min)	**H_2O_2 (mM)**								
	5	**10**	**20**	**30**	**40**	**60**	**100**	**120**	**150**
	(C/Co)								
0	1	1	1	1	1	1	1	1	1
2	0.8423	0.7631	0.6259	0.8974	0.9842	0.9647	0.8465	0.7968	0.7770
5	0.7778	0.5027	0.4888	0.8189	0.7866	0.7765	0.7817	0.7428	0.6847
10	0.6955	0.4264	0.4586	0.6723	0.3215	0.6454	0.6495	0.7325	0.5487
20	0.5911	0.4011	0.4666	0.4439	0.3171	0.4836	0.4319	0.6184	0.2977
40	0.5373	0.3871	0.4287	0.3963	0.2431	0.3648	0.4101	0.4731	0.2282
60	0.4840	0.2337	0.3560	0.3361	0.1806	0.3499	0.3753	0.3370	0.2035
90	0.4321	0.1623	0.2438	0.2556	0.0800	0.2137	0.2059	0.3016	0.1147
120	0.2571	0.1300	0.1922	0.2321	0.0746	0.1732	0.0653	0.2316	0.0952

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, I = 1.43 A

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Table C.9. Effect of applied electric current on 2,6-dimethylaniline degradation by electro-Fenton process

Time (min)	I (A)					
	0.5	**1**	**1.43**	**2**	**4**	**6**
	(C/Co)					
0	1	1	1	1	1	1
2	0.8963	0.6311	0.6259	0.7936	0.7413	0.9325
5	0.8436	0.5039	0.4888	0.5396	0.6434	0.8091
10	0.5776	0.5449	0.4586	0.4782	0.5325	0.4022
20	0.5627	0.3800	0.4666	0.3951	0.5221	0.2970
40	0.3871	0.2207	0.4287	0.3526	0.3171	0.2758
60	0.2728	0.1765	0.3560	0.2354	0.2346	0.1735
90	0.2190	0.1217	0.2438	0.1942	0.1514	0.1233
120	0.2056	0.0891	0.1922	0.1505	0.0926	0.1027

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, H_2O_2 = 20 mM

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Table C.10. Effect of initial pH on 2,6-dimethylaniline degradation by photoelectro-Fenton process

Time	**pH1.5**	**pH2**	**pH2.5**	**pH3**
(min)	**(C/Co)**			
0	1	1	1	1
2	0.6652	0.6160	0.5810	0.6064
5	0.5575	0.4975	0.3785	0.5249
10	0.4214	0.3502	0.3000	0.4357
20	0.2408	0.1909	0.1559	0.2018
40	0.1592	0.0258	0.0674	0.1698
60	0.0840	0	0	0.0738
90	0.0497	0	0	0
120	0	0	0	0

Note: 2,6-Dimethylaniline = 1 mM, Fe^{2+} = 1 mM, H_2O_2 = 20 mM, I = 1.43 A, UVA lamps = 12

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Table C.11. Effect of initial ferrous ion concentration on 2,6-dimethylaniline degradation by photoelectro-Fenton process

Time (min)	Fe^{2+} (mM)				
	0.25	0.5	1	2.5	5
	(C/Co)				
0	1	1	1	1	1
2	0.7225	0.6160	0.6160	0.0939	0.0665
5	0.5788	0.5199	0.4975	0.0323	0.0143
10	0.4190	0.4977	0.3502	0	0
20	0.3325	0.3502	0.1909	0	0
40	0.1820	0.0909	0.0258	0	0
60	0.0822	0.0258	0	0	0
90	0	0	0	0	0
120	0	0	0	0	0

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, H_2O_2 = 20 mM, I = 1.43 A, UVA lamps = 12

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Table C.12. Effect of initial hydrogen peroxide concentration on 2,6-dimethylaniline degradation by photoelectro-Fenton process

Time (min)	**H_2O_2 (mM)**				
	5	**10**	**20**	**40**	**100**
	(C/Co)				
0	1	1	1	1	1
2	0.8423	0.7631	0.6259	0.9842	0.8465
5	0.7778	0.5027	0.4888	0.7866	0.7817
10	0.6955	0.4264	0.4586	0.3215	0.6495
20	0.5911	0.4011	0.4666	0.3171	0.4319
40	0.5373	0.3871	0.4287	0.2431	0.4101
60	0.4840	0.2337	0.3560	0.1806	0.3753
90	0.4321	0.1623	0.2438	0.0800	0.2059
120	0.2571	0.1300	0.1922	0.0746	0.0653

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, I = 1.43 A, UVA lamps = 12

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Table C.13. Effect of applied electric current on 2,6-dimethylaniline degradation by photoelectro-Fenton process

Time (min)	**I (A)**				
	0.5	**1.43**	**2**	**4**	**8**
	(C/Co)				
0	1	1	1	1	1
2	0.6800	0.6160	0.5190	0.6069	0.5661
5	0.5978	0.5199	0.4170	0.5860	0.4455
10	0.5352	0.4975	0.3017	0.5014	0.3002
20	0.4711	0.3502	0.1927	0.3999	0.1832
40	0.2536	0.0909	0.0497	0.2152	0.0076
60	0.1191	0.0258	0	0.0135	0
90	0	0	0	0	0
120	0	0	0	0	0

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, H_2O_2 = 20 mM, UVA lamps = 12

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Table C.14. Effect of number of UVA lamps on 2,6-dimethylaniline degradation by photoelectro-Fenton process

Time (min)	**Number of UVA lamps(lamps)**		
	4	**8**	**12**
	(C/Co)		
0	1	1	1
2	0.5810	0.5633	0.4893
5	0.3785	0.3623	0.34236
10	0.3200	0.3046	0.2669
20	0.1559	0.1448	0.1289
40	0.0674	0.0431	0.0231
60	0	0	0
90	0	0	0
120	0	0	0

Note: 2,6-Dimethylaniline = 1 mM, pH = 2, Fe^{2+} = 1 mM, H_2O_2 = 20 mM, Electric current = 1.43 A

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Aniline degradation

Table C.15. Aniline degradation by various processes

Time	Electrolysis	Photolysis	UV+H_2O_2	Fenton	EF	PF	PEF
(min)	(C/Co)						
0	1	1	1	1	1	1	1
2	0.9898	0.9782	0.9829	0.5363	0.5778	0.2572	0.5025
5	0.9791	0.9811	0.8976	0.3149	0.3393	0.1419	0.1567
10	0.9457	0.9765	0.8857	0.2180	0.2503	0.0209	0.0123
20	0.9266	0.9559	0.8936	0.1515	0.2019	0.0047	0
40	0.9052	0.9397	0.8721	0.1145	0.1891	0	0
60	0.8904	0.9238	0.8602	0.0832	0.0853	0	0
90	0.8630	0.9125	0.8574	0.0389	0	0	0
120	0.8736	0.8901	0.8483	0	0	0	0

Note: Aniline = 1 mM, pH = 3, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM,

Electric current = 1 A, UVA light= 12 lamps

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Table C.16. TOC removal by various processes

Time	**Electrolysis**	**Photolysis**	**UV+H2O2**	**Fenton**	**EF**	**PF**	**PEF**
(min)	**(C/Co)**						
0	1	1	1	1	1	1	1
2	0.9898	0.9836	0.9805	0.8356	0.9569	0.9403	0.7205
5	0.9791	0.9672	0.9708	0.7260	0.8681	0.8656	0.6617
10	0.9457	0.9672	0.9417	0.6712	0.7811	0.7859	0.5882
20	0.9266	0.9344	0.9126	0.6438	0.7507	0.7411	0.5294
40	0.9052	0.9180	0.8835	0.5753	0.6072	0.6134	0.4558
60	0.8904	0.9180	0.8640	0.5468	0.5623	0.5716	0.3970
90	0.8630	0.9016	0.8252	0.5342	0.5204	0.5119	0.3529
120	0.8736	0.8852	0.8252	0.5342	0.497	0.4714	0.2941

Note: Aniline = 1 mM, pH = 3, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM,
Electric current = 1 A, UVA light= 12 lamps

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Table C.17. Effect of initial pH on aniline degradation by photoelectro-Fenton process

Time	pH2	pH2.5	pH3	pH3.5
(min)	(C/Co)			
0	1	1	1	1
2	0.7575	0.8099	0.5715	0.3098
5	0.6829	0.6985	0.0029	0.1033
10	0.5920	0.6568	0.0152	0.0268
20	0.3436	0.5072	0	0
40	0	0.0194	0	0
60	0	0	0	0
90	0	0	0	0
120	0	0	0	0

.

Note: Aniline = 1 mM, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, Electric current = 1 A, UVA light= 12 lamps

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Table C.18. Effect of initial ferrous ion concentration on aniline degradation by photoelectro-Fenton process

Time (min)	Fe^{2+} (mM)				
	0.1	0.25	0.5	1	2.5
	(C/Co)				
0	1	1	1	1	1
2	0.7820	0.6633	0.5715	0.2196	0.0392
5	0.6934	0.5518	0.0029	0.0409	0
10	0.6640	0.1891	0.0152	0	0
20	0.3059	0.0359	0	0	0
40	0.0577	0	0	0	0
60	0.0150	0	0	0	0
90	0	0	0	0	0
120	0	0	0	0	0

Note: Aniline = 1 mM, pH = 3, H_2O_2 = 20 mM, Electric current = 1 A, UVA light= 12 lamps

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Table C.19. Effect of initial hydrogen peroxide concentration on aniline degradation by photoelectro-Fenton process

Time (min)	**H_2O_2 (mM)**				
	1	**5**	**10**	**20**	**40**
	(C/Co)				
0	1	1	1	1	1
2	0.8203	0.7899	0.8096	0.5715	0.8096
5	0.7370	0.5745	0.5812	0.4392	0.5812
10	0.6129	0.2704	0.2503	0.0152	0.2503
20	0.4750	0.0881	0.0869	0	0.0869
40	0.3769	0.0252	0	0	0
60	0.3728	0.0186	0	0	0
90	0.3656	0.0135	0	0	0
120	0.3360	0.0097	0	0	0

Note: Aniline = 1 mM, pH = 3, Fe^{2+} = 0.5 mM, Electric current = 1 A, UVA light= 12 lamps

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Table C.20. Effect of applied electric current on aniline degradation by photoelectro-Fenton process

Time (min)	I (A)				
	0.5	1	2	4	8
	(C/Co)				
0	1	1	1	1	1
2	0.7527	0.8096	0.7315	0.6987	0.7953
5	0.5635	0.5812	0.5860	0.5863	0.6430
10	0.4109	0.2503	0.3161	0.3818	0.3880
20	0.1434	0.0869	0.0763	0.1111	0.1059
40	0.0160	0.0077	0	0	0.0063
60	0	0	0	0	0
90	0	0	0	0	0
120	0	0	0	0	0

Note: Aniline = 1 mM, pH = 3, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, UVA light= 12 lamps

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Table C.21. Effect of number of UVA lamps on aniline degradation by photoelectro-Fenton process

Time (min)	**Number of UVA lamps(lamps)**		
	4	**8**	**12**
		(C/Co)	
0	1	1	1
2	0.5715	0.4396	0.5025
5	0.0029	0.1316	0.1567
10	0.0152	0.0091	0.0123
20	0	0	0
40	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0

Note: Aniline = 1 mM, Fe^{2+} = 0.5 mM, H_2O_2 = 20 mM, pH 2, Electric current = 1 A

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APPENDIX D

Journal and Conference Publication Lists

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Journal publication lists

1. Nalinrut Masomboon, Ming-Chun Lu and Chavalit Ratanatamskul “Effect of hydrogen peroxide on the degradation of 2,6-dimethylaniline by Fenton processes” , Fresenius Environmental Bulletin (FEB) Vol.17; No. 8 (2008)

2. Nalinrut Masomboon, Chavalit Ratanatamskul and Ming-Chun Lu “Kinetics of 2,6- Dimethylaniline Degradation by Fenton and Electro-Fenton Processes” (submitted to Journal of Environmental Management).

3. Nalinrut Masomboon, Chavalit Ratanatamskul and Ming-Chun Lu “Oxidative Degradation of 2,6-dimethylaniline by electro-Fenton process” (submitted to Journal of Environmental, Science and Technology (ES&T)).

Conference paper publication lists

1. Nalinrut Masomboon, Chavalit Ratanatamskul, Ming-Chun Lu “Effect of H_2O_2 on 2,6-dimethylaniline degradation using electro-Fenton process”, 2007 International Conference on Environmental Quality Concern, Control and Conservation, July 2, 2007, Tainan, Taiwan ROC

2. Nalinrut Masomboon, Chavalit Ratanatamskul, Ming-Chun Lu “Chemical oxidation of 2,6-dimethylaniline by electro-Fenton process”, Asian-Pacific Regional Conference on Practical Environmental Technologies (APRC 2007).

3. Nalinrut Masomboon, Chavalit Ratanatamskul, Ming-Chun Lu “Effect of hydrogen peroxide on the degradation of 2,6-dimethylaniline by Fenton processes” 中華民國環境工程學會 2007 廢水處理技術研討會 (Taiwan National Conference 2007 Environmental Engineering).

4. Nalinrut Masomboon, Chavalit Ratanatamskul, Ming-Chun Lu “Degradation of 2,6-Dimethylaniline by Electro-Fenton Technology”, 2008 International Conference on Environmental Quality Concern, Control and Conservation, May 23, 2008, Tainan, Taiwan, ROC.

5. Sutthinee Narkwittaya, Nalinrut Masomboon, Chavalit Ratanatamskul, Ming-Chun Lu “Oxidation of 2,6-dimethylaniline by fluidized –bed Fenton process”, 2008 International Conference on Environmental Quality Concern, Control and Conservation, May 23, 2008, Tainan, Taiwan, ROC.

6. Nalinrut Masomboon, Chavalit Ratanatamskul, Ming-Chun Lu “2,6-Dimethylaniline Oxidation by Fenton and Electro-Fenton Processes – The Kinetic Study”, Asian-Pacific Regional Conference on Practical Environmental Technologies (APRC 2008).

7. Sutthinee Narkwittaya, Nalinrut Masomboon, Ming-Chun Lu, Chavalit Ratanatamskul”Kinetic of 2,6-dimethylaniline oxidation by fluidized-bed Fenton process”, Asian-Pacific Regional Conference on Practical Environmental Technologies (APRC 2008).

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BIOGRAPHY

Miss Nalinrut Masomboon was born on April 14, 1982 in Bangkok, Thailand. She received her Bachelor’s degree in Degree with honor in Department of Biology from Faculty of Science, Silpakorn University in 2004. She pursued her Degree of Doctor of Philosophy studies in Inter-Department of Environmental Science, Chulalongkorn University, Bangkok, Thailand on May 3, 2004. She finished her Degree of Doctor of Philosophy in October 2008.

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