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苯環類化合物在電解芬頓程序中之反應動力與反應槽設計 (2/2)

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Abstract

In this study, a novel electrochemical method for treating wastewater containing benzene compound, aniline, has been investigated. In the electrolytic cell, the organic compound is ionized or is oxidized by direct electrolysis on the anode. Meanwhile, this method applied H_2O_2 and ferrous ion to produce hydroxyl radicals for oxidizing the contaminants, in which ferrous ion is regenerated via the reduction of ferric ion on the cathode.

This is a two-year project. In the first year, attention were paid on the effect of oxidation intermediates on the inhibition of parent compound oxidation during the reaction based on the operation parameters, such as concentration of contaminants, pH, catalyst concentration, oxidant concentration, catalytic ability of ferrous and ferric ions and the effects of inorganic anions on the electro-Fenton process. The reaction kinetics of aniline by electro-Fenton processes has been proposed.

This is the first time in Taiwan to collect the data concerning the oxidation of benzene compounds by electro-Fenton processes. The results of this study can help our government in managing these kinds of benzene compounds, and also can be the basis of making regulations to control their remaining in environment.

Key word: electro-Fenton processes, benzene compound, kinetic model, half-life

中文摘要

為改良傳統 Fenton 法於實際應用上因添加亞鐵、過氧化氫與酸鹼等藥品，所造成的高操作成本及反應後續之氫氧化鐵污泥($Fe(OH)_3$)處理處置問題，本計畫欲

於傳統 Fenton 法中加入電流，使用過氧化氫與亞鐵反應產生的氫氧自由基與陽極，直接氧化污染物，並在陰極還原 Fenton 反應所產生的三價鐵離子，使系統中存在足量的亞鐵持續與過氧化氫作用，形成一循環反應，可有效地減少亞鐵的加藥和污泥產生量，解決高操作成本及高污泥產量等相關問題。

計畫中使用 electro-Fenton 氧化法處理含苯胺廢水，模擬其分解反應的動力模式與中間產物之抑制行為，以俾利於充分掌握分解過程中各方面的變化，藉以做為實廠設計與反應器操作的依據。本研究根據過去一系列 electro-Fenton 氧化苯環類化合物廢水的反應控制因子試驗結果進行研究，包括污染物的種類、濃度、酸鹼值、亞鐵離子濃度、過氧化氫濃度、三價鐵離子濃度及陰離子添加試驗等最適條件，建立分解反應動力模式，並藉由分解反應中間產物，探討苯環類化合物的分解反應機構與反應速率之快慢差異現象，經改變不同苯環類化合物初始濃度，建立一套分解半生期動力預測模式。

本計畫的執行與完成，預期在學術理論與實際應用方面，建立國內首批一系列苯環類化合物的 electro-Fenton 氧化反應模式與分解機制資料，輔之以其半生期模式的研究，提供其日後實廠設計應用之重要依據。

關鍵詞: 電解芬頓法、苯環類化合物、反應動力模式、半生期

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LIST OF TECHNICAL VOCABULARY AND ABBREVIATIONS

| | | |
|----------------|---|--------------------------------|
| M | = | molar |
| m | = | meter |
| °C | = | Celsius degree |
| η | = | efficiency |
| Pt | = | Platinum |
| Ti | = | Titanium |
| Pb | = | Lead |
| ml | = | milliliter |
| mg | = | milligram |
| mm | = | millimeter |
| cm | = | centimeter |
| g/l | = | gram per liter |
| $M^{-1}s^{-1}$ | = | per molar per second |
| A/m^2 | = | ampere per meter |
| $\mu g/l$ | = | microgram per liter |
| mM | = | millimolar |
| mg/l | = | milligram per liter |
| g/cm^3 | = | gram per cubic meter |
| wt/wt | = | weight per weight |
| mol/min | = | molar per minute |
| kW/h/kg | = | kilowatt per hour per kilogram |
| ppb | = | part per billion |
| ppm | = | part per million |
| TOC | = | total organic carbon |
| COD | = | chemical oxygen demand |
| BOD | = | biochemical oxygen demand |
| DSA | = | dimension stable anode |
| CPM | = | constant potential modes |
| CCM | = | constant current modes |
| DC | = | direct current |

CHAPTER 1 INTRODUCTION

1.1 Rational

Pollution of water and environment by toxic and nonbiodegradable organic material of industrial or agriculture origin brings about very serious health hazards for all living species of the nature. The pollutants of different chemical composition excludes the possibility of using an universal treatment method and led to the development of special treatment methods.

Recent progress in chemical water treatment has lead to the development of Advanced Oxidation Processes (AOPs). Common oxidants involved in AOPs are Fenton's reagent, Ozone, Ozone/H₂O₂, and UV/H₂O₂ of which the primary intermediate is the hydroxyl radical (\bullet OH). Fenton's reagent, a mixture of hydrogen peroxide and a ferrous, is an effective and simple oxidant of organic contaminants. It has been proven to be effective in treating various organic contaminants such as nitrophenol, dye, aromatic amines, polycyclic aromatic, ethers, and photographic wastewater (Korenaga, et al., 1998; Ewa et al., 1991). The Fenton reagent as an oxidant for wastewater treatment is attractive due to the facts that iron is a highly abundant and non toxic element and H₂O₂ is easy to handle and environmental benign making (Munter, 2001; Pignatello, 1992). Moreover this process is easy to operate with low cost (Lu, 2003) 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. There is a development of new advanced electrochemical oxidation process (AEOP) which the 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.

Aniline was chosen as a target compound. It is widely used as an intermediate in the synthesis of dyes. It is also used in the manufacture of pharmaceuticals, photographic developers, shoe polish, etc. Exposure to aniline is toxic because it produces methemoglobin. In humans, blood methemoglobin levels are often measured as an index of exposure to aniline. This research study intends to investigate the efficiency of aniline removal by Fenton, electro-Fenton, and combined Fenton&electro-Fenton processes at pH 2.0.

1.2 Objectives

The main objectives of this study are:

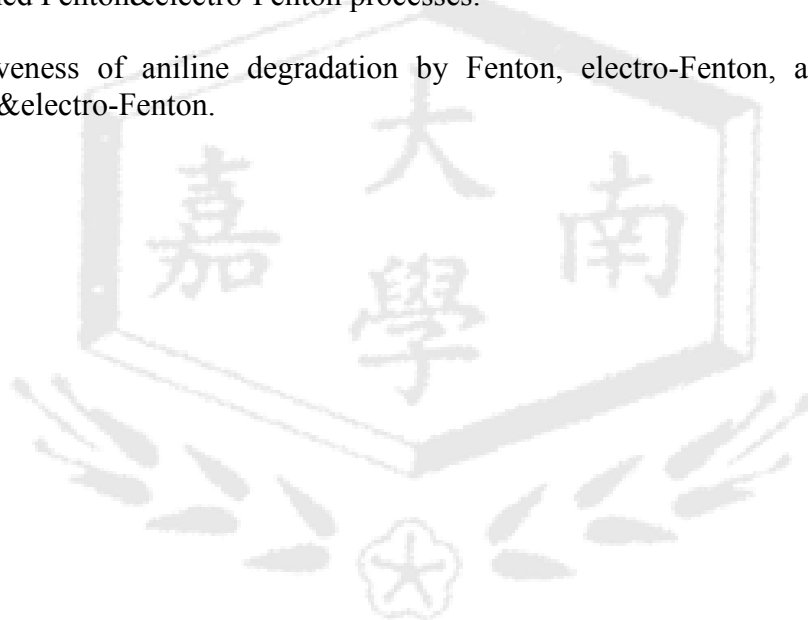
1. To compare the aniline removal efficiency of Fenton, electro-Fenton, and combined Fenton&electro-Fenton processes.
2. To determine the effects of H₂O₂ dosage, initial concentration of Fe²⁺, and initial concentration of aniline on the aniline removal efficiency of Fenton, electro-Fenton, and combined Fenton&electro-Fenton processes.

1.3 Scope of Investigation

1. Using lab scale reactor of 5 liters.
2. Using synthetic wastewater at pH 2.0.
3. For the electro-Fenton and combined Fenton&electro-Fenton, the anode is a special net made from Ti/Pt or dimensionally stable anodes (DSA) and the cathode is stainless steel and the current is 4 ampere constantly.

1.4 Expecting Results

1. Kinetics information of aniline degradation by Fenton, electro-Fenton, and combined Fenton&electro-Fenton processes.
2. Effectiveness of aniline degradation by Fenton, electro-Fenton, and combined Fenton&electro-Fenton.



CHAPTER 2 THEORIES AND LITERATURE REVIEW

2.1 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes have been defined as those which involve the generation of hydroxyl radicals ($\bullet\text{OH}$) in sufficient quantity to carry out the destruction of toxic pollutants (Glaze et al, 1987). The AOPs is the use of high energy oxidants that can generate $\bullet\text{OH}$. The $\bullet\text{OH}$ is a powerful, non-selective chemical oxidant, which acts very rapidly with most organic compounds. The reaction rate constants of $\bullet\text{OH}$ are shown in Table 2.1.

Table 2.1 Reaction rate constants (k , $\text{M}^{-1} \text{s}^{-1}$) of hydroxyl radical (Richard, 1998)

| Compound | Reaction rate constant of $\bullet\text{OH}$ |
|---------------------------------|--|
| Monocyclic Aromatic Hydrocarbon | |
| - Benzene | 7.8×10^9 |
| - Ethylbenzene | 7.5×10^9 |
| - Toluene | 3.0×10^9 |
| Chlorinated 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 |

The rate of destruction of a contaminant is proportional to the rate constant for the contaminant with $\bullet\text{OH}$. AOPs can often achieve oxidative destruction of refractory compounds to convention ozonation or H_2O_2 oxidation. AOPs is used to treat a variety of industrial wastes containing a wide range of toxic organic compounds (phenols, formaldehyde, BTEX, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals). The process may be applied to wastewater, sludge, or contaminated soils, with the effects being: organic pollutant destruction, toxicity reduction, biodegradability improvement, COD/BOD removal, and odor & color removal.

In general, the AOPs when applied in right placed, give a good opportunity to reduce the contaminants from several hundreds ppm to less than 5 ppb. That is why they are called the water treatment process of the 21st century (Parsons, 2004).

2.2 Advanced Oxidation Methods

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

2.2.1 Non-photochemical

The well known methods for generating $\bullet\text{OH}$ without using light energy. Two methods involve the reaction of ozone while one use ferrous ion as the catalyst. These methods are ozonation at elevated values of pH up to 8.5, combining ozone with hydrogen peroxide, ozone with catalyst, and the Fenton system.

2.2.2 Photochemical

Conventional ozone or hydrogen peroxide oxidations of organic compounds do not completely oxidize organic to CO_2 and H_2O . In some reaction, certain oxidation products still remain in the solution. Completing of oxidation reaction, as well as oxidative destruction, can be achieved by supplementing the reaction with UV radiation.

2.3 Fenton and Electro-Fenton Reactions.

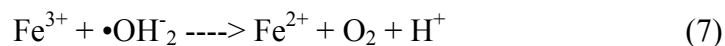
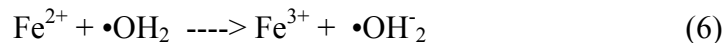
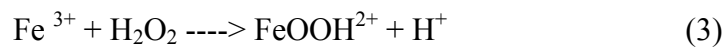
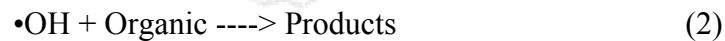
The Fenton process was introduced by Fenton, in 1884. The rate constant for the reaction of ferrous ion (Fe^{2+}) with hydrogen peroxide (H_2O_2) is high and Fe^{2+} is oxidized to ferric ion (Fe^{3+}) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. For the reason, it is believed that most waste destruction catalyzed by Fenton's reagent is simply a $\text{Fe(III)-H}_2\text{O}_2$ (Fenton-like reagent) system catalyzed destruction process. Reaction rates with Fenton's Reagent are generally limited by the rate of $\bullet\text{OH}$ generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. Typical $\text{Fe:H}_2\text{O}_2$ 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.

In recent years, another wastewater treatment method, using electrochemically generated hydroxyl radicals, has been investigated. Since electrochemical techniques

are more environmentally friendly than typical chemical methods used in polluted water treatment. One of them, 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 electrogenerated via two-electron reduction of O_2 at the cathode. When Fe^{2+} is added to the solution, pollutants can be mainly destroyed by $\bullet\text{OH}$ produced via Fenton reaction. And Fe^{3+} can be continuously transformed to Fe^{2+} via one-electron reduction at the cathode.

Electro-Fenton process can be generally divided into three groups. The first group (EF- H_2O_2 method) uses Fe^{2+} and electrogenerate 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 radical of $\bullet\text{OH}$, $\bullet\text{OH}_2$ and $\bullet\text{OH}_2^-$ are consumed and regenerated in the reaction system, which is influenced by H_2O_2 , Fe^{2+} and Fe^{3+} as shown in Figure 2.1 and equation (8) to (11). When electricity is employed in the process, Fe^{3+} can be reduced to Fe^{2+} more efficiently and rapidly, and then increases the reaction rate. In addition, low pH and anaerobic condition are employed to prevent the oxidation of ferrous ion by many investigators. However, over-low pH will decrease reaction rate. Therefore, solution pH should be kept at optimum value. Then, the high efficiency of hydrogen peroxide decompose to hydroxyl radical is maintained.



Iron salt acts as a catalyst for hydrogen peroxide decomposition, further reaction (4) and (5) 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. Because of the sensitivity of Fenton's Reagent to different wastewater, it is recommended that the reaction always be characterized through laboratory treatability tests before proceeding to plant scale.

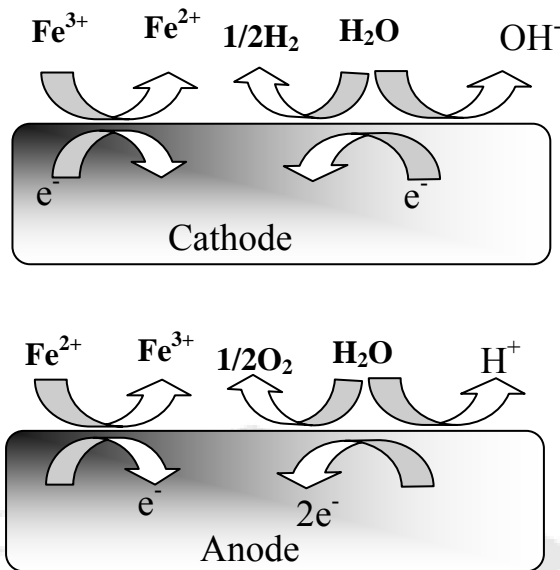
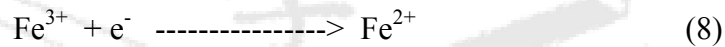
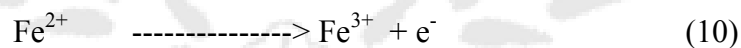


Figure 2.1 Electro-Fenton reaction

On Cathode Side



On Anode Side



2.4 Aniline

Aniline is a colorless to brown oily liquid which is aromatic. It is miscible with all conventional organic solvents, sparingly soluble in water. The formula of aniline is $\text{C}_6\text{H}_7\text{N}$ with the molecular structure as shown in figure 2.2. It is 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 sorb onto sediment and particulate matter. In soil most of it will be broken down by bacteria and other microorganisms. Aniline will partially sorb to the soil. Small amounts may evaporate into air or pass through the soil into groundwater. Aniline does not typically accumulate in the food chain.

2.4.1 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.

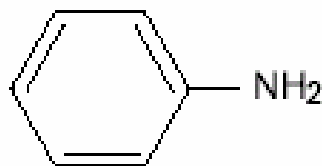


Figure 2.2 Structure of aniline

Aniline is also important in the manufacture of rubber-processing chemicals and [antioxidants](#). Its physical and chemical properties are shown in Table 2.

2.4.2 Toxicology of Aniline

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, resulting 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 symptoms 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 2.2 Physical and chemical properties of aniline (Schuchardt, 2000)

| Properties | |
|---|---------------------------------|
| Molecular formula | C ₆ H ₇ N |
| Molecular Weight; g/mole | 93.13 |
| pH value @ 36 g/l H ₂ O; 20 °C | 8.8 |
| Melting Point; °C | -6.2 |
| Boiling Point; °C | 184.4 |
| Density @ 20 °C; g/cm ³ | 1.022 |
| Flash Point; °C | 70 |
| Ignition Temperature; °C | 615 |
| Solubility in | |
| Water @ 20°C; g/L | 36 |
| Ethanol @ 20°C | free soluble |
| Organic Solvents | miscible |
| Thermal Decomposition 20°C | 190 |

2.4.3 First Aid Measures

Aniline is the chemical substance that can be toxic (that was said above) with organisms in the body if ingested or contact. The first aid measures are shown in Table 2.3

2.4.4 Storage and Handling

Aniline has an almost unlimited shelf life, original containers when properly stored in a protected storage area. Upon prolonged storage, aniline assumes a yellow to reddish brown coloration.

Table 2.3 First aid measures of aniline (Schuchardt, 2000)

| Contact by | How to first aid |
|------------|---|
| Inhalation | Taking to fresh air. 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. |
| Swallowing | Make victim drink plenty of water, induce vomiting. Immediately summon doctor. |

2.5 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is one of the most powerful oxidizers known, stronger than chlorine, chlorine dioxide, and potassium permanganate as shown in Table 2.4 and through catalysis, H_2O_2 can be converted into hydroxyl radicals ($\bullet OH$) with reactivity second only to fluorine.

Despite its power, H_2O_2 is a natural metabolite of many organisms, which decompose the H_2O_2 to oxygen and water. H_2O_2 is also formed by the action of sunlight on water, a natural purification system for our environment. Consequently, H_2O_2 has none of the problems of gaseous release or chemical residues that are associated with some other chemical oxidants. And since H_2O_2 is totally miscible in water, the issue of safety is one of concerns.

2.5.1 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, destroys residual chlorine and reduced sulfur compounds thiosulfates, sulfites, and sulfides, which form corrosive acids when condensed onto processing equipment and oxidized by air.
- BOD/COD removal, 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 catalysis, 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.

2.5.2 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.

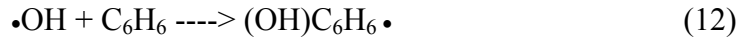
Advanced Oxidation Processes represent the newest development in H_2O_2 technology. Typically, this means combining H_2O_2 with ozone or ultraviolet light. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely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

Table 2.4 Value of oxidation power (Carey, 1992)

| Reactive Species | Oxidation(Oxidant Potential Voltage) | Relative Oxidation Power ($Cl_2=1.0$) |
|------------------------|--------------------------------------|---|
| Fluorine | 3.06 | 2.25 |
| Hydroxy radical | 2.80 | 2.05 |
| Ozone | 2.07 | 1.52 |
| Hydrogen peroxide | 1.77 | 1.30 |
| Potassium permanganate | 1.67 | 1.23 |
| Chlorine dioxide | 1.50 | 1.10 |
| Chlorine | 1.36 | 1.0 |

Chemical reactions of the hydroxyl radical in water. There are four typical types of reaction occurring when $\bullet OH$ presents in water.

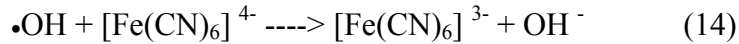
- Addition, the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product such as cyclohexadienyl radical as shown below.



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



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



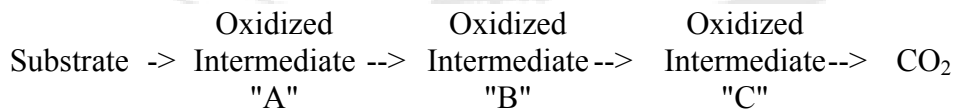
- Radical Interaction, the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product as shown below.



2.6 Effect of Substances and Conditions in Fenton Process

2.6.1 Effect of H₂O₂

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 reactions will occur



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 H₂O₂ 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 H₂O₂ results in a rapid decrease in wastewater toxicity.

2.6.2 Effect of Iron Concentration

In the absence of iron, there is no evidence of hydroxyl radical formation when, for example, H₂O₂ 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 (an optimal dose range for iron catalyst) is a characteristic of Fenton's Reagent, although the definition of the range varies between wastewaters.

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 H₂O₂ dose. Typical ranges are 1 part Fe per 5-25 parts H₂O₂ (wt/wt).

2.6.3 Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether Fe²⁺ or Fe³⁺ salts are used to catalyze the reaction, the catalytic cycle begins quickly if H₂O₂ and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L H₂O₂), Bishop, 1968 suggests ferrous iron may be preferred. 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 floc, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

2.6.4 Effect of pH

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 H₂O₂ 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 side is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates.

The first inflection is caused by the addition of FeSO₄ catalyst which typically contains residual H₂SO₄. A second, more pronounced drop in pH occurs as the H₂O₂ 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 H₂O₂ 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.

2.6.5 Effect of Reaction Time

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 H₂O₂ will interfere with many wastewater analyses. Residual H₂O₂ may be removed by raising

the pH to e.g., pH 7-10, or by neutralizing with bisulfite solution. Often, observing 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.

2.7 Literature Reviews

Tang and Tassos (1996) determined the oxidation kinetics and mechanisms of trihalomethanes (THMs) by Fenton's reagent. All the experiments were carried out in air-tight and well-mixed batch reactors in which no headspace was allowed in order to minimize volatilization of any THM during reaction. The optimum dosages of H_2O_2 and Fe^{2+} in the oxidation of bromoform was 3.7 and 1.9 mM for all the initial concentration at pH 3.5. The maximum bromoform degradations of 85, 78 and 65% at 3 minutes were achieved for bromoform concentrations of 295, 98.3 and 49.2 $\mu\text{g}/\text{l}$, respectively. The pseudo-first-order oxidation constants of THMs increase with increasing number of bromine atoms present in a THM molecule, with bromoform being oxidized the fastest and bromodichloromethane being oxidized the slowest.

Brillas, et al. (1998) studied on aniline mineralization by AOPs through anodic oxidation, photocatalysis, electro-Fenton, and photoelectro-Fenton processes. The aniline degradation in acidic medium of $\text{pH} \approx 3$ under photocatalytic and electrochemical condition has been investigated. The electrochemical experiments performed in the presence of both species (electro-Fenton conditions) led to a fast aniline mineralization, which is notably increased by UVA irradiation (photoelectron-Fenton process). A general pathway for aniline mineralization is proposed in which products are formed via hydroxyl radical degradation.

Chou, et al. (1999) studied on the treatment of high strength hexamine contaminating wastewater by electro-Fenton method. The performance of Fe^{2+} generation in the electrolytic system was first evaluated, including the factors of the cathode material, initial pH, initial ferric concentration, and current density. When initial pH exceeded 2.5, the current efficiency dramatically decreased, which was due the formation of $\text{Fe}(\text{OH})_3$. Between 3,000 and 10,000 mg/l of Fe^{2+} , the initial current efficiency of Fe^{2+} generation was almost constant (85-87%), which dropped sharply to 39% at 1,000 mg/l . The COD removal efficiency attained above 94% after 5 hours of reaction. The changes in hexamine and its oxidation intermediates (methanol, formaldehyde, formate, ammonium and nitrate) during the reaction were also investigated.

Lu, et al. (1999) investigated on the decomposition of dichlorvos insecticide by Fenton process. Results showed that dichlorvos decomposed through a two stage reaction. The first stage is a $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ reaction in which dichlorvos decomposed swiftly. In the second stage, dichlorvos decomposed somewhat less rapidly than the first stage. The detection of ferrous ions also supports the theory of the two stage reaction for the dichlorvos oxidation with Fenton's reagent. The dissolved oxygen of the solution decreased rapidly in the first stage reaction, but it slowly increased in the second stage with a zero-order kinetics. The Fenton system decomposed dichlorvos most rapidly when the initial pH in solution between 3-4. In addition, increasing either the concentration of hydrogen peroxide or ferrous ion can enhance the decomposition of dichlorvos.

Oturan, et al. (2000) used electro-Fenton method to degrade of *p*-Nitrophenol in aqueous medium. This method is based on electrocatalytical generation of Fenton's

reagent to produce hydroxyl radical. The major intermediary degradation products were hydroquinone, benzoquinone, 4-nitrocatechol, 1,2,4-trihydroxybenzene and 3,4,5-trihydroxynitrobenzene. The rate constants of the hydroxylation reaction were also determined. The mineralization of the initial pollutant and the intermediates formed during electro-Fenton treatment was studied using total organic carbon (TOC) analyses. 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, i.e., from aromatics to aliphatics which are more resistant to mineralization by ring disrupting reactions. Under optimum condition, the mineralization process reached 95% efficiency.

Lin, et al. (2000) treated old-aged landfill leachate by combined chemical and biological methods. The electro-Fenton method assisted by chemical coagulation was employed and found to be highly efficient in removing a large amount of refractory organic and inorganic compounds in the leachate. The electro-Fenton oxidation employed was able to greatly enhance the COD removal of the leachate effluent from chemical coagulation. At optimum pH 4, the oxidation process rendered the leachate effluent totally colorless (i.e. 100% color removal). An optimum H_2O_2 dosage of 750 mg/L yield a very good COD, color, $\text{NH}_3\text{-N}$ and phosphorus removal in less than 30 minutes. Final treatment of the leachate effluent by sequencing batch reactor (SBR), was able to achieve the quality up to the standard for direct discharge or for reuse as non-potable water.

Brillas, et al. (2001) studied about 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 a Ti/Pt or DSA anode yields an insoluble violet polymer, while the soluble total organic carbon (TOC) is gradually remove, reaching 61% degradation after 2 hours at 20 Ampere. In this treatment, aniline was preferentially oxidized by hydroxyl radicals formed in solution from reaction of Fe^{2+} with H_2O_2 . The peroxi-coagulation process with an Fe anode has higher degradation power, allowing to remove more than 95% of pollutants at 20 ampere.

Huang, et al. (2001) compare a novel electro-Fenton method with 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 ($\text{Pb} = 7,500 \text{ mg/l}$) and high organic concentration ($\text{COD} = 11,000 \text{ mg/l}$). 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. Furthermore, 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 an industrial wastewater mainly containing naphthalene- and anthraquinone-sulphonic acids by electrogenerated Fenton's reagent. The hydrogen peroxide was produced in situ by electrochemical reduction of oxygen on 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 saturated calomel electrode (SCE). The maximum COD removal of 87% and color fading of 89% were obtained with a Fe^{2+} of concentration of 3 mM in electro-Fenton treatment process. The COD removal kinetics followed a pseudo-first-order reaction. Chemical or electrochemical surface pre-treatment had no significant impact on organics oxidation.

Arapoglou, et al. (2002) detoxified commercial methyl-parathion (MeP) by using an electrochemical method that employed a Ti/Pt anode and a stainless steel 304 as a cathode. Sodium chloride was added as an electrolyte and the mixture was passed through an electrolytic cell for 2 hours. 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.

Chun, et al. (2002) were designed a three-phase three-dimensional electrode reactor (TTER) for wastewater treatment. The intrinsic performances of TTER were characterized by potential distribution and SEM micrograph. The experimental results showed that it could effectively degrade aniline. Its degradation efficiency mainly depended on applied voltage, Fe^{2+} concentration, pH, and electrolysis time. It was found that the degradation of aniline in the presence of Fe^{2+} was faster than in the absence of Fe^{2+} .

Qiang, et al. (2002) established the optimal condition for the minimization of iron sludge produced in Fenton oxidation processes by electro-regenerating Fe^{2+} with constant potential (CPM) or constant current modes (CCM). Results indicate 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 Fe^{3+} hydrolysis curve. Increasing cathode surface area and solution temperature notably increases Fe^{2+} regeneration rate. The maximum current efficiency (η) that is obtained under the optimal condition is 96-98%. The unit energy consumption is 2.0-3.0 kW.h per kg Fe^{2+} regenerated.

Qiang, et al. (2002) used electro-Fenton oxidation process to remove selected hazardous organic compounds from aqueous solution. Hydrogen peroxide is electro-generated by the reduction of dissolved oxygen in acidic solution. The optimum conditions are 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+} is electro-regenerated from ferric salt or Fenton's iron sludge. The Fenton oxidation process can effectively degrade all selected polycyclic aromatic hydrocarbons (PAHs), namely, naphthalene, fluorene and anthracene. Fe^{2+} can also be effectively regenerated from Fenton's iron sludge. The dosing mode of H_2O_2 and Fe^{2+} significantly affects the reaction efficiency. Electro-Fenton oxidation process is more efficient than conventional Fenton oxidation process to the continuous regeneration of Fe^{2+} at the cathode.

Ventura, et al. (2002) investigated on electrochemical generation of the Fenton's reagent. Atrazine was chosen as a model organic compound since its reaction with $\bullet\text{OH}$ has been extensively studied. With regards to the atrazine degradation by the classical Fenton's reaction under similar condition, it appears that the electro-Fenton system seems to be more efficient. Hence, despite a faster degradation at the initial stage of the experiment in case of the Fenton's system, the degradation after 15 min appeared to be quite limited. As a consequence, in the second stage of the experiment, the electro-

Fenton system was more efficient and enable more thorough atrazine degradation. The results show that the Fenton's reagent can be electrochemically produced in aqueous solution, thereby leading to an efficient and continuous $\bullet\text{OH}$ production, with limited competitive reaction. This simple system produces ferrous iron in situ by the reduction of ferric iron, with the simultaneous reduction of oxygen into hydrogen peroxide.

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 and aniline as a yielded the silica. When the aging time 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.

Boye, et al. (2003) compared anodic oxidation, electro-Fenton and photoelectron-Fenton treatment of 2,4,5-trichlorophenoxyacetic acid. The methods are carried out in an undivided cell with a Pt anode and O_2 -diffusion cathode within the pH 2.0-4.0, operating at low current and with 1 mM Fe^{2+} . Photoelectro-Fenton treatment yields fast and complete depollution of solution with 2,4,5-T concentration up to about saturation. An electro-Fenton reaction leads to 60-65% of mineralization. The anodic oxidation is very poorly mineralized the pollutant. The herbicide decay always follows a pseudo-first-order. Several intermediates can detected including 2,4,5-trichlorophenol, 2,5-dichlorohydroquinone, 4,6-dichlororesorcinol, and carboxylic acid group.

Brillas, et al. (2003) studied on the mineralization of acid aqueous solution with herbicide 3,6-dichloro-2-methoxybenzoic acid (dicamba) by electro-Fenton and photoelectro-Fenton using a Pt anode and an O_2 -diffusion cathode. While electro-Fenton yield 60-70% mineralization, photoelectro-Fenton allows a fast and complete depollution of herbicide solution. In both treatment, the initial chlorine is rapidly released to the medium as 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+} -oxalato complexes in the solution.

Brillas, et al. (2003) determined electrochemical degradation of chlorophenoxy and chlorobenzoic herbicide in acidic aqueous medium by the peroxi-coagulation method. This electrochemical method yields a very effective depollution of all compounds in acidic aqueous medium of pH 3.0. Target compounds are oxidized substantially by hydroxyl radicals produced from Fenton's reagent between Fe^{2+} and H_2O_2 generated by the corresponding Fe anode and O_2 -diffusion cathode. Their products can then be removed by mineralization or coagulation with the $\text{Fe}(\text{OH})_3$ precipitate formed. Both degradation paths complete at low currents. The efficiency of this method decreases with increasing electrolysis time and current. The decay of all herbicides follows a pseudo-first-order reaction.

CHAPTER 3 EXPERIMENTS AND METHODS

3.1 Chemical Substances

Aniline, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 (30%), HClO_4 , NaOH , and all other chemical substances were reagent grade. Aqueous solution used for oxidation reaction was prepared from demineralized water.

3.2 Analysis Methods

The aniline was analyzed by HP 19095J-321 gas chromatography with 0.53 mm in inside diameter, and 15 m long. Hydrogen peroxide was analyzed by an iodometric titration with $\text{Na}_2\text{S}_2\text{O}_3$ solution as shown at Appendix A (Kolthof et al., 1969). TOC was detected by Model 700 which is the classic persulfate oxidation method for samples containing 4 ppb to 10,000 ppm of organic carbon. COD was measured by closed reflex titrimetric method. The solution pH was measured by Orion model 210 A meter.

3.3 Experimental Procedures

3.3.1 Reactor

The reactor was shown in Figure 3.1 and Appendix B, it was made of acrylic (15cmx21cmx20cm). The electro-Fenton anode is a special net made from Ti/Pt or DSA and the cathode was stainless steel as shown in Figure 3.2 and 3.3. The anode and cathode were connected with DC power supply. Figure 3.4 shows the DC power supply, which was operated at constant current (I) of 4 ampere. Mixers were installed in the reactor to provide agitation.

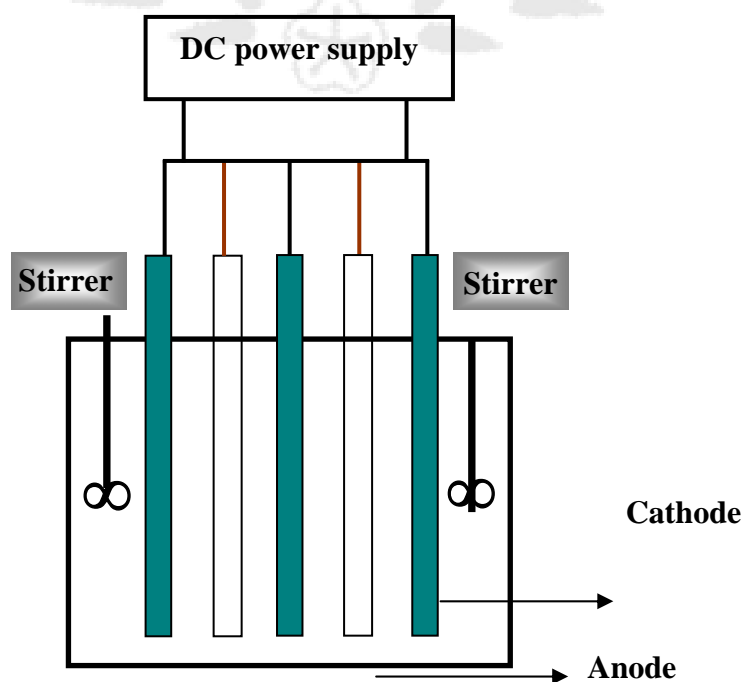


Figure 3.1 Reactor configuration.

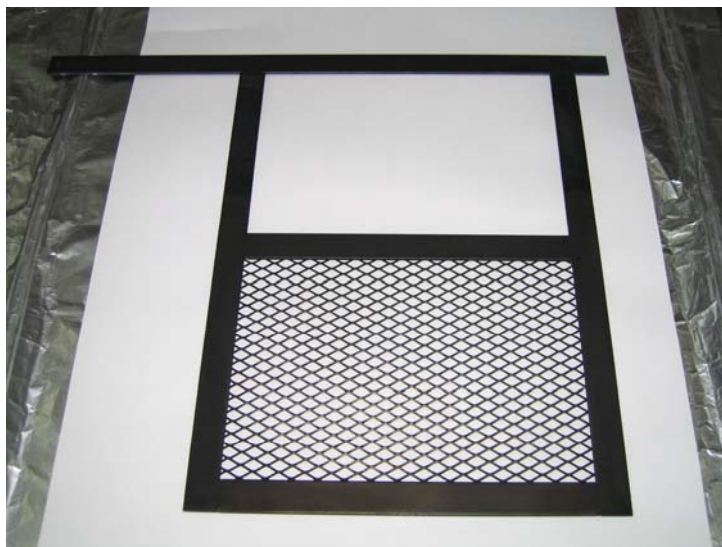


Figure 3.2 Anode sheet



Figure 3.3 Cathode sheet



Figure 3.4 DC power supply

3.3.2 Procedures

3.3.2.1 Fenton Experiment

As shown in Figure 3.2, the aniline solution was adjusted to pH 2.0 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 hydrogen peroxide was supplied into the solution with six-step addition. The sample of 1 ml was taken every 20 minutes and was immediately injected into a tube containing 9 ml of NaOH to stop the reaction. The experiment was terminated in 2 hours. Samples were analyzed for COD, TOC, and aniline concentration.

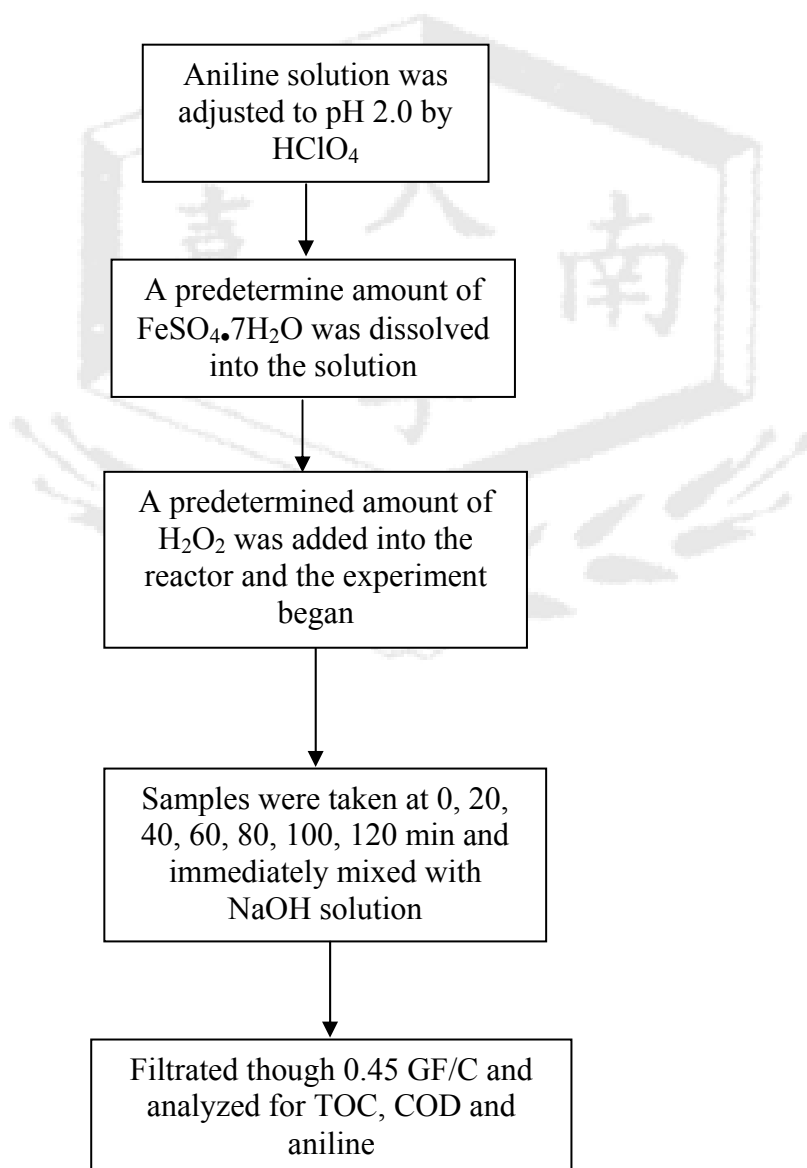


Figure 3.5 Flow chart for Fenton experiment

3.3.2.2 Electro-Fenton Experiment

In this experiment, an electrical supply unit which consisted of a stainless steel cathode, a Ti/Pt anode, and a regulator DC power supply was installed additionally in the reactor. Most procedures were similar to those of typical Fenton reaction, however, in this scenario, the electrical current at 4 ampere was delivered through out the experimental period as shown in Figure 3.3.

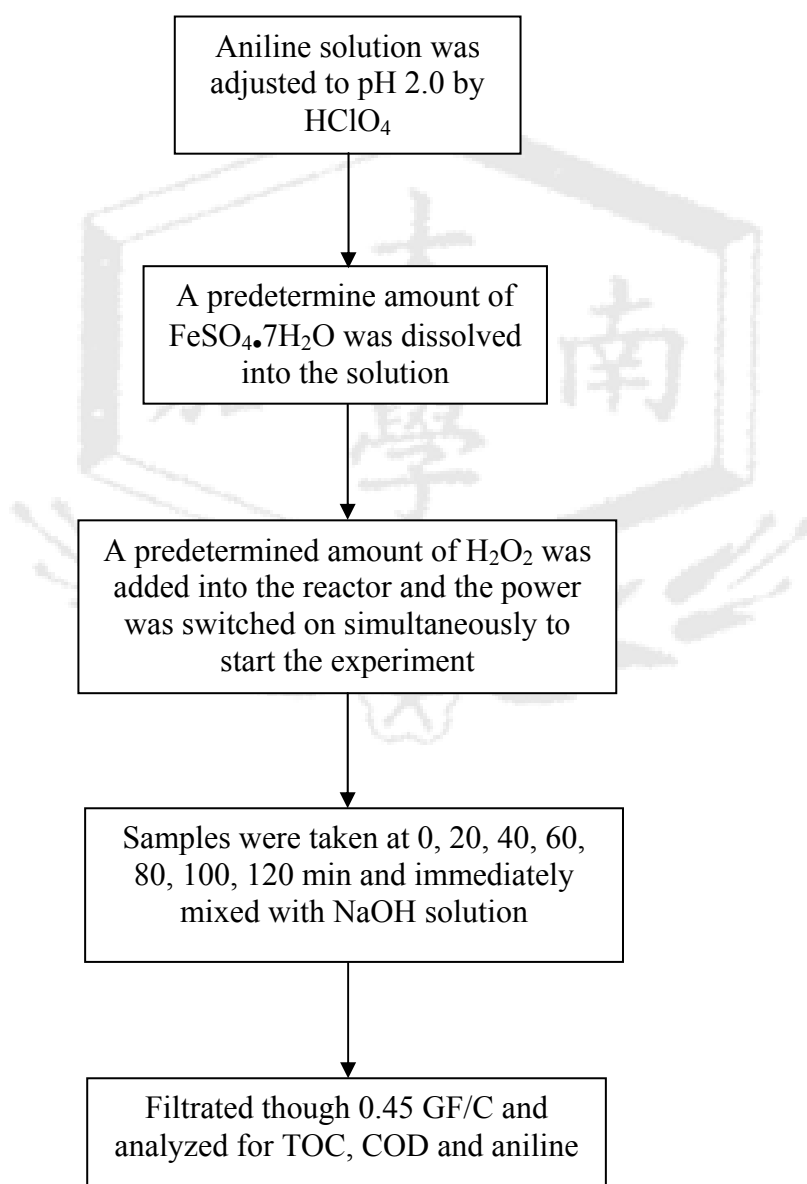


Figure 3.6 Flow chart for electro-Fenton experiment

3.3.2.3 Combined Fenton&electro-Fenton Experiment

The experimental scenario was divided into 2 sequential parts. The typical Fenton reaction was initiated at the beginning stage and then followed by the electro-Fenton reaction for the second stage. System operation and configuration are as mentioned previously in the cases of Fenton and electro-Fenton experiments as shown in Figure 3.4

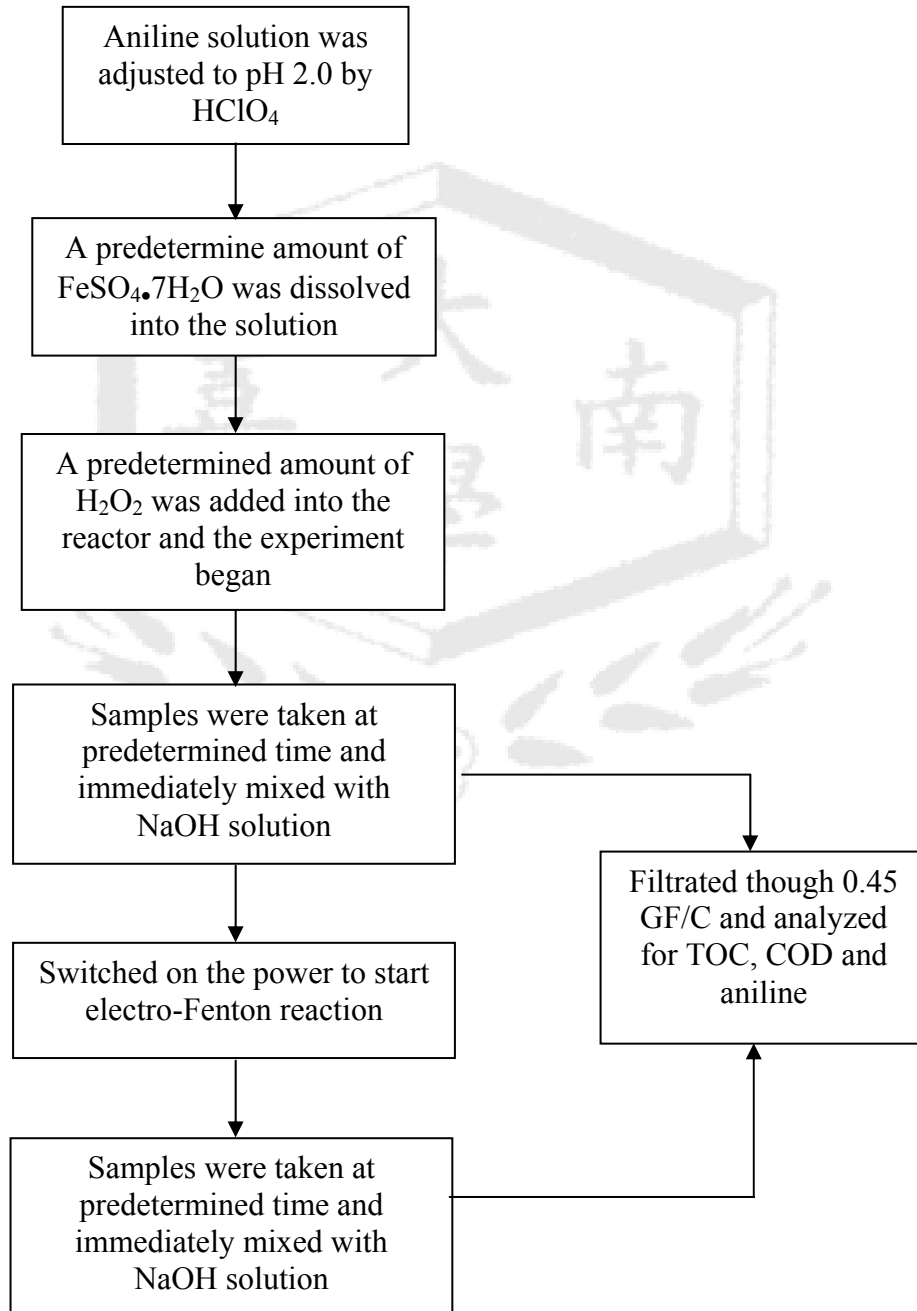


Figure 3.7 Flow chart for combined Fenton&electro-Fenton experiment

3.4 Experimental Scenarios

Before starting the experiments, several pre-tests have been performed to determine the appropriate ranges for each chemical as well as the optimum conditions such as pH, current density, 6-step of H₂O₂ addition, etc.

Scenario A

Determination of effects of Fe²⁺, H₂O₂, and current as shown in Table 3.1

Table 3.1 Detail for scenario A

| Aniline (M) | pH | Control parameters |
|-------------|-----|-------------------------------|
| 0.01 | 2.0 | Fe ²⁺ |
| | | H ₂ O ₂ |
| | | Current density |

Scenario B

Determination of effect of Fe²⁺ on the degradation of aniline by Fenton and electro-Fenton processes with the conditions as shown in Table 3.2

Table 3.2 Detail for scenario B

| Aniline (M) | pH | H ₂ O ₂ (M) | Fe ²⁺ (M) |
|-------------|-----|-----------------------------------|----------------------|
| 0.01 | 2.0 | 0.3 | 0.0056 |
| | | | 0.017 |
| | | | 0.028 |

Scenario C

Determination of effect of H₂O₂ concentration on the degradation of aniline by Fenton and electro-Fenton with the conditions as shown in Table 3.3

Table 3.3 Detail for scenario C

| Aniline (M) | pH | Fe ²⁺ (M) | H ₂ O ₂ (M) |
|-------------|-----|----------------------|-----------------------------------|
| 0.01 | 2.0 | 0.017 | 0.2 |
| | | | 0.3 |
| | | | 0.4 |

Scenario D

Determination of effect of initial aniline concentration on the degradation of aniline by Fenton and electro-Fenton processes with the condition as shown in Table 3.4

Table 3.4 Detail for scenario D

| pH | H ₂ O ₂ (M) | Fe ²⁺ (M) | Aniline (M) |
|-----|-----------------------------------|----------------------|-------------|
| 2.0 | 0.3 | 0.017 | 0.005 |
| | | | 0.01 |
| | | | 0.05 |

Scenario E

Determination of effect of current discharge time on the degradation of aniline by combined Fenton&electro-Fenton processes with the conditions as shown in Table 3.6

Table 3.5 Detail for scenario E

| Aniline (M) | pH | H ₂ O ₂ (M) | Fe ²⁺ (M) | Fenton reaction time (min) | Current discharge time (min) |
|-------------|-----|-----------------------------------|----------------------|----------------------------|------------------------------|
| 0.01 | 2.0 | 0.3 | 0.017 | 40 | 80 |
| | | | | 60 | 60 |
| | | | | 80 | 40 |

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Control Experiments

The results of control study are summarized in Figures 4.1 and 4.2. It was found that aniline and TOC were not removed significantly during the experiments when the Fe^{2+} or H_2O_2 or electricity current was applied individually as an oxidant. Therefore, all the aniline degradation observed in next sections was solely due to hydroxyl radical oxidation.

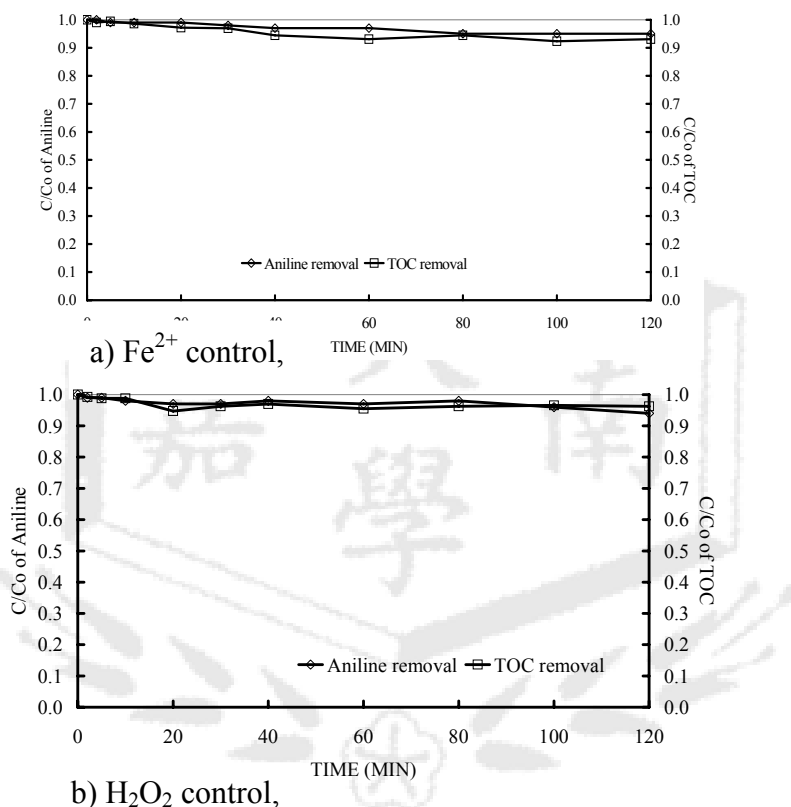


Figure 4.1 Aniline degradation and TOC removal in control experiment for 0.01 M of aniline, at pH 2.0, a) 0.017 M of Fe^{2+} b) 0.3 M of H_2O_2

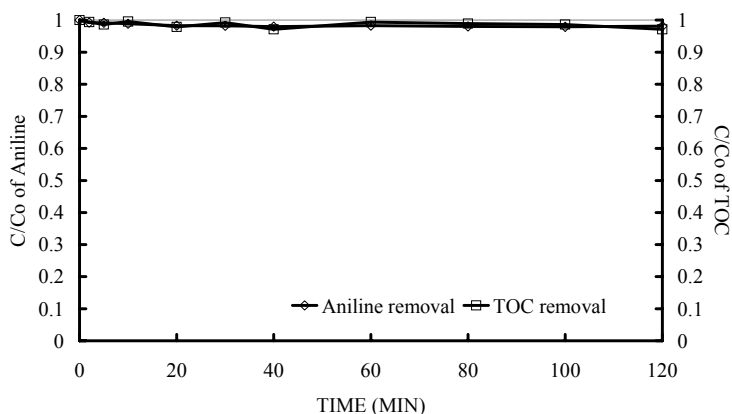


Figure 4.2 Aniline degradation and TOC removal in current constant of 4 ampere in control experiment for 0.01 M of aniline, pH 2.0

4.2 Comparison of Fenton and Electro-Fenton Processes

Figure 4.3 shows the comparative aniline degradation between Fenton and electro-Fenton processes, which each experiment was done duplicated. In Fenton process, it can be seen that only 40% of aniline was degraded within 120 minutes under the study conditions and the degradation rate was already tailing-off. The retardation in the reaction rate is expected to be due to ferrous depletion since H_2O_2 was still available in the solution (greater than 200 mg/l at all time) as shown in Figure 4.4. The result is opposed to the electro-Fenton experiment where the H_2O_2 was almost consumed within 20 minutes after addition.

In contrast, electro-Fenton process could completely degrade aniline in just 60 minutes due to the ability to regenerate Fe^{2+} from Fe^{3+} as shown in equation (8). Due to an ambiguous reaction mechanism between aniline and hydroxyl radicals.

The initial rate technique is used to explain kinetic behavior of the system. It was found that, under the same condition, electro-Fenton could accelerate the initial degradation of aniline over Fenton process more than four times from 7.12×10^{-5} to 3.01×10^{-4} M/min (The details of initial reate calculations are provided in Appendix D)

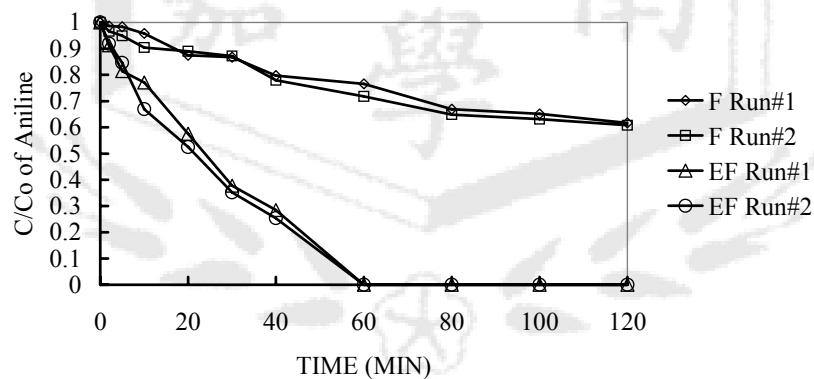


Figure 4.3 Aniline degradation by Fenton and electro-Fenton processes for 0.01 M aniline, pH 2.0, 0.017 M of Fe^{2+} and 0.3 M of total H_2O_2

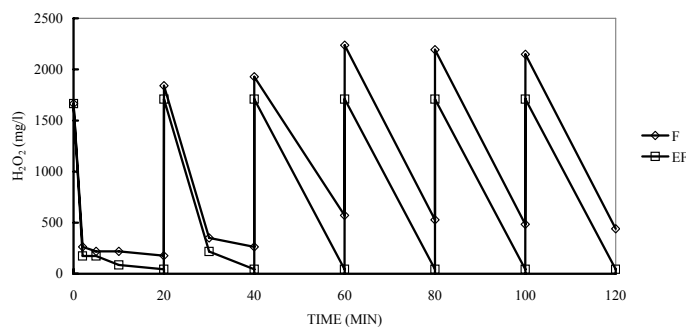


Figure 4.4 H_2O_2 concentration during the experiment.

The results from TOC analysis as shown in Figure 4.5 reveal that some organic products from aniline degradation can be further oxidized or mineralized to carbon dioxide; i.e., approximately 25 and 50% reduction for Fenton and electro-Fenton processes, respectively.

However, it is important to note that the removal efficiency of aniline and TOC were quite different. In fact, in the case of electro-Fenton, the TOC reduction still occurred after aniline disappearance. This indicates that the certain products from aniline destruction were less vulnerable to hydroxyl radical than aniline; therefore were attacked after the completed depletion of aniline. Nonetheless, since the TOC reduction occurred simultaneously with the aniline degradation, it implies that some other intermediates were as susceptible to hydroxyl radical as the aniline. As a result, they competed with each other for hydroxyl radical.

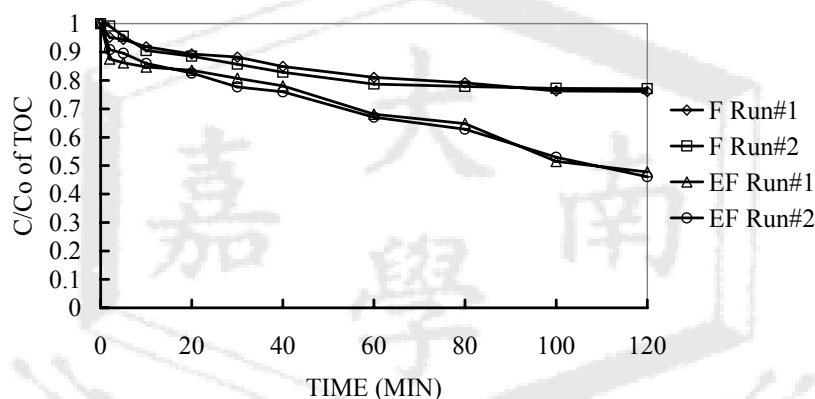


Figure 4.5 TOC removal by Fenton and electro-Fenton processes for 0.01 M aniline, pH 2.0, 0.017 M of Fe^{2+} and 0.3 M of total H_2O_2 , The initial TOC is 720 mg/l

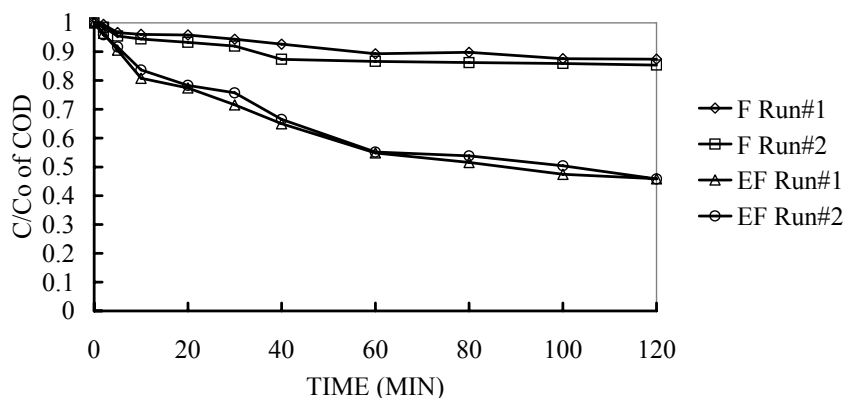


Figure 4.6 COD removal by Fenton and electro-Fenton processes for 0.01 M aniline, pH 2.0, 0.017 M of Fe^{2+} and 0.3 M of total H_2O_2 , The initial COD is 2,240 mg/l

Figure 4.6 shows the time-related COD reduction of which the trend is quite similar to those of TOC. Nonetheless, TOC and COD reduction efficiencies during the experimental period were not similar which indicates that the mechanism for COD reduction was not only complete mineralization to carbon dioxide. In fact, the reduction in COD can also result from the addition of hydroxyl radical onto the carbon atoms of organic molecule, addition mechanism, which will increase the oxygen to carbon ratio.

Brillas et al. (1998) proposed reaction pathways for aniline degradation by hydroxyl radicals to form intermediates with increasing oxygen to carbon ratio, i.e., from aniline (0 O / 6 C) to phenol (1 O / 6 C), hydroquinone, benzoquinone, and nitrobenzene (2 O / 6 C), 1,2,4 benzenetriol (3 O / 6 C), and maleic and fumaric acids (12 O / 6 C).

4.3 Effect of Ferrous ion (Fe^{2+}) Concentration

For traditional Fenton reaction, an increase in ferrous ion concentration from 0.0056 to 0.017 and 0.028 M could obviously increase the removal efficiencies of aniline, TOC, and COD as illustrated in Figures 4.7, 4.8, and 4.9, respectively.

The results strongly support the explanation for reaction retardation of Fenton reaction in previous section. Aniline removal of 90% was achieved within 120 minutes at ferrous ion dosage of 0.028 M. However, when compared to those of electro-Fenton as shown in Figure 4.10, completed oxidation of aniline occurred only at 0.017 M of Fe^{2+} at 60 minutes. 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 typical Fenton process.

Effect of Fe^{2+} on the removal efficacy of electro-Fenton process was more evident than those of Fenton process as shown in Figures 4.10 to 4.12. However, unlike the TOC and COD, the impact on aniline degradation became diminutive as the Fe^{2+} concentration increased from 0.017 to 0.028 M; i.e., completion of aniline degradation occurred at 60 minutes for both concentrations. This may be due to the susceptibility of aniline by hydroxyl radical oxidation under excess Fe^{2+} .

However, it is important to point that the improvement in aniline oxidation is not linearized with increasing Fe^{2+} ; i.e., efficiency increased from 15% to 40 and 85% in the case of Fenton and from 55% to 100% for electro-Fenton processes as the Fe^{2+} concentration increased from 0.0056 M to 0.017 and 0.028 M respectively. In fact, with steady H_2O_2 concentration, the removal of aniline is expected to be accelerated as the concentration of Fe^{2+} increased until a point is reached where further addition of Fe^{2+} became insufficient (Brillas et al., 1998)

The similarity of the removal patterns of aniline, TOC, and COD of Fenton process at 0.028 M of Fe^{2+} with those of electro-Fenton process in Figures 4.11 and 4.12 implies that both processes proceeded through the same pathway by the powerful hydroxyl radical formed in the solution from reaction of Fenton reagents as shown in equation (1) and (2). As seen in both Figures 4.11 and 4.12 that the removal in terms of TOC and COD were improved as the Fe^{2+} dose increased, this implies that the electrical regeneration of Fe^{2+} might not be fast enough for by-product oxidation, therefore

required addition Fe^{2+} . Increasing either Ti/Pt or DSA anode surface area or current intensity could sufficiently rectify ferrous regeneration further. It can be concluded that electro-Fenton process at its optimum conditions should be able to completely removal aniline at a much lower Fe^{2+} concentration than typical Fenton process.

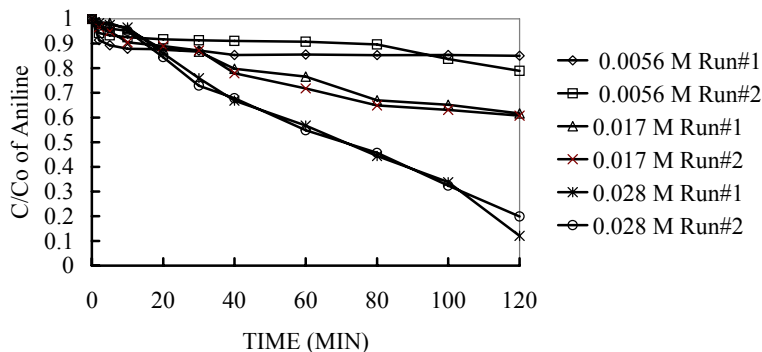


Figure 4.7 Effect of Fe^{2+} concentration on aniline degradation by Fenton process for 0.0056 M, 0.017 M, and 0.028 M of Fe^{2+} , 0.01 M aniline, pH 2.0, and 0.3 M of total H_2O_2 .

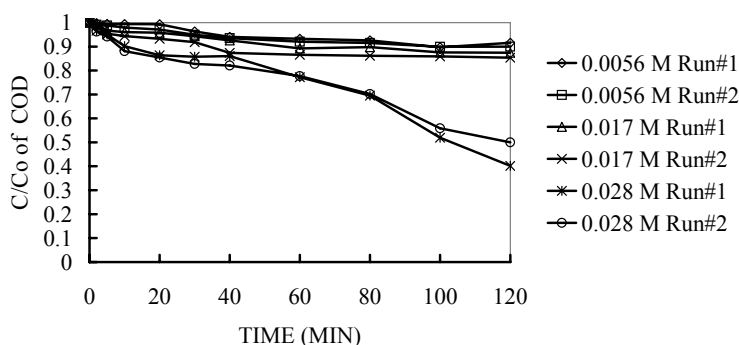


Figure 4.8 Effect of Fe^{2+} concentration on TOC removal (720 mg/l of initial TOC) by Fenton process for 0.0056 M, 0.017 M, and 0.028 M of Fe^{2+} , 0.01 M aniline, pH 2.0, and 0.3 M of total H_2O_2 .

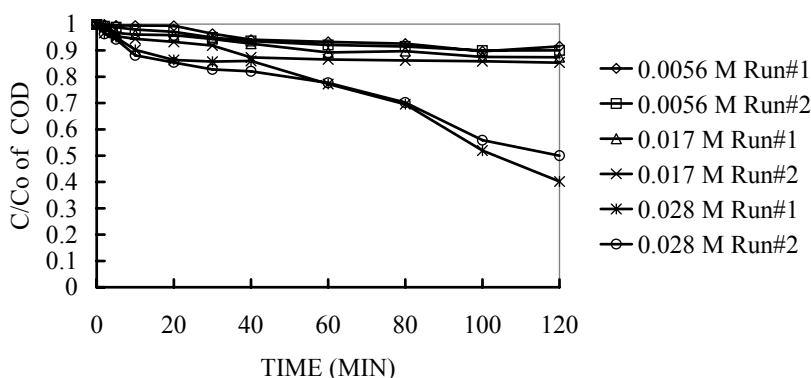


Figure 4.9 Effect of Fe^{2+} concentration on COD removal (2,240mg/l of initial COD) by Fenton process for 0.0056 M, 0.017 M, and 0.028 M of Fe^{2+} , 0.01 M aniline, pH 2.0, and 0.3 M of total H_2O_2 .

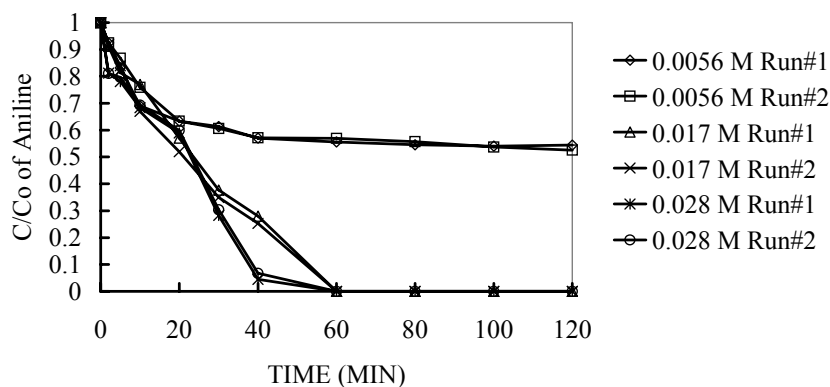


Figure 4.10 Effect of Fe^{2+} concentration on aniline degradation by electro-Fenton process for 0.0056 M, 0.017 M, and 0.028 M of Fe^{2+} , 0.01 M aniline, pH 2.0, and 0.3 M of total H_2O_2 .

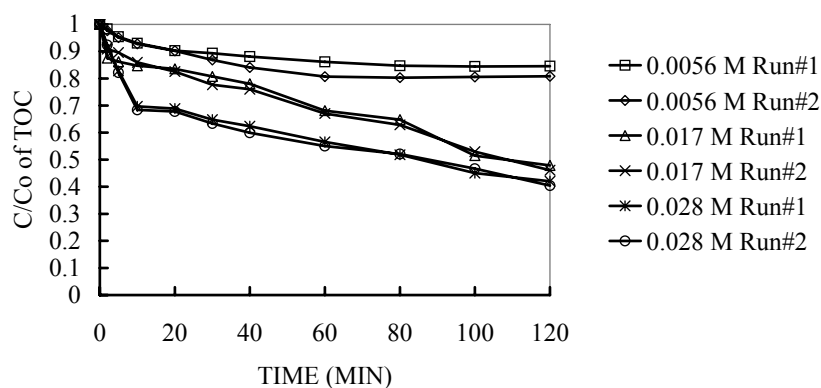


Figure 4.11 Effect of Fe^{2+} concentration on TOC removal (720 mg/l of initial TOC) by electro-Fenton process for 0.0056 M, 0.017 M, and 0.028 M of Fe^{2+} , 0.01 M aniline, pH 2.0, and 0.3 M of total H_2O_2 .

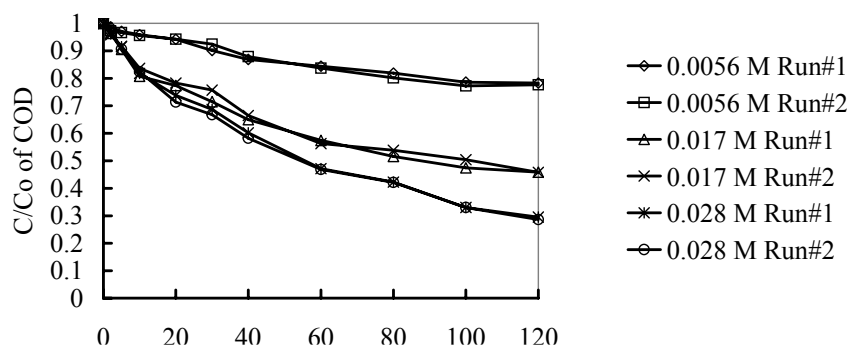
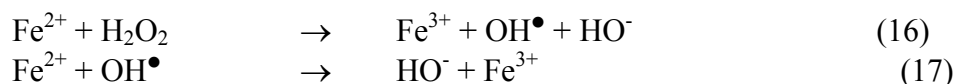


Figure 4.12 Effect of Fe^{2+} concentration on COD removal (2,240 mg/l of initial COD) by electro-Fenton process for 0.0056 M, 0.017 M, and 0.028 M of Fe^{2+} , 0.01 M aniline, pH 2.0, and 0.3 M of total H_2O_2 .

From kinetics point of view, it is interesting that, despite the overall removal efficiency was improved, an increase in ferrous from 0.0056 to 0.017 and 0.028 M in Fenton experiment reduced the initial oxidation rate of aniline from 2.0×10^{-4} to 7.12×10^{-5} and 5.65×10^{-5} M/min, respectively. This observation is understandable since Fe^{2+} can react with H_2O_2 to generate hydroxyl radicals as well as scavenge the hydroxyl radicals being generated (Pignatello, 1992) as shown in the following equations:



In other word, the competition of Fe^{2+} and organic compounds for the hydroxyl radicals became significant as the Fe^{2+} concentration increased. After excess Fe^{2+} had been oxidized to Fe^{3+} at the expense of H_2O_2 , the radicals can react with aniline exclusively. On the other hand, the effect of Fe^{2+} on the initial rate in electro-Fenton experiment was opposite to what happened in Fenton experiment, i.e., the rate increased from 2.83×10^{-4} to 3.01×10^{-4} and 3.54×10^{-4} M/min in the presence of 0.0056, 0.017 and 0.028 M of Fe^{2+} , respectively. This implies that the supplied electrons with extra Fe^{2+} can somehow increase the overall efficiency of hydroxyl radical generation. Further analysis in Figure 4.13 indicated that obtained initial rates from Fenton and electro-Fenton experiments under the conditions used in this study were linear-dependent with reciprocal ferrous concentration and ferrous concentration, respectively. Therefore, the redox kinetics can be described by the following equations

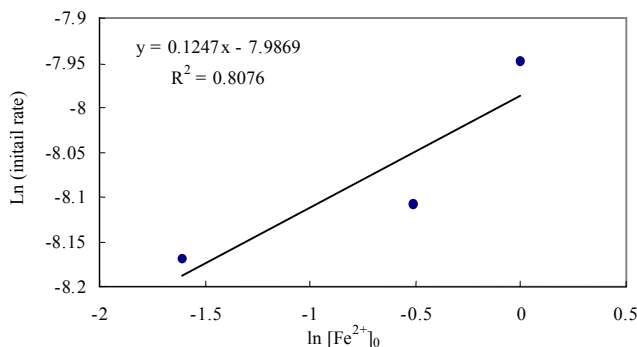
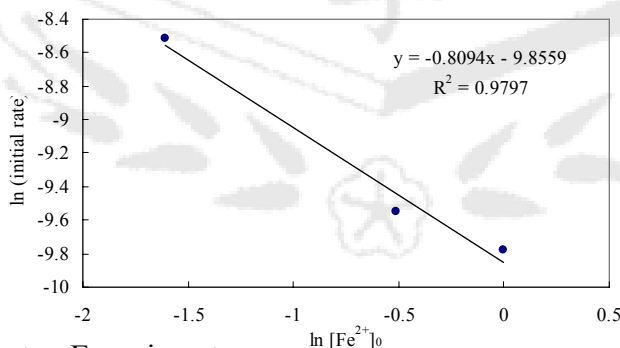


Figure 4.13 Initial rate of aniline oxidation as a function of Fe^{2+} concentration.

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{\text{Fenton}} = k_{\text{Fe}} [\text{Fe}^{2+}]^{-0.8} \quad (18)$$

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{\text{electro-Fenton}} = k_{\text{Fe}} [\text{Fe}^{2+}]^{0.1} \quad (19)$$

Where " k_{Fe} " and " k_{Fe} " are apparent rate constants.

4.4 Effect of Hydrogen Peroxide (H₂O₂) Concentration

Figure 4.14 shows the effect of H₂O₂ on aniline removal by Fenton reaction. It was found that the degradation rates of aniline in 120 minutes were comparable within 30 to 40% regardless on H₂O₂ concentration ranging between 0.2 and 0.4 M. This can be explained by the limitation of available Fe²⁺ in the solution. Lu et al. (1999) also reported that most of Fe²⁺ was transform to Fe³⁺ very fast. The concentration transformation of H₂O₂ has significant effect on the elimination rate of aniline. The reason is may be the concentration of H₂O₂ is much higher than Fe²⁺, and it will not become the limiting factor of reaction.

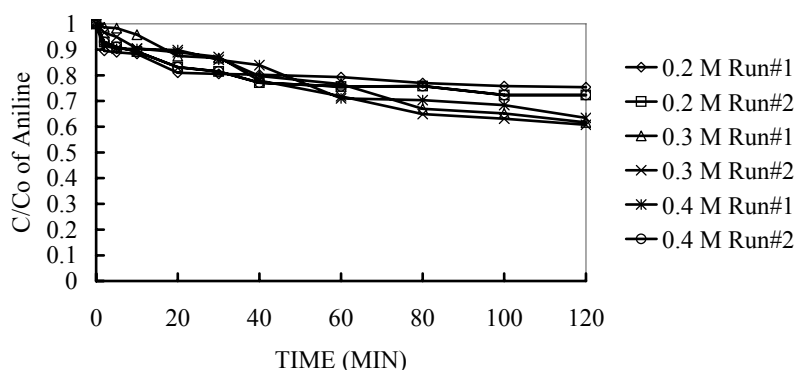


Figure 4.14 Effect of H₂O₂ concentration on aniline degradation by Fenton process for 0.2 M, 0.3 M, and 0.4 M of H₂O₂, 0.01 M aniline, pH 2.0, and 0.017 M of Fe²⁺.

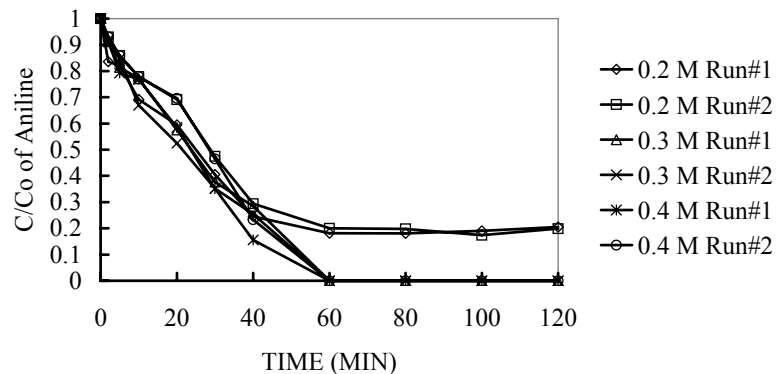


Figure 4.15 Effect of H₂O₂ concentration on aniline degradation by electro-Fenton process for 0.2 M, 0.3 M, and 0.4 M of H₂O₂, 0.01 M aniline, pH 2.0, and 0.017 M of Fe²⁺.

A similar trend was also observed for electro-Fenton experiments as shown in Figure 4.15. However, in the experiment with 0.2 M of H₂O₂, the degradation of aniline was not completed; i.e., approximately 20% of initial aniline still remained in the solution after 120 minutes due to H₂O₂ limitation. Nonetheless in the other scenarios, aniline was totally removed within one hour.

In conclusion, in the electro-Fenton process without oxygen supply at the cathodes, the amount of H₂O₂ initially exists in the solution is one of the most important factor which controlling the degradation efficiency.

Further analysis on the effect of H₂O₂ on the initial rate of aniline oxidation reveals a linear relationship for both scenarios as shown in Figure 4.16. The initial rates increased from 5.2×10⁻⁵ to 7.12×10⁻⁵ and 3.28×10⁻⁴ M/min for Fenton experiment and from 2.87×10⁻⁴ to 3.01×10⁻⁴ and 2.56×10⁻⁴ M/min as the H₂O₂ increased from 0.2 to 0.3 and 0.4 M, respectively. In addition, with the linear relationship, the oxidation rate of aniline can be written in the pseudo-first order rate law as shown in equations (20) and (21):

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{\text{Fenton}} = -k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]^{2.5} \quad (20)$$

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{\text{electro-Fenton}} = -k'_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]^{2.7} \quad (21)$$

Where "k_{H₂O₂}" and "k'_{H₂O₂}" are apparent rate constants.

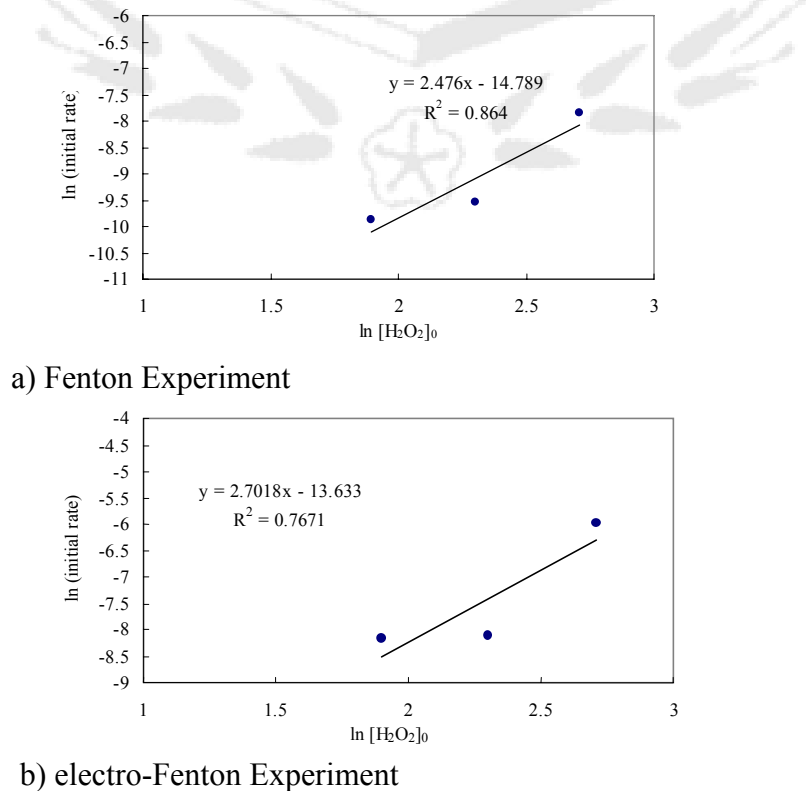


Figure 4.16 Initial rate of aniline oxidation as a function of H₂O₂ concentration.

4.5 Effect of Aniline Concentration.

The results from this experimental scenario are shown in Figures 4.17 to 4.22. The aniline degradation efficiency increased as the initial aniline concentration increased as shown in Figures 4.17 and 4.20. Aniline degradation was 20% to 40% by Fenton process. However, the effect was more pronounced in the case of electro-Fenton process, that aniline was completely degraded within 60 min at 0.01 M and 0.005 M of aniline.

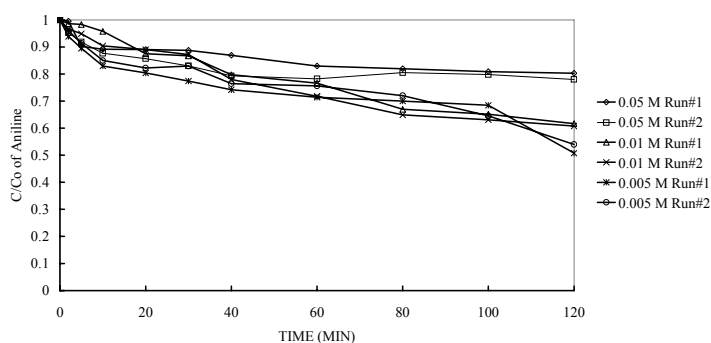


Figure 4.17 Effect of aniline concentration on aniline degradation by Fenton process for 0.3 M of H_2O_2 , 0.005 M, 0.01 M, and 0.05 M of aniline, pH 2.0, and 0.017 M of Fe^{2+}

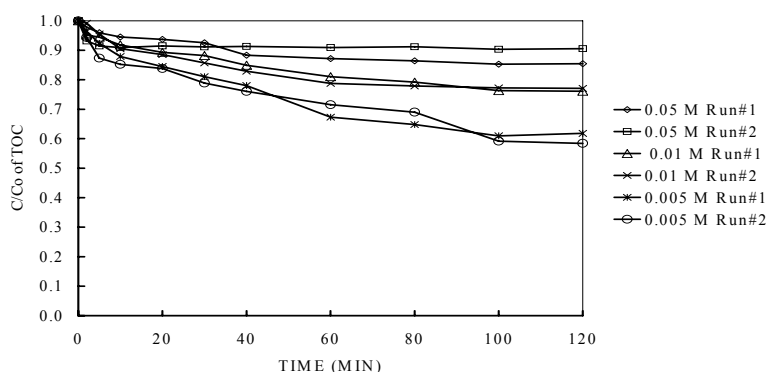


Figure 4.18 Effect of aniline concentration on TOC removal by Fenton process for 0.3 M of H_2O_2 , 0.005 M, 0.01 M, and 0.05 M aniline, pH 2.0, and 0.017 M of Fe^{2+}

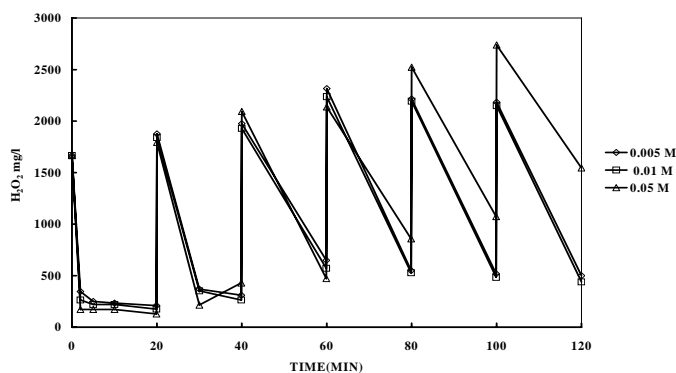


Figure 4.19 H_2O_2 concentration during Fenton experiment

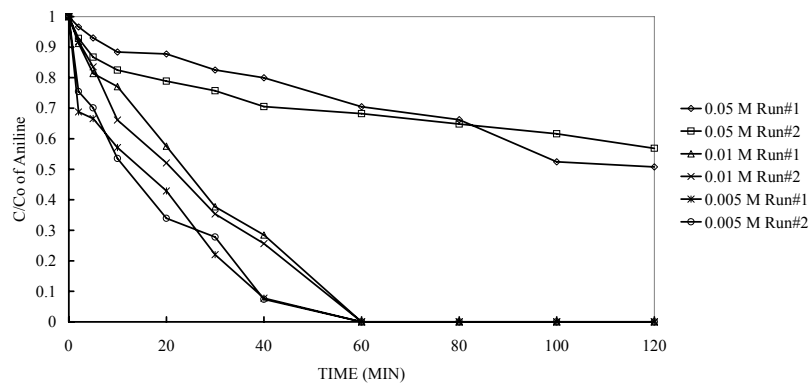


Figure 4.20 Effect of aniline concentration on aniline degradation by electro-Fenton process for 0.3 M of H_2O_2 , 0.005 M, 0.01 M, and 0.05 M aniline, pH 2.0, and 0017 M of Fe^{2+} .

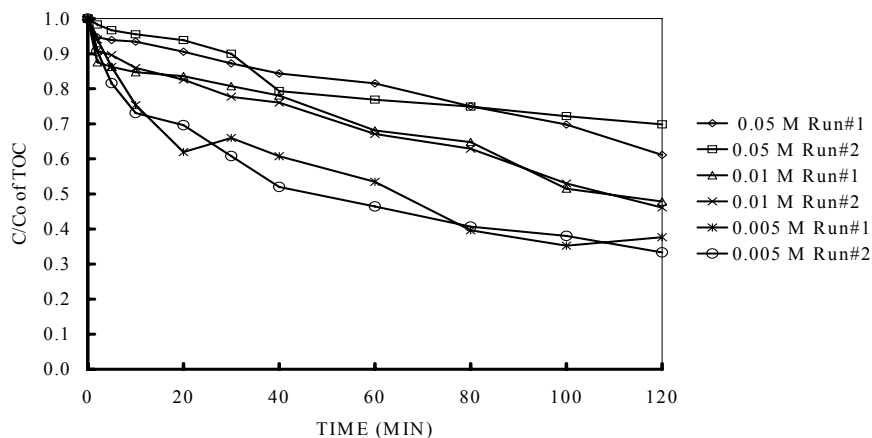
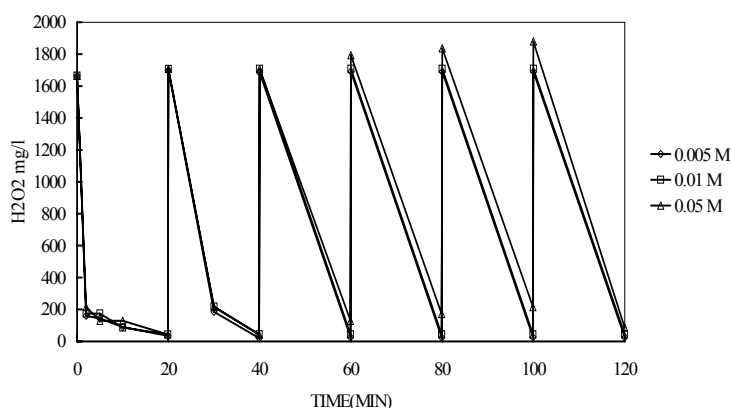


Figure 4.21 Effect of aniline concentration on TOC removal by electro-Fenton process for 0.3 M of H_2O_2 , 0.005 M, 0.01 M, and 0.05 M aniline, pH 2.0, and 0017 M of Fe^{2+} .

Figure 4.22 H_2O_2 concentration during electro-Fenton experiment



The results from TOC analysis in Fenton and electro-Fenton processes as shown in Figures 4.18 and 4.21. In Fenton, it was found 10% to 40% of aniline degradation at 0.05 M to 0.005 M aniline concentration. In electro-Fenton, aniline was degraded about 30% to 60% at 0.05 M to 0.005 M. The results indicate a similar trend although was not as evident as in the case of aniline. As a result, it can be concluded that degradation kinetics of aniline by hydroxyl radical depend on aniline concentration in the solution. Again, it can be seen from Figure 4.19 and 4.22 that H_2O_2 was consumed almost completely in the presence of electrical current.

Further analysis indicated that the initial rates for both Fenton and electro-Fenton experiments increased linearly with initial aniline concentration as shown in Figure 4.23, i.e., increasing from 6.36×10^{-5} to 7.12×10^{-5} and 8.69×10^{-4} M/min and from 2.57×10^{-4} to 3.01×10^{-4} and 1.06×10^{-3} M/min as initial aniline concentration increased from 0.005 to 0.01 and 0.05 M, respectively. The kinetic rate law can be shown as follows:

$$\left(\frac{d[\text{Aniline}]}{dt} \right)_{\text{Fenton}} = -k_{\text{Aniline}} [\text{Aniline}]^{1.2} \quad (22)$$

$$\left(\frac{d[\text{Aniline}]}{dt} \right)_{\text{electro-Fenton}} = -k'_{\text{Aniline}} [\text{Aniline}]^{0.6} \quad (23)$$

4.6 Determination of Reaction Rate Constant

As mentioned previously, the initial rates of aniline oxidation from both Fenton and electro-Fenton experiments behaviors with respect to Fe^{2+} , H_2O_2 , and aniline concentrations as shown in equations (18) to (23). Equations (24) and (25) represent the overall kinetic rate for aniline oxidation by Fenton and electro-Fenton processes, respectively.

$$\left(\frac{d[\text{Aniline}]}{dt} \right)_{\text{Fenton}} = k[\text{Aniline}]^{1.2} [Fe^{2+}]^{-0.8} [H_2O_2]^{2.5} \quad (24)$$

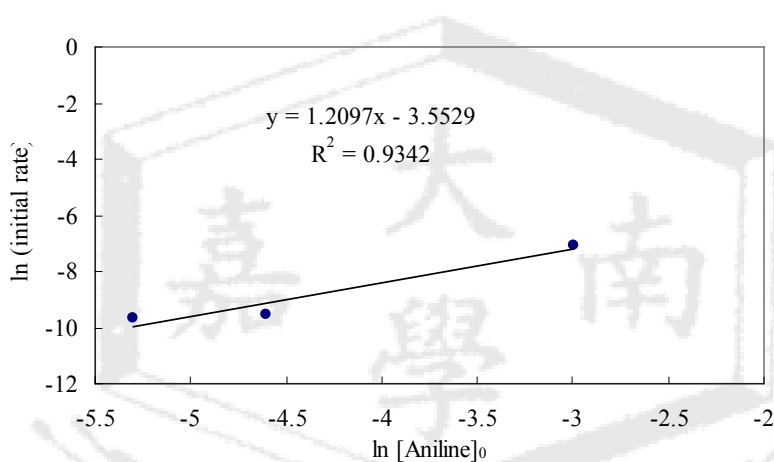
$$\left(\frac{d[\text{Aniline}]}{dt} \right)_{\text{electro-Fenton}} = k'[\text{Aniline}]^{0.6} [Fe^{2+}]^{0.1} [H_2O_2]^{2.7} \quad (25)$$

Where "k" and "k'" are the overall rate constants for aniline degradation by Fenton and electro-Fenton processes, respectively.

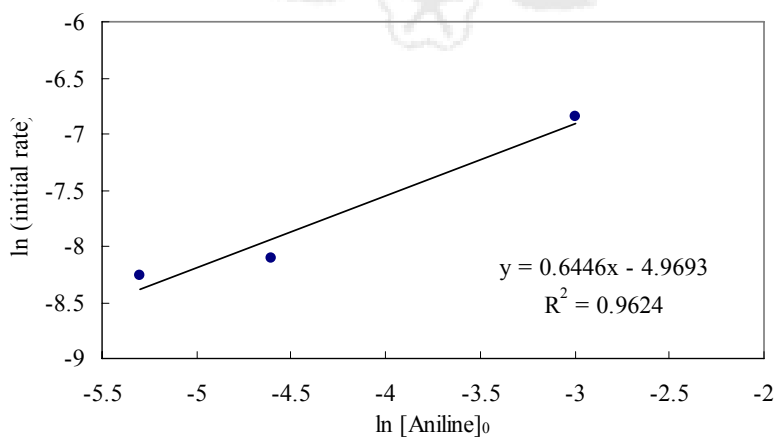
By using a non-linear least squares method which minimizing the sum of error squares between the measured initial rates from the experiments and the calculated initial rates from equations (24) and (25), the "k" and "k'" can be determined as shown in Table 4.1 and equations (24) and (25) become

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{\text{Fenton}} = 6.41 \times 10^{-5} [\text{Aniline}]^{1.2} [\text{Fe}^{2+}]^{-0.8} [\text{H}_2\text{O}_2]^{2.5} \quad (26)$$

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{\text{electro-Fenton}} = 8.37 \times 10^{-6} [\text{Aniline}]^{0.6} [\text{Fe}^{2+}]^{0.1} [\text{H}_2\text{O}_2]^{2.7} \quad (27)$$



a) Fenton Experiment



b) electro-Fenton Experiment

Figure 4.23 Initial rate of aniline oxidation as a function of aniline concentration.

Table 4.1 Optimum rate constants from non-linear least squares regression

| Processes | optimum rate constant | minimum sum of error squares |
|----------------|-----------------------|------------------------------|
| Fenton | 6.41×10^{-5} | 2.07×10^{-8} |
| electro-Fenton | 8.34×10^{-6} | 4.74×10^{-7} |

4.7 Effect of Combined Fenton&Electro-Fenton Process

The results from combined Fenton&electro-Fenton experiments including aniline degradation and H_2O_2 residuals are summarized in Figures 4.24 to 4.25. Aniline was degraded much more rapidly when the power supply had been switched on. Comparing aniline degradation rates under similar reactant concentrations of solely electro-Fenton process and combined Fenton&electro-Fenton process, the combined Fenton&electro-Fenton process seems to be more effective than fully electro-Fenton process.

Hence, in field practice, significant reduction in power consumption can be obtained by delaying the current supply and allowing traditional Fenton process to proceed to certain period.

However, when considering on the TOC removal rate, it was surprisingly that the efficiency during typical Fenton and electro-Fenton periods of the 60-minute Fenton + 60-minute electro-Fenton and 80-minute Fenton + 40-minute electro-Fenton experiments were comparable rather than being accelerated as expected in the presence of electricity as observed in the 40-minute Fenton + 80-minute electro-Fenton run which was expecting.

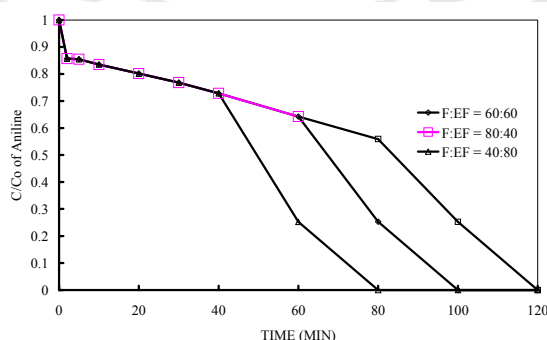


Figure 4.24 Aniline degradation by combined Fenton&electro-Fenton process for 0.01 M of aniline, pH 2.0, 0.017 M of Fe^{2+} , and 0.3 M of total H_2O_2

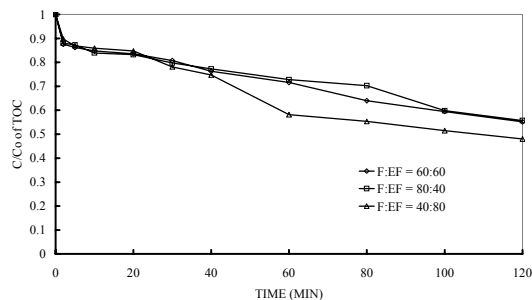


Figure 4.25 TOC removal by combined Fenton&electro-Fenton process for 0.01 M of aniline, pH 2.0, 0.017 M of Fe^{2+} , and 0.3 M of total H_2O_2

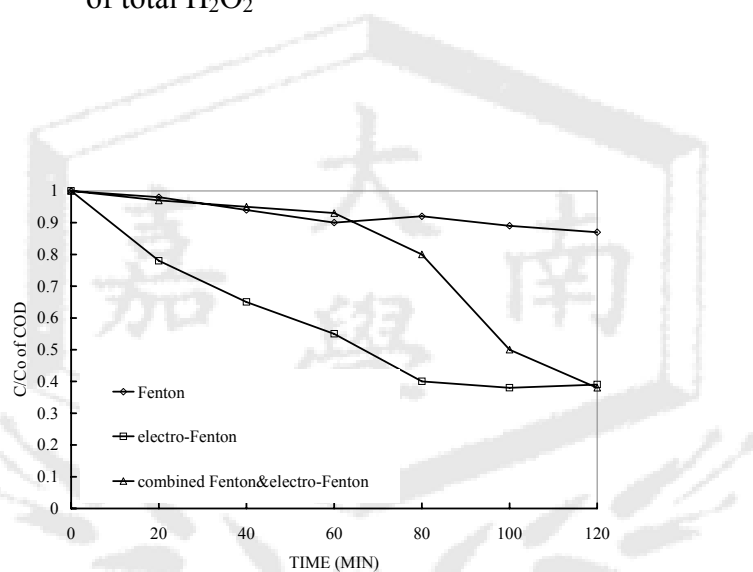


Figure 4.26 COD removal by Fenton, electro-Fenton and combined Fenton&electro-Fenton process for 0.01 M of aniline, pH 2.0, 0.017 M of Fe^{2+} , and 0.3 M of total H_2O_2

Further investigations need to be done in order to explain this observation. In addition, it was found that the Fenton&electro-Fenton process could reduce the COD very efficiently as shown in Figure 4.26 of which up to 60 minutes of power supply can be saved as compared to typical electro-Fenton process.

CHAPTER 5 CONCLUSIONS

5.1 Conclusion

The following conclusions for aniline degradation by Fenton, electro-Fenton and combined Fenton&electro-Fenton processes at pH 2 are as follows:

5.1.1 On its own, none of the ferrous ion, hydrogen peroxide, and electrical current within the ranges and conditions used in this study has significant effect on aniline degradation.

5.1.2 Under similar chemical dosages, electro-Fenton process degraded aniline and its oxidation products much more rapidly and effectively than typical Fenton process.

5.1.3 Even with electro-Fenton process, complete mineralization of aniline could not be obtained under studied conditions within 2 hours of reaction time.

5.1.4 In Fenton process, increasing Fe^{2+} concentration dramatically increased the overall degradation of aniline whereas, in electro-Fenton process, the efficiency was increased until a point was reached where further addition of ferrous ion became unnecessary.

5.1.5 An increase in H_2O_2 concentration from 0.2 to 0.4 M slightly increased the overall oxidation of aniline by both Fenton and electro-Fenton processes.

5.1.6 Degradation kinetics for aniline degradation by Fenton and electro-Fenton processes can be described by the following equations

$$\left(\frac{d[Aniline]}{dt}\right)_{Fenton} = 6.41 \times 10^{-5} [Aniline]^{1.2} [Fe^{2+}]^{-0.8} [H_2O_2]^{2.5}$$
$$\left(\frac{d[Aniline]}{dt}\right)_{electro-Fenton} = 8.37 \times 10^{-6} [Aniline]^{0.6} [Fe^{2+}]^{0.1} [H_2O_2]^{2.7}$$

5.1.7 The delay in electrical current supply in Fenton-electro-Fenton process still allowed the aniline to decompose as completely as in electro-Fenton process; hence, provides a potential reduction in power consumption.

5.2 Future Works

5.2.1 Determination the decomposition of aniline at other pHs comparing to this study.

5.2.2 Use different cathode and anode in both materials and surface area and compare the results to this study.

5.2.3 Determination on the effect of current density and electrical potential on the degradation of aniline by electro-Fenton process.



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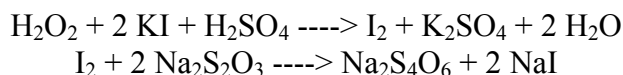
APPENDIX A

Analytical Method of Hydrogen Peroxide (Iodometric Titration)



A.1 PRINCIPLE

H₂O₂ oxidizes iodide to iodine in the presence of acid and molybdate catalyst. The iodine formed is titrated with thiosulfate solution, incorporating a starch indicator.



A.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.

A.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 H₂O₂ should not be stopper, but rather vented or covered loosely with aluminum foil or paraffin film.

A.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 indicates some air oxidation to iodine, which can be removed by adding a 1-2 drops of dilute sodium thiosulfate solution.
2. Ammonium molybdate solution. Dissolve 9 grams ammonium molybdate in 10 ml 6N NH₄OH. Add 24 grams NH₄NO₃ and dilute to 100 ml.
3. Sulfuric acid solution. Carefully add one part H₂SO₄ -98% to four parts demineralized water.
4. Starch indicator.
5. Sodium thiosulfate solution (0.1N).

A.5 Apparatus

1. Analytical balance (+/- 0.1 mg/l)
2. Small weighing bottle (< 5 ml)
3. 250 ml Erlenmeyer flask
4. 50 ml buret (Class A)
5. Medicine dropper

A.6 Procedure

1. Weigh to the nearest 0.1 mg an amount of H₂O₂ equivalent to a titer of 30 ml (0.06 grms of H₂O₂) using a 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 two 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 H₂O₂).

A.7 Calculation

$$\text{Weight \% H}_2\text{O}_2 = \frac{(A - B) \times (\text{Normality of Na}_2\text{S}_2\text{O}_3) \times 1.7}{\text{Sample weight in grams}}$$

where: A = ml Na₂S₂O₃ for sample; B = ml Na₂S₂O₃ for blank

APPENDIX B

Experimental Figures





Figure B.1 Aniline solution for 5 liters before treatment

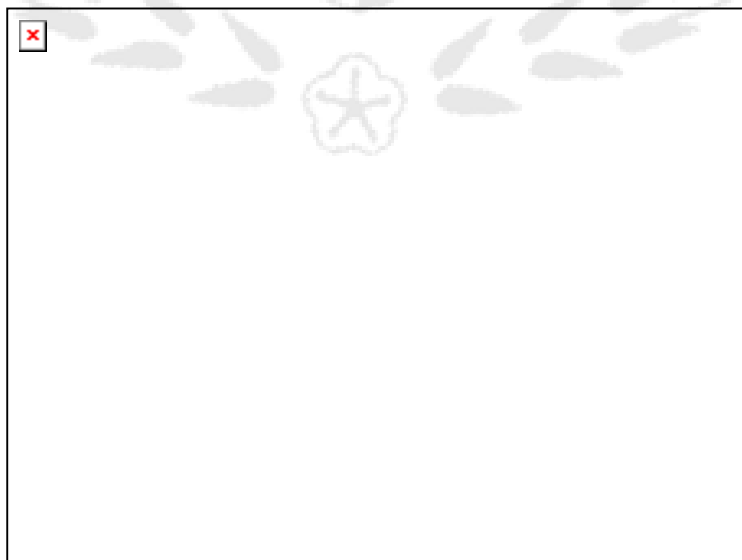


Figure B.2 Reactor setup

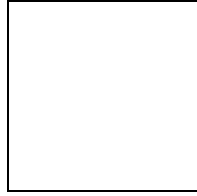


Figure B.3 Electro-Fenton reactor setup

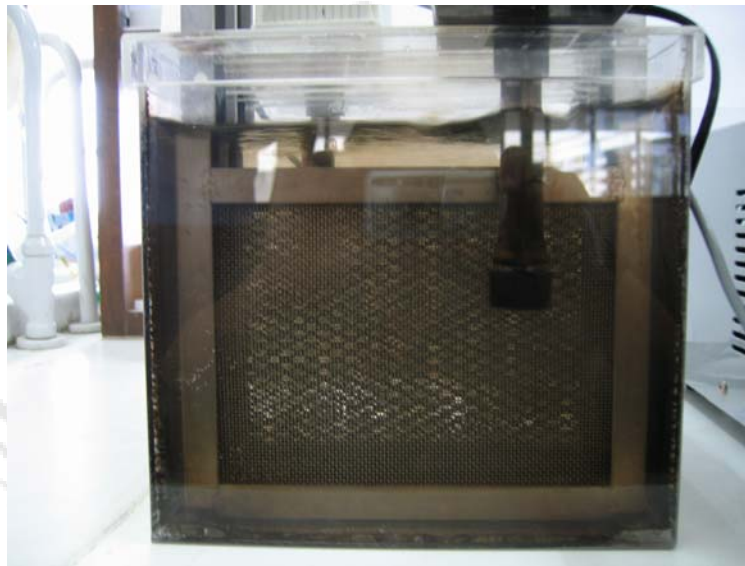


Figure B.4 Aniline solution between experiment (1)



Figure B.5 Aniline solution between experiment (2)



Figure B.6 Aniline solution from the right hand, aniline solution before treatment; the middle, aniline solution after treatment (no filtrated); the left hand, aniline solution after treatment (filtrated)

APPENDIX C

Experimental Data



Table C.1 Aniline Degradation of control experiment of Fenton process.

| Time (MIN) | Aniline | | | | | |
|---------------|------------------------------|-------|---|-------|-------------------------------|-------|
| | Control Fe ²⁺ (a) | | Control H ₂ O ₂ (b) | | Control Current Constant © | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 |
| 2 | 0.00996 | 0.996 | 0.00999 | 0.999 | 0.00992 | 0.992 |
| 5 | 0.00992 | 0.992 | 0.00994 | 0.994 | 0.00992 | 0.992 |
| 10 | 0.00993 | 0.993 | 0.00986 | 0.986 | 0.00988 | 0.988 |
| 20 | 0.00991 | 0.991 | 0.00985 | 0.985 | 0.00983 | 0.983 |
| 30 | 0.00990 | 0.990 | 0.00983 | 0.983 | 0.00982 | 0.982 |
| 40 | 0.00979 | 0.979 | 0.00984 | 0.984 | 0.00980 | 0.980 |
| 60 | 0.00985 | 0.985 | 0.00984 | 0.984 | 0.00983 | 0.983 |
| 80 | 0.00982 | 0.982 | 0.00986 | 0.986 | 0.00980 | 0.980 |
| 100 | 0.00979 | 0.979 | 0.00991 | 0.991 | 0.00790 | 0.790 |
| 120 | 0.00980 | 0.980 | 0.00987 | 0.987 | 0.00981 | 0.981 |

Note: 0.01 M Aniline, pH 2.0, (a) 0.017 M of Fe²⁺, (b) 0.3 M of total H₂O₂, (c) Current constant of 4 ampere.

Table C.2 TOC removal of control experiment of Fenton process

| Time (MIN) | TOC | | | | | |
|------------|--------------------------|-------|---------------------------------------|-------|--------------------------|-------|
| | Control Fe ²⁺ | | Control H ₂ O ₂ | | Control Current Constant | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 720 | 1.0 | 665 | 1.0 | 659 | 1.0 |
| 2 | 713 | 0.990 | 660 | 0.992 | 655 | 0.994 |
| 5 | 716 | 0.994 | 657 | 0.988 | 650 | 0.986 |
| 10 | 710 | 0.986 | 657 | 0.988 | 656 | 0.995 |
| 20 | 700 | 0.972 | 630 | 0.947 | 645 | 0.979 |
| 30 | 698 | 0.969 | 640 | 0.962 | 654 | 0.992 |
| 40 | 680 | 0.944 | 645 | 0.970 | 640 | 0.971 |
| 60 | 670 | 0.931 | 635 | 0.955 | 655 | 0.994 |
| 80 | 680 | 0.944 | 640 | 0.962 | 652 | 0.989 |
| 100 | 665 | 0.924 | 642 | 0.965 | 650 | 0.986 |
| 120 | 670 | 0.931 | 640 | 0.962 | 640 | 0.971 |

Note: 0.01 M Aniline, pH 2.0, (a) 0.017 M of Fe²⁺, (b) 0.3 M of total H₂O₂, (c) Current constant of 4 ampere.

Table C.3 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:49.95]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 |
| 2 | 0.0091 | 0.914 | 0.0094 | 0.942 | 0.0092 | 0.924 | 0.0092 | 0.925 |
| 5 | 0.0089 | 0.893 | 0.0093 | 0.933 | 0.0083 | 0.832 | 0.0086 | 0.868 |
| 10 | 0.0088 | 0.878 | 0.0092 | 0.925 | 0.0069 | 0.690 | 0.0075 | 0.759 |
| 20 | 0.0088 | 0.877 | 0.0091 | 0.917 | 0.0063 | 0.634 | 0.0063 | 0.633 |
| 30 | 0.0087 | 0.872 | 0.0091 | 0.913 | 0.0061 | 0.614 | 0.0060 | 0.606 |
| 40 | 0.0085 | 0.854 | 0.0091 | 0.910 | 0.0057 | 0.570 | 0.0057 | 0.572 |
| 60 | 0.0085 | 0.855 | 0.0090 | 0.907 | 0.0055 | 0.556 | 0.0057 | 0.570 |
| 80 | 0.0085 | 0.853 | 0.0089 | 0.896 | 0.0054 | 0.546 | 0.0055 | 0.557 |
| 100 | 0.0085 | 0.854 | 0.0083 | 0.837 | 0.0054 | 0.540 | 0.0053 | 0.537 |
| 120 | 0.0085 | 0.851 | 0.0078 | 0.789 | 0.0054 | 0.544 | 0.0052 | 0.525 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.0056$ M and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.4 TOC removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:49.95]$

| Time (MIN) | TOC Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 711 | 1.0 | 715 | 1.0 | 702 | 1.0 | 710 | 1.0 |
| 2 | 703 | 0.989 | 703 | 0.983 | 694 | 0.989 | 693 | 0.976 |
| 5 | 680 | 0.956 | 670 | 0.937 | 675 | 0.962 | 682 | 0.961 |
| 10 | 671 | 0.944 | 664 | 0.929 | 662 | 0.943 | 655 | 0.923 |
| 20 | 670 | 0.942 | 658 | 0.920 | 642 | 0.915 | 640 | 0.901 |
| 30 | 666 | 0.937 | 652 | 0.912 | 635 | 0.905 | 615 | 0.866 |
| 40 | 662 | 0.931 | 649 | 0.908 | 626 | 0.892 | 598 | 0.842 |
| 60 | 661 | 0.930 | 646 | 0.903 | 612 | 0.872 | 567 | 0.799 |
| 80 | 659 | 0.927 | 645 | 0.902 | 602 | 0.858 | 560 | 0.789 |
| 100 | 658 | 0.925 | 643 | 0.899 | 600 | 0.855 | 564 | 0.794 |
| 120 | 659 | 0.927 | 642 | 0.898 | 602 | 0.858 | 560 | 0.789 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.0056$ M and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.5 COD removal between Fenton and electro- Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:49.95]$

| Time (MIN) | COD Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|----------------------|-------|----------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro- Fenton#1 | | Electro- Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 1940 | 1.0 | 1990 | 1.0 | 2084 | 1.0 | 1970 | 1.0 |
| 2 | 1920 | 0.990 | 1975 | 0.992 | 2013 | 0.966 | 1930 | 0.980 |
| 5 | 1915 | 0.987 | 1940 | 0.975 | 2015 | 0.967 | 1890 | 0.959 |
| 10 | 1910 | 0.985 | 1910 | 0.960 | 1960 | 0.940 | 1833 | 0.930 |
| 20 | 1913 | 0.986 | 1902 | 0.956 | 1944 | 0.933 | 1810 | 0.919 |
| 30 | 1870 | 0.964 | 1864 | 0.937 | 1870 | 0.897 | 1710 | 0.868 |
| 40 | 1825 | 0.941 | 1842 | 0.926 | 1805 | 0.866 | 1648 | 0.837 |
| 60 | 1812 | 0.934 | 1840 | 0.925 | 1764 | 0.846 | 1600 | 0.812 |
| 80 | 1798 | 0.927 | 1811 | 0.910 | 1699 | 0.815 | 1547 | 0.785 |
| 100 | 1742 | 0.898 | 1785 | 0.897 | 1665 | 0.799 | 1540 | 0.782 |
| 120 | 1790 | 0.923 | 1800 | 0.905 | 1660 | 0.797 | 1535 | 0.779 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.0056 \text{ M}$ and $\text{H}_2\text{O}_2 = 0.3 \text{ M}$

Table C.6 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.57]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 |
| 2 | 0.0098 | 0.986 | 0.0096 | 0.966 | 0.0091 | 0.912 | 0.0091 | 0.918 |
| 5 | 0.0098 | 0.983 | 0.0094 | 0.945 | 0.0081 | 0.814 | 0.0083 | 0.835 |
| 10 | 0.0095 | 0.958 | 0.0090 | 0.904 | 0.0077 | 0.771 | 0.0066 | 0.661 |
| 20 | 0.0087 | 0.875 | 0.0089 | 0.890 | 0.0057 | 0.575 | 0.0052 | 0.520 |
| 30 | 0.0086 | 0.867 | 0.0087 | 0.872 | 0.0037 | 0.377 | 0.0035 | 0.353 |
| 40 | 0.0079 | 0.797 | 0.0078 | 0.780 | 0.0028 | 0.284 | 0.0025 | 0.256 |
| 60 | 0.0076 | 0.766 | 0.0071 | 0.718 | 0.0 | 0.0 | 0.0 | 0.0 |
| 80 | 0.0067 | 0.670 | 0.0064 | 0.648 | 0.0 | 0.0 | 0.0 | 0.0 |
| 100 | 0.0065 | 0.651 | 0.0063 | 0.631 | 0.0 | 0.0 | 0.0 | 0.0 |
| 120 | 0.0061 | 0.617 | 0.0060 | 0.607 | 0.0 | 0.0 | 0.0 | 0.0 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017 \text{ M}$ and $\text{H}_2\text{O}_2 = 0.3 \text{ M}$

Table C.7 TOC removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.57]$

| Time (MIN) | TOC Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 704 | 1.0 | 715 | 1.0 | 602 | 0.9 | 716 | 1.0 |
| 2 | 680 | 0.956 | 705 | 0.986 | 527 | 0.751 | 650 | 0.915 |
| 5 | 667 | 0.938 | 680 | 0.951 | 519 | 0.739 | 641 | 0.903 |
| 10 | 652 | 0.917 | 650 | 0.909 | 510 | 0.726 | 615 | 0.866 |
| 20 | 639 | 0.899 | 628 | 0.878 | 503 | 0.717 | 591 | 0.832 |
| 30 | 630 | 0.886 | 608 | 0.850 | 486 | 0.692 | 556 | 0.783 |
| 40 | 598 | 0.841 | 585 | 0.818 | 470 | 0.670 | 544 | 0.766 |
| 60 | 574 | 0.807 | 556 | 0.778 | 410 | 0.584 | 480 | 0.676 |
| 80 | 561 | 0.789 | 542 | 0.758 | 390 | 0.556 | 450 | 0.634 |
| 100 | 540 | 0.759 | 543 | 0.759 | 310 | 0.442 | 379 | 0.534 |
| 120 | 542 | 0.762 | 542 | 0.758 | 288 | 0.410 | 330 | 0.465 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017 \text{ M}$ and $\text{H}_2\text{O}_2 = 0.3 \text{ M}$

Table C.8 COD removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.57]$

| Time (MIN) | COD Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 2090 | 1.0 | 2180 | 1.0 | 1975 | 1.0 | 1970 | 1.0 |
| 2 | 2065 | 0.988 | 2118 | 0.972 | 1904 | 0.964 | 1880 | 0.954 |
| 5 | 2012 | 0.963 | 2080 | 0.954 | 1782 | 0.902 | 1810 | 0.919 |
| 10 | 2004 | 0.959 | 2048 | 0.939 | 1610 | 0.815 | 1630 | 0.827 |
| 20 | 1996 | 0.955 | 2020 | 0.927 | 1534 | 0.777 | 1550 | 0.787 |
| 30 | 1960 | 0.938 | 1993 | 0.914 | 1420 | 0.719 | 1490 | 0.756 |
| 40 | 1914 | 0.916 | 1911 | 0.877 | 1272 | 0.644 | 1310 | 0.665 |
| 60 | 1875 | 0.897 | 1879 | 0.862 | 1105 | 0.559 | 1080 | 0.548 |
| 80 | 1870 | 0.895 | 1863 | 0.855 | 1007 | 0.510 | 1052 | 0.534 |
| 100 | 1831 | 0.876 | 1860 | 0.853 | 957 | 0.485 | 997 | 0.506 |
| 120 | 1828 | 0.875 | 1864 | 0.855 | 900 | 0.456 | 915 | 0.464 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017 \text{ M}$ and $\text{H}_2\text{O}_2 = 0.3 \text{ M}$

Table C.9 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:9.99]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 |
| 2 | 0.0098 | 0.982 | 0.0097 | 0.995 | 0.0081 | 0.812 | 0.0081 | 0.811 |
| 5 | 0.0097 | 0.975 | 0.0096 | 0.989 | 0.0078 | 0.780 | 0.0079 | 0.796 |
| 10 | 0.0096 | 0.965 | 0.0095 | 0.978 | 0.0068 | 0.683 | 0.0069 | 0.693 |
| 20 | 0.0085 | 0.859 | 0.0084 | 0.869 | 0.0058 | 0.589 | 0.0059 | 0.598 |
| 30 | 0.0075 | 0.759 | 0.0072 | 0.751 | 0.0028 | 0.282 | 0.0030 | 0.304 |
| 40 | 0.0066 | 0.668 | 0.0067 | 0.698 | 0.0004 | 0.044 | 0.0006 | 0.067 |
| 60 | 0.0056 | 0.566 | 0.0054 | 0.564 | 0.0 | 0.000 | 0.0 | 0.000 |
| 80 | 0.0044 | 0.443 | 0.0045 | 0.470 | 0.0 | 0.000 | 0.0 | 0.000 |
| 100 | 0.0033 | 0.338 | 0.0032 | 0.333 | 0.0 | 0.000 | 0.0 | 0.000 |
| 120 | 0.0012 | 0.120 | 0.0015 | 0.163 | 0.0 | 0.000 | 0.0 | 0.000 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.028$ and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.10 TOC removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:9.99]$

| Time (MIN) | TOC Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 721 | 1.0 | 715 | 1.0 | 718 | 1.0 | 716 | 1.0 |
| 2 | 705 | 0.978 | 700 | 0.979 | 663 | 0.923 | 650 | 0.908 |
| 5 | 630 | 0.874 | 640 | 0.895 | 590 | 0.822 | 592 | 0.827 |
| 10 | 582 | 0.807 | 580 | 0.811 | 491 | 0.684 | 490 | 0.684 |
| 20 | 530 | 0.735 | 541 | 0.757 | 487 | 0.678 | 482 | 0.673 |
| 30 | 500 | 0.693 | 510 | 0.713 | 455 | 0.634 | 460 | 0.642 |
| 40 | 470 | 0.652 | 452 | 0.632 | 430 | 0.599 | 440 | 0.615 |
| 60 | 456 | 0.632 | 445 | 0.622 | 395 | 0.550 | 401 | 0.560 |
| 80 | 430 | 0.596 | 430 | 0.601 | 374 | 0.521 | 365 | 0.510 |
| 100 | 428 | 0.594 | 432 | 0.604 | 335 | 0.467 | 330 | 0.461 |
| 120 | 428 | 0.594 | 430 | 0.601 | 290 | 0.404 | 305 | 0.426 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.028 \text{ M}$ and $\text{H}_2\text{O}_2 = 0.3 \text{ M}$

Table C.11 COD removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:9.99]$

| Time (MIN) | COD Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 2055 | 1.0 | 1996 | 1.0 | 2107 | 1.0 | 2095 | 1.0 |
| 2 | 1980 | 0.964 | 1920 | 0.962 | 2020 | 0.959 | 2050 | 0.979 |
| 5 | 1950 | 0.949 | 1880 | 0.942 | 1896 | 0.900 | 1870 | 0.893 |
| 10 | 1850 | 0.900 | 1770 | 0.887 | 1710 | 0.812 | 1700 | 0.811 |
| 20 | 1800 | 0.876 | 1710 | 0.857 | 1534 | 0.728 | 1490 | 0.711 |
| 30 | 1785 | 0.869 | 1650 | 0.827 | 1420 | 0.674 | 1380 | 0.659 |
| 40 | 1758 | 0.855 | 1620 | 0.812 | 1388 | 0.659 | 1350 | 0.644 |
| 60 | 1566 | 0.762 | 1530 | 0.767 | 1205 | 0.572 | 1180 | 0.563 |
| 80 | 1452 | 0.707 | 1380 | 0.691 | 889 | 0.422 | 870 | 0.415 |
| 100 | 1100 | 0.535 | 1100 | 0.551 | 710 | 0.337 | 710 | 0.339 |
| 120 | 870 | 0.423 | 980 | 0.491 | 620 | 0.294 | 650 | 0.310 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.028 \text{ M}$ and $\text{H}_2\text{O}_2 = 0.3 \text{ M}$

Table C.12 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:11.04]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|---------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 |
| 2 | 0.0089 | 0.895 | 0.0093 | 0.958 | 0.0083 | 0.835 | 0.0093 | 0.930 |
| 5 | 0.0088 | 0.889 | 0.0091 | 0.937 | 0.0082 | 0.820 | 0.0085 | 0.857 |
| 10 | 0.0088 | 0.883 | 0.0089 | 0.917 | 0.0069 | 0.691 | 0.0077 | 0.778 |
| 20 | 0.0081 | 0.810 | 0.0083 | 0.855 | 0.0059 | 0.594 | 0.0069 | 0.690 |
| 30 | 0.0080 | 0.805 | 0.0081 | 0.834 | 0.0040 | 0.405 | 0.0047 | 0.474 |
| 40 | 0.0080 | 0.802 | 0.0077 | 0.794 | 0.0024 | 0.245 | 0.0029 | 0.294 |
| 60 | 0.0079 | 0.793 | 0.0076 | 0.784 | 0.0018 | 0.181 | 0.0020 | 0.200 |
| 80 | 0.0076 | 0.769 | 0.0072 | 0.742 | 0.0018 | 0.180 | 0.0019 | 0.198 |
| 100 | 0.0075 | 0.757 | 0.0072 | 0.743 | 0.0019 | 0.190 | 0.0017 | 0.174 |
| 120 | 0.0075 | 0.753 | 0.0072 | 0.742 | 0.0020 | 0.205 | 0.0019 | 0.199 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.2$ M

Table C.13 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:24.98]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|---------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 | 0.01 | 1.0 |
| 2 | 0.0091 | 0.915 | 0.0093 | 0.930 | 0.0091 | 0.911 | 0.0093 | 0.930 |
| 5 | 0.0090 | 0.902 | 0.0091 | 0.910 | 0.0079 | 0.792 | 0.0085 | 0.857 |
| 10 | 0.0090 | 0.902 | 0.0089 | 0.890 | 0.0076 | 0.768 | 0.0077 | 0.778 |
| 20 | 0.0089 | 0.898 | 0.0083 | 0.830 | 0.0058 | 0.583 | 0.0069 | 0.695 |
| 30 | 0.0085 | 0.859 | 0.0081 | 0.810 | 0.0035 | 0.351 | 0.0046 | 0.468 |
| 40 | 0.0083 | 0.839 | 0.0077 | 0.770 | 0.0015 | 0.156 | 0.0023 | 0.232 |
| 60 | 0.0071 | 0.710 | 0.0076 | 0.760 | 0.0 | 0.0 | 0.0 | 0.0 |
| 80 | 0.0070 | 0.703 | 0.0076 | 0.761 | 0.0 | 0.0 | 0.0 | 0.0 |
| 100 | 0.0068 | 0.683 | 0.0072 | 0.723 | 0.0 | 0.0 | 0.0 | 0.0 |
| 120 | 0.0063 | 0.634 | 0.0072 | 0.721 | 0.0 | 0.0 | 0.0 | 0.0 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.4$ M

Table C.14 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.67]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|---------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.05 | 1.0 | 0.05 | 1.0 | 0.05 | 1.0 | 0.05 | 1.0 |
| 2 | 0.0497 | 0.994 | 0.0476 | 0.952 | 0.0483 | 0.966 | 0.0464 | 0.928 |
| 5 | 0.0451 | 0.902 | 0.0459 | 0.918 | 0.0465 | 0.930 | 0.0433 | 0.866 |
| 10 | 0.0445 | 0.890 | 0.0438 | 0.876 | 0.0442 | 0.884 | 0.0412 | 0.824 |
| 20 | 0.0444 | 0.888 | 0.0428 | 0.856 | 0.0438 | 0.877 | 0.0394 | 0.788 |
| 30 | 0.0443 | 0.886 | 0.0415 | 0.830 | 0.0412 | 0.825 | 0.0378 | 0.756 |
| 40 | 0.0434 | 0.868 | 0.0396 | 0.792 | 0.0399 | 0.800 | 0.0352 | 0.704 |
| 60 | 0.0414 | 0.828 | 0.0391 | 0.782 | 0.0352 | 0.705 | 0.0341 | 0.682 |
| 80 | 0.0409 | 0.818 | 0.0405 | 0.811 | 0.0331 | 0.662 | 0.0324 | 0.648 |
| 100 | 0.0404 | 0.808 | 0.0399 | 0.798 | 0.0262 | 0.525 | 0.0307 | 0.614 |
| 120 | 0.0401 | 0.802 | 0.0390 | 0.780 | 0.0253 | 0.508 | 0.0284 | 0.568 |

Note: 0.05 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.15 TOC removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.67]$

| Time (MIN) | TOC Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 3527 | 1.0 | 3500 | 1.0 | 3520 | 1.0 | 3511 | 1.0 |
| 2 | 3449 | 0.978 | 3287 | 0.939 | 3339 | 0.949 | 3460 | 0.985 |
| 5 | 3384 | 0.959 | 3226 | 0.922 | 3311 | 0.941 | 3409 | 0.971 |
| 10 | 3333 | 0.945 | 3206 | 0.916 | 3296 | 0.936 | 3369 | 0.960 |
| 20 | 3304 | 0.937 | 3226 | 0.922 | 3194 | 0.907 | 3310 | 0.943 |
| 30 | 3265 | 0.926 | 3214 | 0.918 | 3076 | 0.874 | 3172 | 0.903 |
| 40 | 3116 | 0.883 | 3220 | 0.920 | 2974 | 0.845 | 2798 | 0.797 |
| 60 | 3075 | 0.872 | 3206 | 0.916 | 2875 | 0.817 | 2711 | 0.772 |
| 80 | 3048 | 0.864 | 3216 | 0.919 | 2645 | 0.751 | 2642 | 0.752 |
| 100 | 3008 | 0.853 | 3186 | 0.910 | 2641 | 0.750 | 2546 | 0.725 |
| 120 | 3013 | 0.854 | 3194 | 0.913 | 2155 | 0.612 | 2463 | 0.702 |

Note: 0.05 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.16 Aniline degradation between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.67]$

| Time (MIN) | Aniline Concentration | | | | | | | |
|------------|-----------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | M | C/Co | M | C/Co | M | C/Co | M | C/Co |
| 0 | 0.005 | 1.0 | 0.005 | 1.0 | 0.005 | 1.0 | 0.005 | 1.0 |
| 2 | 0.00469 | 0.938 | 0.00479 | 0.958 | 0.00344 | 0.688 | 0.00377 | 0.754 |
| 5 | 0.00447 | 0.894 | 0.00456 | 0.912 | 0.00332 | 0.664 | 0.00350 | 0.700 |
| 10 | 0.00414 | 0.828 | 0.00443 | 0.886 | 0.00285 | 0.570 | 0.00267 | 0.534 |
| 20 | 0.00441 | 0.882 | 0.00440 | 0.880 | 0.00214 | 0.428 | 0.00169 | 0.338 |
| 30 | 0.00437 | 0.874 | 0.00411 | 0.822 | 0.00110 | 0.220 | 0.00139 | 0.278 |
| 40 | 0.00418 | 0.836 | 0.00411 | 0.822 | 0.00038 | 0.076 | 0.00036 | 0.072 |
| 60 | 0.00413 | 0.826 | 0.00395 | 0.790 | 0.0 | 0.000 | 0.0 | 0.000 |
| 80 | 0.00371 | 0.742 | 0.00981 | 1.962 | 0.0 | 0.000 | 0.0 | 0.000 |
| 100 | 0.00341 | 0.682 | 0.00322 | 0.644 | 0.0 | 0.000 | 0.0 | 0.000 |
| 120 | 0.00253 | 0.506 | 0.00269 | 0.538 | 0.0 | 0.000 | 0.0 | 0.000 |

Note: 0.005 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.17 TOC removal between Fenton and electro-Fenton processes
 $[\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.67]$

| Time (MIN) | TOC Concentration | | | | | | | |
|---------------|-------------------|-------|----------|-------|------------------|-------|------------------|-------|
| | Fenton#1 | | Fenton#2 | | Electro-Fenton#1 | | Electro-Fenton#2 | |
| | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co | mg/L | C/Co |
| 0 | 358 | 1.0 | 350 | 1.0 | 362 | 1.0 | 354 | 1.0 |
| 2 | 345 | 0.964 | 338 | 0.944 | 347 | 0.940 | 315 | 0.907 |
| 5 | 330 | 0.923 | 310 | 0.873 | 319 | 0.862 | 282 | 0.816 |
| 10 | 315 | 0.879 | 302 | 0.852 | 280 | 0.753 | 273 | 0.731 |
| 20 | 302 | 0.845 | 300 | 0.838 | 222 | 0.619 | 249 | 0.696 |
| 30 | 290 | 0.810 | 282 | 0.788 | 236 | 0.659 | 218 | 0.608 |
| 40 | 279 | 0.780 | 272 | 0.760 | 217 | 0.607 | 186 | 0.520 |
| 60 | 241 | 0.670 | 256 | 0.715 | 191 | 0.534 | 160 | 0.464 |
| 80 | 232 | 0.648 | 250 | 0.690 | 150 | 0.396 | 146 | 0.406 |
| 100 | 218 | 0.610 | 213 | 0.591 | 126 | 0.352 | 136 | 0.380 |
| 120 | 221 | 0.618 | 209 | 0.584 | 135 | 0.377 | 129 | 0.333 |

Note: 0.005 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.3$ M

Table C.18 Aniline degradation and TOC removal on combined Fenton&electro-Fenton process[Fe²⁺:H₂O₂ = 1:16.67]

| Time (MIN) | Aniline Concentration | | TOC Concentration | |
|------------|-----------------------|-------|-------------------|-------|
| | M | C/Co | mg/L | C/Co |
| 0 | 0.01 | 1.0 | 602 | 1.0 |
| 2 | 0.00857 | 0.857 | 527 | 0.875 |
| 5 | 0.00854 | 0.854 | 519 | 0.862 |
| 10 | 0.00835 | 0.835 | 510 | 0.847 |
| 20 | 0.00801 | 0.801 | 503 | 0.836 |
| 30 | 0.00767 | 0.767 | 486 | 0.807 |
| 40 | 0.00728 | 0.728 | 459 | 0.762 |
| 60 | 0.00250 | 0.250 | 355 | 0.590 |
| 80 | 0.0 | 0.0 | 333 | 0.553 |
| 100 | 0.0 | 0.0 | 310 | 0.515 |
| 120 | 0.0 | 0.0 | 289 | 0.480 |

Note: 0.01 M Aniline, pH 2.0, Fe²⁺ = 0.017 M and H₂O₂ = 0.3 M, Fenton time = 60 min and electro-Fenton time = 60 min.

Table C.19 Aniline degradation and TOC removal combined Fenton&electro-Fenton process [$\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.67$]

| Time (MIN) | Aniline Concentration | | TOC Concentration | |
|------------|-----------------------|-------|-------------------|-------|
| | M | C/Co | mg/L | C/Co |
| 0 | 0.01 | 1.0 | 612 | 1.0 |
| 2 | 0.00877 | 0.877 | 530 | 0.880 |
| 5 | 0.00862 | 0.862 | 524 | 0.870 |
| 10 | 0.00824 | 0.824 | 515 | 0.855 |
| 20 | 0.00786 | 0.786 | 503 | 0.836 |
| 30 | 0.00754 | 0.754 | 482 | 0.801 |
| 40 | 0.00705 | 0.705 | 449 | 0.746 |
| 60 | 0.00240 | 0.240 | 360 | 0.598 |
| 80 | 0.0 | 0.0 | 321 | 0.533 |
| 100 | 0.0 | 0.0 | 304 | 0.505 |
| 120 | 0.0 | 0.0 | 275 | 0.457 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.3$ M, Fenton time = 80 min and electro-Fenton time = 40 min.

Table C.20 Aniline degradation and TOC removal combined Fenton&electro-Fenton process [$\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:16.67$]

| Time (MIN) | Aniline Concentration | | TOC Concentration | |
|------------|-----------------------|-------|-------------------|-------|
| | M | C/Co | mg/L | C/Co |
| 0 | 0.01 | 1.0 | 655 | 1.1 |
| 2 | 0.00857 | 0.857 | 537 | 0.892 |
| 5 | 0.00855 | 0.855 | 529 | 0.879 |
| 10 | 0.00840 | 0.840 | 521 | 0.865 |
| 20 | 0.00801 | 0.801 | 496 | 0.824 |
| 30 | 0.00768 | 0.768 | 482 | 0.801 |
| 40 | 0.00728 | 0.728 | 459 | 0.762 |
| 60 | 0.00642 | 0.642 | 433 | 0.719 |
| 80 | 0.00559 | 0.559 | 380 | 0.631 |
| 100 | 0.00240 | 0.240 | 371 | 0.616 |
| 120 | 0.0 | 0.0 | 328 | 0.545 |

Note: 0.01 M Aniline, pH 2.0, $\text{Fe}^{2+} = 0.017$ M and $\text{H}_2\text{O}_2 = 0.3$ M, Fenton time = 40 min and electro-Fenton time = 80 min.

行政院國家科學委員會補助國內專家學者出席國際學術會議報告

| | | | |
|----------------|--|--------------------|-----------------------------|
| 報 告 人 姓 名 | 盧 明 俊 | 服 務 機 構 及 職 稱 | 嘉南藥理科技大學 環境資源管理系 專任教授 |
| 會 議 時 間 地 點 | 95 年 9 月 25 日 至 28 日 美 國 , 匹 茲 堡 | 本 會 核 定 補 助 文 號 | |
| 會 議 名 稱 | 第十二屆國際高級氧化技術處理水、空氣及土壤研討會 The 12 th International Conference on Advanced Oxidation Technologies for Treatment of Water, Air and Soil | | |
| 發 表 論 文 題 目 | 1. Treatment of Petrochemical Wastewater by Electro-Fenton Technology in a Pilot Reactor 2. Application of Goethite/Hydrogen Peroxide on the Treatment of Chlorophenols | | |

一、參加會議經過：

本人 9 月 24 日搭乘華航 CI008 到洛山機轉全美航空於當地時間 9 月 25 日早上六點到達匹茲堡，會議結束後於 9 月 29 日飛往舊金山轉搭 CI003 回台灣本次研討會是由氧化還原技術公司舉辦，除原有之高級氧化技術研討會，並與光觸媒技術研討會及地下水現場處理技術研討會在相同場地舉行。內容共有兩大部份：口頭報告及海報發表論文發表地點在 Omni William Penn Hotel 17 樓進行不同主題論文的發表，9 月 25 日上午 8 點開始第一場發表會。本研討會海報論文發表，在 17 樓另闢大廳展示。此外現場亦有許多顧問工程公司或製造廠商在現場展覽。本人的兩篇論文分別於 9 月 27 日 15:40 至 16:05 及 9 月 28 日 10:20 至 10:45 發表。其餘時段則選擇相關主題，進入相關會場聽取簡報。

二、與會心得

奈米微粒粒徑介於 1-100nm 之間，而其特有的尺寸效應、量子侷限效應及表面效應，應用在二氧化鈦奈米材料上，可大幅提升其物性、化性及光電性質。二氧化鈦光觸媒的效率決定因素有很多，以觸媒本身性質而言，採用較大的比表面積且粒徑較一致的二氧化鈦，可接受較多且較穩定的光照量，有利於催化反應的進行。

二氧化鈦的「毒化現象」正是目前工業污染物光催化技術最大的瓶頸。在工業污染物的去除技術中，紫外線/二氧化鈦光催化程序能有效處理易分解性的有機污染物，醇類、酮類及醛類的低碳鏈化合物，但在處理對人體毒害性較強的難分解性有機物，例如苯類、酚類或其他長碳鏈

的聚合物，光分解後的中間產物有可能比之前的化合物更具毒性、更難分解；此外，中間產物更可能會吸附在二氧化鈦的表面，且不易脫附去除，最後造成觸媒活性喪失、毒化觸媒。

塗佈固定技術會影響二氧化鈦的均勻度、堅硬度及耐久度，且並非每一種基材都可直接塗佈二氧化鈦。在日本已有廠商提供專門的塗佈技術，為客戶所需的環境或物品塗佈二氧化鈦。日本學者的研究著重於弱紫外光搭配二氧化鈦反應的影響。目前的研究目標則是開發以可見光為主要能量光源的二氧化鈦光觸媒，使光觸媒技術能更有效應用於日常生活上；在此方面也提及在醫療上的應用，如果能採用 450nm 或 500nm 的可見光能量搭配二氧化鈦滅菌，可使生物體在較安全的狀況下進行醫療的工作。此外，目前已開發許多光觸媒商品，但由於測試方法的不同，所表現出來的結果也不同，某些產品是否具有廠商說明的功效的確讓人質疑。因此本次會議特別提出標準檢驗方法之窠論，希望未來對光觸媒之活性鑑定有相同之準則。

四、攜回資料名稱及內容

1. 程序冊：介紹研討會各項活動名稱, 時間及地點。
2. 論文集壹冊

Treatment of Petrochemical Wastewater by Electro-Fenton Technology in a Pilot Reactor

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Abstract

The chemical wastewater for this study came from the petrochemical plant, which mainly produced aromatic compounds, organic acid, epoxidized soybean oil (ESBO), poly vinyl alcohol (PVA), hexamethylene tetramine (HEXA), etc., in Taiwan. The discharging quantity from the plant was about 3000 CMD. The electro-Fenton method was applied for treating the bioeffluent of petrochemical manufacturing wastewater. The major pollutant in the bioeffluent was identified as hexamine, which is nonbiodegradable and contributed 20% of COD to the wastewater. The goal of this study was to treat the biotreatment effluent with more than 50% of COD removal efficiency to meet the Effluent standard of 2003 in Taiwan.

Electro-Fenton and traditional Fenton were employed to treat this effluent for comparison. The onsite pilot reactor was operated at continuous mode for 800 hours. Results show that wastewater treated by traditional Fenton process could not meet the effluent standard in the range of operating conditions. However, more than 80% of COD was removed with the electro-Fenton process and the effluent quality can meet the standard; the consumed energy was 65 kWh/m³.

Keywords: Electro-Fenton process; electrolysis; petrochemical wastewater; pilot reactor

Introduction

Innovative technologies of wastewater treatment, advanced oxidation processes (AOPs), are developed to treat specific toxic and non-biodegradable organics. It is demonstrated that AOPs have been proven as an effective technology for treating hazardous organics in aqueous solution. Pignatello *et al.*, (2006) have already reviewed numerous AOPs investigation, including homogeneous Fenton and electro-Fenton reactions with various organic compounds. There is no study focusing on the treatment of petrochemical wastewater by Fenton or electro-Fenton processes.

Petrochemical wastewater often contains a high concentration of biodegradable compounds that possess either toxicity or activity inhibition to the biological unit. Numerous streams of wastewaters contain significant amounts of toxic organic compounds. While the wastewater contains toxic, inhibitory or refractory to biological cultures, chemical oxidation can pretreat the wastewater to produce biogenic intermediates. Conversely, biological pretreatment can initially remove the biodegradable fraction of

wastewater containing a mixture of refractory and biogenic compounds, and thereby conserve subsequent use of expensive chemical oxidant for the small remaining recalcitrant fraction. Consequently, there were used potential advantages of Fenton and electro-Fenton processes treating of petrochemical wastewater.

The Fenton process, one of the advanced oxidation processes (AOPs), is widely used as a suitable treatment method for highly concentrated wastewater due to its effectiveness in producing hydroxyl radical (Barbeni *et al.*, 1987; Kang *et al.*, 2002; Rivas *et al.*, 2001). It combines hydrogen peroxide and ferrous salt to produce hydroxyl radical with powerful oxidizing abilities to degradation certain toxic contaminants (Kitis *et al.*, 1999; Lu *et al.*, 2001; Yoon *et al.*, 2001). One of the drawbacks for Fenton method is the production of a significant amount of ferric hydroxide sludge that needs further separation and disposal.

Therefore, this paper presents a pilot scale electro-Fenton process, which is utilizing H_2O_2 and electrogenerated ferrous ion (Pratap and Lemley, 1994; Huang *et al.*, 1997). The bench and pilot scale Fenton processes were carried out for comparing the feasibility of traditional Fenton and electro-Fenton processes.

Materials and Methods

Site description

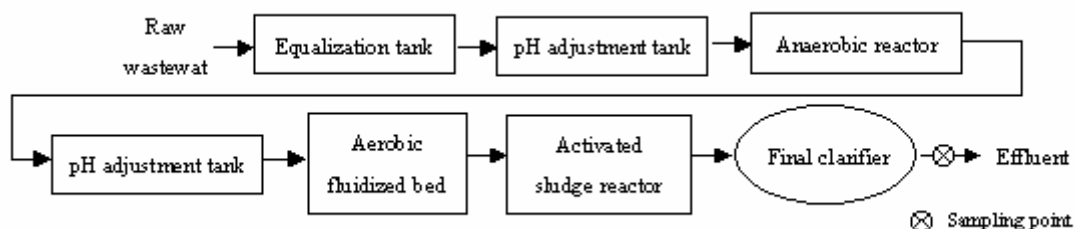


Figure 1. The flowchart of the biotreatment process in the petrochemical plant

Fig. 1 shows the unit of biotreatment process in this plant and sampling points. The raw wastewater was treated by two upflow anaerobic sludge beds (UASB), and then discharged in one adjustment tank for low strength wastewater. Subsequently, the mixing wastewater was treated through an aerobic fluidized bed reactor and an activated sludge reactor. The sampling points were located at the discharge of final clarifier for the aerobic biotreatment process. The average COD concentration of the bioeffluent was 250 ~ 400 mg/L.

Electro-Fenton and traditional Fenton methods

A batch-scale Fenton process and a pilot-scale electro-Fenton process were operated at room temperature.

The dimensions of electrolytic reactor was 10 cm (L) x 10 cm (W) x 10 cm (H). Both the anode and the

cathode were stainless steel. The initial COD concentrations of bench-scale trials were all controlled at 200 ~ 255 mg/L. The electro-Fenton method was performed by continuously feeding the wastewater, which was controlled at pH = 3.5 in the pH adjustment tank. H₂O₂ was continuously added to the electrolytic reactor for treating the wastewater at constant current mode.

Results and discussion

Characteristics of raw wastewater

Table 1. The composition of petrochemical wastewater treated in this study

| Stream | Composition |
|-------------------------------|--|
| PVB | N-butanal, PVB product, Anion |
| PVA | MeOH, Acetate, PVA, Aldehy |
| BUAC | Butanol, Solvent |
| Hexa | Formaldehyde, NH ₄ -N, Hexa methyltetramine |
| ESBO | Oil, Organic acid, Anion |
| Acrylic | Styrene, MMA |
| TMP | Ketone, Formaldehyde, N-butanal |
| H ₂ O ₂ | Aromatic solvent, H ₂ O ₂ |

Table 2. The qualities of bioeffluent

| pH | Cl ⁻ (mg/L) | COD _t (mg/L) | COD _s (mg/L) |
|-----------|------------------------|-------------------------|-------------------------|
| 7.32~8.20 | 103~128 | 226~435 | 231~398 |

The wastewater for this study came from the petrochemical plant in Taiwan, which mainly produced wastewater containing organic acid, epoxidized soybean oil (ESBO), poly vinyl alcohol (PVA), hexamethylene tetramine (HEXA), etc. The discharge quantity of treated wastewater from the plant was about 3000 CMD. Table 1 lists the composition of petrochemical wastewater. The characteristics of raw wastewater generally contained 3000 mg/L COD. The effluent qualities of the biotreatment process are shown in Table 2.

Treatment by traditional Fenton process

As mentioned above, COD concentration in the aerobic biotreatment process was about 220–400 mg/L. It should contain a large amount of recalcitrant organics in wastewater, and the effluent did not meet the effluent standard. Thus, the Fenton process was applied for promoting the COD removal ratio.

Fenton process was employed to treat bioeffluent by jar tests only. The reaction time was set at 30 minutes and the reaction pH was 3.5. Fig. 2 shows the effect of H₂O₂ dosage ranging from 0 to 600 mg/L COD removal. It was found that the maximum COD removal efficiency was 40 %, 600 mg/L of H₂O₂ and 1200

mg/L of Fe(II). Fig. 3 shows the effect of reaction time on the COD removal efficiency. Apparently, increasing the reaction time at optimum dosage still cannot meet the effluent standard. This result indicates that only applying Fenton process is not enough to comply with the regulation.

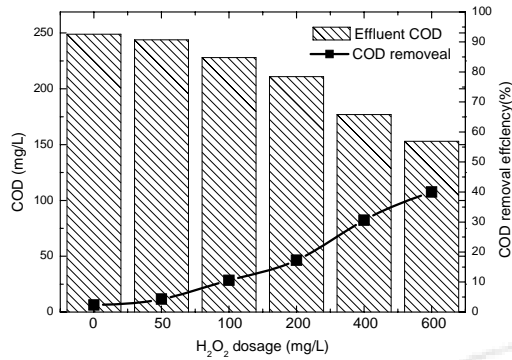


Figure. 2. Effect of H₂O₂ dosage on the COD removal efficiency for Fenton process (COD_t=255 mg/L, COD_s=255 mg/L, pH=3.5, reaction time 30 min, [Fe²⁺]/[H₂O₂]=2)

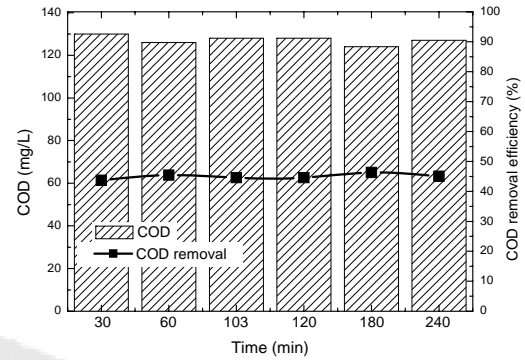
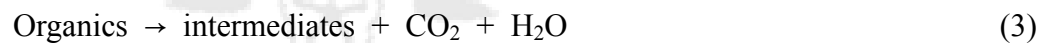


Figure. 3. Effect of reaction time on the COD removal efficiency for Fenton process (COD_t=266 mg/L, COD_s=231 mg/L, pH=3.5, [Fe²⁺]=1200 mg/L, [H₂O₂]=600 mg/L)

Treatment by electro-Fenton process

Electro reactions on both anode and cathode are shown by equations (1) ~ (5).



In the solution phase, organic contaminants react with OH· produced according to Fenton's reaction and then are oxidized.

Table 3. The experimental conditions of the batch-scale electro-Fenton process

| pH | HRT (hr) | Current (A) | Voltage (V) | Influent COD (mg/L) |
|-----|----------|-------------|-------------|---------------------|
| 3.0 | 2 | 0.6 | 6 | 255 |

Feasibility and treatability studies using this electro-Fenton method to treat bioeffluent were performed in batch-scale and pilot-scale processes, respectively. Table 3 lists the experimental conditions of the batch-scale electro-Fenton process. This finding suggests that more than 80 % of COD was removed, where the theoretical H_2O_2 dosage (i.e. 600 mg/L) was used, as shown in Fig. 4. The above screening tests indicate that only the electro-Fenton process can meet the treatment goal. Fig. 5 indicates the changes of influent and effluent COD concentrations and COD removal efficiency of this process during the operation. The influent COD concentrations ranged from 307 mg/L to 420 mg/L. The applied average H_2O_2 dosage, current and average total voltage were 940 mg/L, 4.4 amperes and 9 volts, respectively. The final pH values of the effluent ranged from 6.0 to 7.0 after neutralization, while the pH of the electrochemic cell ranged from 2.1 to 3.2. The final effluent COD concentrations ranged from 86 mg/L to 214 mg/L with an average COD removal efficiency of 58 %.

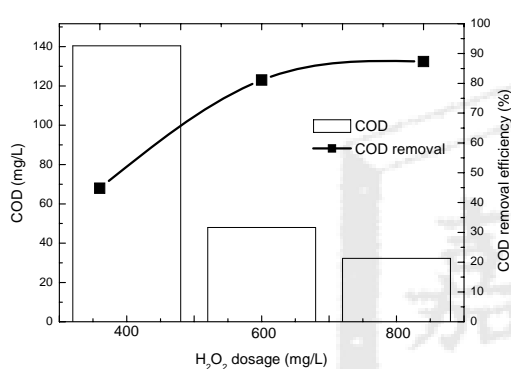


Figure 4. Effect of H_2O_2 dosage on the COD removal efficiency for Electro-Fenton process ($COD_t=254.4$ mg/L, $pH=3.5$, reaction time 180 min)

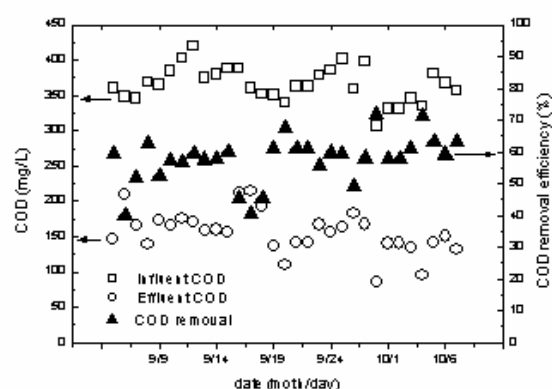


Figure 5. COD removal efficiency of the on-site electro-Fenton process ($COD_{avg}=366$ mg/L, $H_2O_{2,avg}=940$ mg/L, $pH_{avg}=3.02$)

Conclusions

The electrode can keep stable at continuous operation for 792 hours. Traditional Fenton process could not treat this biotreatment effluent of petrochemical wastewater with more than 50% of COD removal efficiency. Only the novel electro-Fenton method is effective in treating this wastewater. It is revealed that the electro-Fenton process could polish the effluent of the current biotreatment to meet the effluent standard in Taiwan.

Acknowledgement

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Application of Goethite/Hydrogen Peroxide on the Treatment of Chlorophenols

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Keywords: Goethite, Hydrogen Peroxide, AOPs, Chlorophenols

Abstract

The use of goethite and hydrogen peroxide was recently found that they could effectively oxidize organic compounds. This research was to investigate the effect of adsorption, pH, Fe^{2+} and Fe^{3+} on the 2-CP oxidation. Results indicated that 2-CP can be decomposed with hydrogen peroxide catalyzed by goethite and the oxidation rate increased with decreasing goethite particle size. The optimum oxidation rate was observed at the pH below 3.0. Addition of Fe^{2+} and Fe^{3+} can enhance the catalytic oxidation rate of 2-CP very efficiently. The main mechanism of goethite catalyzing hydrogen peroxide to oxidize 2-CP may be due to the catalysis of ferrous ions and goethite surface.

1. INTRODUCTION

Fenton process, a widely used and studied catalytic treatment system, has been applied to treat various wastes such as those found in the textile and chemical industries. It was first used to reduce odor in wastewater treatment plants, and from then on, hydrogen peroxide entered the realm of wastewater treatment. The Fenton system uses ferrous ions to react with hydrogen peroxide, subsequently producing hydroxyl radicals with a powerful oxidizing ability to degrade various toxic contaminants (Lipczynskakochany, Sprah et al. 1995; Spacek, Bauer et al. 1995; Miller, Valentine et al. 1996). Recent observations that various organic contaminants in water or soil can be oxidized by H_2O_2 in the presence of iron oxide minerals (Tyre, Watts et al. 1991; Watts, Udell et al. 1993; Ravikumar and Gurol 1994; Gates and Siegrist 1995; Lin and Gurol 1995) provided the motivation for this work. Furthermore, H_2O_2 and iron oxides are common constituents of natural and atmospheric waters (Moffett and Zika 1987; Cunningham, Goldberg et al. 1988).

Besides, contaminants may be oxidized into biologically degradable matter by just adding hydrogen peroxide, and oxygen produced from hydrogen peroxide enhances the decomposition abilities of microorganisms. It can also be used on soil remediation, because ferrous ions are often present in groundwater (Tyre, Watts et al. 1991; Kong, Watts et al. 1998). This study has focused on goethite (α -FeOOH) since it was found to be most reactive with H_2O_2 among the crystalline iron oxides tested (Gurol, Lin et al. 1997). Goethite, which has a very low solubility in water, is also the most abundant crystalline iron oxide mineral in nature (Bolt and van Riemsdijk 1987; Stumm and Morgan 1996). Recently, the use of goethite and hydrogen peroxide was found that they could effectively oxidize organic compounds due to the catalysis of goethite surface and ferrous ion generation. Gurol and Ravikumar (1994) pointed out that hydrogen peroxide can oxidize pentachlorophenol and trichloroethylene adsorbed on sand particles by interacting with the natural iron content of sand particles. Lin and Gurol (1997) also found that n-butyl chloride was oxidized by hydroxyl radicals generated from the interaction of hydrogen peroxide with goethite particles. In previous studies, ferrous ions and hydrogen peroxide have been used to oxidize dichlorvos with an attempt to explore the behavior of dichlorvos oxidation and how factors such as pH, $[H_2O_2]$ and $[Fe^{2+}]$ may influence the dichlorvos decomposition (Lu, Chen et al. 1997).

This study was to investigate the oxidation of 2-Chlorophenols (2-CP) with hydrogen peroxide in the presence of goethite. 2-CP was selected as the model compound to explore the effect of goethite particle size and pH on the oxidation efficiency. Fe^{2+} and Fe^{3+} were also added to study their effect on the 2-CP oxidation to provide insight into the mechanism of catalytic decomposition of H_2O_2 on goethite in aqueous medium.

2. MATERIAL AND METHODS

Goethite used in this study was purchased from Aldrich. Goethite particles have a diameter between 0.21 and 0.044 μm . The density of granular goethite were ranged from 3.99 to 4.58 g/cm^3 . The concentration of the replaceable surface hydroxyl groups of the goethite was determined to be 5×10^{-4} mol/g. All other chemicals were of reagent grade. Solutions containing goethite and 2-CP were prepared and then were poured into 250 ml flasks after the pH adjustment. In homogeneous solutions of hydrogen peroxide and iron salts, the pH was observed to have a significant effect on the decomposition of hydrogen peroxide and the oxidation efficiencies of organic chemicals. In this study, we therefore selected initial pH of 3 as the reaction condition using solution of $HClO_4$ but did not control a constant pH during the period of oxidation reaction. The pH variation during the reaction was $< \pm 0.1$ pH unit. A

thermal oscillator tank was used to maintain completely mixed at 30°C with a constant speed. The oxidation reaction was initiated after adding hydrogen peroxide. Samples were regularly taken to be filtered through Whitman filter papers upon withdrawal to separate goethite from the solutions, and the residual quantities of 2-CP were measured by an HPLC (Waters LC module 1). The total dissolved Fe was measured by an AA (Hitachi, z-8100) and ferric and ferrous ions was measured by colorimetric procedure. Hydrogen peroxide was analyzed by was analyzed by an iodometric titration with Na₂S₂O₃ solution (17). A DO meter (MTW Microprocessor Oximeter OXI 196) was used to monitor the concentration of dissolved oxygen.

3. RESULTS AND DISCUSSION

The effect of goethite adsorption

In our previous studies, 2-CP can be decomposed with hydrogen peroxide catalyzed by goethite before 500 min and oxidation rate increased with decreasing goethite particle size. Based on the results, it is three-stage reaction; the initial decomposition rate 2-CP was slow, and then it slightly increased after 90min. After the transition step, a rapid oxidation rate of 2-CP was observed. The amount of 2-CP adsorbed onto goethite surface was less than 10% under various particle size of goethite at initial pH 3.0 as shown in Fig. 1. It is clear that the removal of 2-CP from solution is not due to the adsorption.

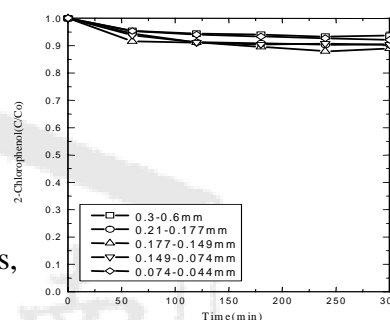


Figure 1: Effect of particle size for the 2-CP sorption on the goethite. Experimental conditions: [2-CP]= 3.9×10^{-4} M; [α -FeOOH]=0.2 g/L; [NaClO₄]=0.1 M; pH_i=3.0; Temp.=30°C

The effect of pH

The effect of pH on catalytic action of goethite in the oxidation of 2-CP with hydrogen peroxide was examined in a set experiment, the pH slight increased with time of reaction. Only the effect of initial pH on 2-CP decomposition will be discussed here. Typical changes in 2-CP concentration over time are shown in Fig. 2 for the range of pH, i.e. 2.0 to 5.0. The optimum oxidation rate was observed at the pH below 3.0. According to the findings of Sedlak

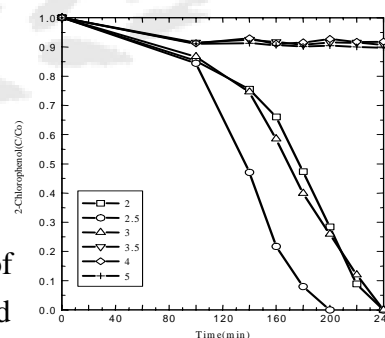


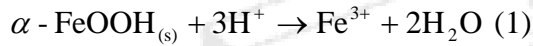
Figure 2: Effect of pH for the 2-CP oxidation. Experimental conditions: [2-CP]= 3.9×10^{-4} M; [α -FeOOH]=0.2 g/L; [NaClO₄]=0.1 M; pH_i=3.0; Temp.=30°C; particle size=0.074 – 0.149 mm.

and Andren (Sedlak and Andren 1991), the most ideal pH for chlorodiphenyl and chlorobenzene is between 2 and 3. Sudouh found the optimum pH of phenol decomposition using Fenton's reagent is between 2 and 3. At high pH, the degradation of 2-CP decreased because ferric ions will form Fe(OH)₃. It has low activity and will not react with hydrogen peroxide (Pignatello 1992). When the pH is too low, the

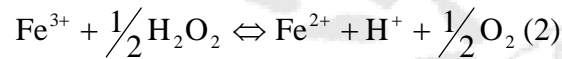
hydrogen ion will cause the formation of FeOOH^{2+} to slow down the reaction, which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well.

The dissolution behavior of goethite

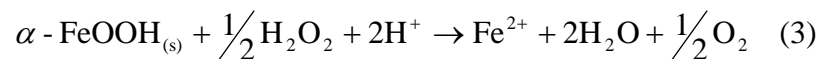
The dissolution of goethite under acidic conditions requires protons which may bind to the surface and weaken critical bonds, resulting in the detachment of the metal species into solution (Stumm 1992). In addition, the dissolution rate increases with decrease of pH and increase of goethite dosage. The phenomenon is known as the proton-promoted dissolution reaction as described below:



Hydrogen peroxide was used as the oxidant in the system. Although there were ferrous ions generated in solution, the total amount of soluble iron did not significantly change with the various H_2O_2 concentration added in the solution without 2-CP (data not shown). Lin and Guro (1998) demonstrated that a low concentration of H_2O_2 does not affect the surface reactivity and the structure of the goethite particle. Ferric ions detached from the surface in acidic solution Eq. (1), and subsequently followed by a homogeneous redox reaction Eq.(2).



Combining Eq. (1) and (2), the following equation is obtained:



To investigate the effect of goethite dissolution on the oxidation rate of 2-CP, ferrous iron were monitored at initial pH 3.0. as shown in Fig. 3. Based on the results, iron ions in the solution were mostly ferrous ions (>90%) during the experiment. Within the 90 min, the ferrous ions were negligible, and then the amount of dissolved ferrous ions slightly increased in the following transition region. The appearance of ferrous ions could be attributed to (1) the interaction between ferric ions and H_2O_2 (Eq.(2)), (2) Organic reductant (2-CP) can react with ferric ion to form a complex and then produce ferrous ions due to electron transformation (Eq.(4))(Dong 1993), and (3) the reductant bind to the surface of goethite to release ferrous ions (Eq. (5-7))(Zinder, Furrer et al. 1986).

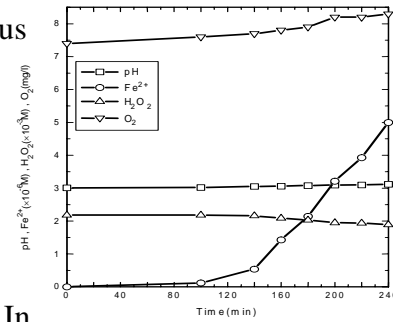
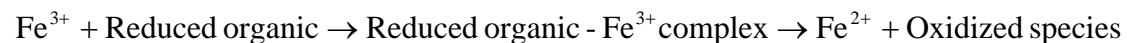
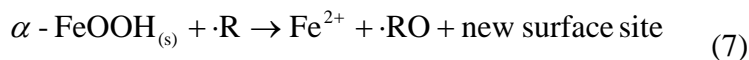
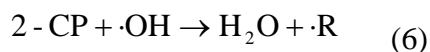
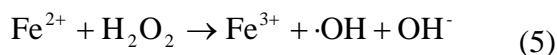


Figure 3: Changes in the concentration of ferrous/ferric ion, hydrogen peroxide, dissolved oxygen and pH. Experimental conditions: [2-CP]= 3.9×10^{-4} M; [α -FeOOH]=0.2 g/L; [H_2O_2]_i= 2.2×10^{-3} M, [NaClO_4]=0.1 M; pH_i=3.0; Temp.=30°C; particle size=0.074 – 0.149 mm.

(4)



The reaction mechanism

The mechanism of goethite catalyzing hydrogen peroxide to oxidize 2-CP are: (1) the surface of goethite catalyzing hydrogen peroxide to produce hydroxyl radicals; (2) the ferrous ions generated from goethite combined with hydrogen peroxide and (3) the ferric ions generated from goethite combined with hydrogen peroxide. Therefore, it was compared the goethite/H₂O₂

process with other systems such as Fe²⁺/H₂O₂, Fe³⁺/H₂O₂, goethite/Fe³⁺/H₂O₂ and goethite/Fe²⁺/H₂O₂ processes. As shown in Fig. 4, the rate of 2-CP degradation using Fe³⁺ is almost zero, and goethite

as the catalyst is lower than that using Fe²⁺. Based on the results, the dissolution should be the main mechanism of goethite catalyzing H₂O₂ to oxidize 2-CP in this study. The proton-promoted dissolution is the initial rate-determining step. After a transition stage, the reductive dissolution of ferrous ions initiates Fenton's reaction, thereby becoming the overall oxidation rate-determining step for the oxidation of 2-CP.

Conclusion

Particle size of goethite and the pH of solution are important factors affecting the oxidation rate of 2-CP, because both of them can influence the concentration of ferrous ions due to goethite dissolution. Smaller size of goethite and acid condition will enhance the degradation of 2-CP with hydrogen peroxide. The main mechanism of goethite catalyzing hydrogen peroxide to oxidize 2-CP may be considered to be the mixture of ferrous salts and hydrogen peroxide, known as Fenton's reagent, producing hydroxyl radicals with powerful oxidizing abilities to degrade 2-CP.

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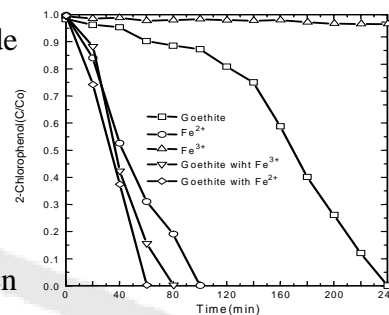


Figure 4: Effect of Catalyst on the 2-CP oxidation. Experimental conditions: [2-CP]=3.9×10⁻⁴ M; [α-FeOOH]=0.2 g/L; [Fe²⁺]=[Fe³⁺]=8.2×10⁻⁶ M, [NaClO₄]=0.1 M; pH=3.0; Temp.=30°C; particle size=0.074 – 0.149 μm.

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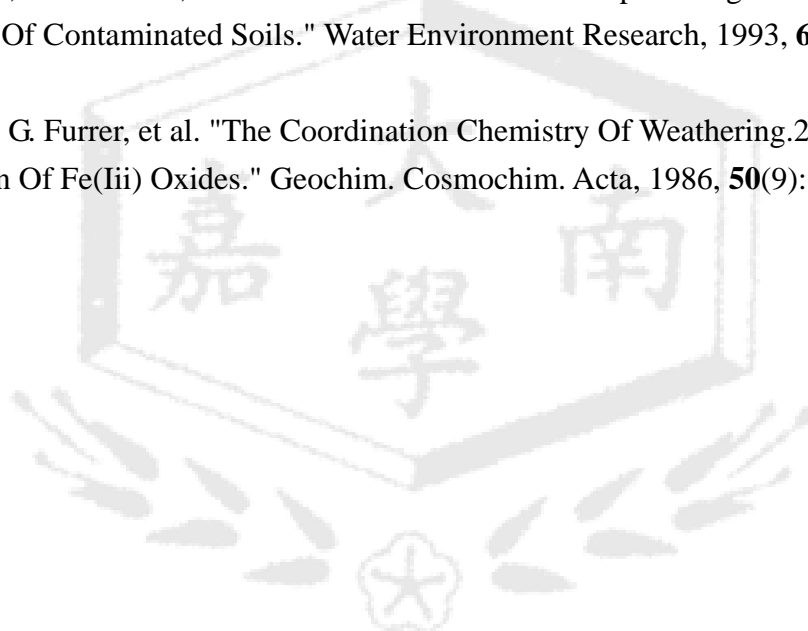
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行政院國家科學委員會補助國內專家學者出席國際學術會議報告

| | | | |
|----------------|--|--------------------|-----------------------------|
| 報 告 人 姓 名 | 盧 明 俊 | 服 務 機 構 及 職 稱 | 嘉南藥理科技大學 環境資源管理系 專任教授 |
| 會 議 時 間 地 點 | 95 年 9 月 25 日 至 28 日 美 國 , 匹 茲 堡 | 本 會 核 定 補 助 文 號 | |
| 會 議 名 稱 | 第十二屆國際高級氧化技術處理水、空氣及土壤研討會 The 12 th International Conference on Advanced Oxidation Technologies for Treatment of Water, Air and Soil | | |
| 發 表 論 文 題 目 | 1. Treatment of Petrochemical Wastewater by Electro-Fenton Technology in a Pilot Reactor 2. Application of Goethite/Hydrogen Peroxide on the Treatment of Chlorophenols | | |

一、參加會議經過：

本人 9 月 24 日搭乘華航 CI008 到洛山機轉全美航空於當地時間 9 月 25 日早上六點到達匹茲堡，會議結束後於 9 月 29 日飛往舊金山轉搭 CI003 回台灣本次研討會是由氧化還原技術公司舉辦，除原有之高級氧化技術研討會，並與光觸媒技術研討會及地下水現場處理技術研討會在相同場地舉行。內容共有兩大部份：口頭報告及海報發表論文發表地點在 Omni William Penn Hotel 17 樓進行不同主題論文的發表，9 月 25 日上午 8 點開始第一場發表會。本研討會海報論文發表，在 17 樓另闢大廳展示。此外現場亦有許多顧問工程公司或製造廠商在現場展覽。本人的兩篇論文分別於 9 月 27 日 15:40 至 16:05 及 9 月 28 日 10:20 至 10:45 發表。其餘時段則選擇相關主題，進入相關會場聽取簡報。

二、與會心得

奈米微粒粒徑介於 1-100nm 之間，而其特有的尺寸效應、量子侷限效應及表面效應，應用在二氧化鈦奈米材料上，可大幅提升其物性、化性及光電性質。二氧化鈦光觸媒的效率決定因素有很多，以觸媒本身性質而言，採用較大的比表面積且粒徑較一致的二氧化鈦，可接受較多且較穩定的光照量，有利於催化反應的進行。

二氧化鈦的「毒化現象」正是目前工業污染物光催化技術最大的瓶頸。在工業污染物的去除技術中，紫外線/二氧化鈦光催化程序能有效處理易分解性的有機污染物，醇類、酮類及醛類的低碳鏈化合物，但在處理對人體毒害性較強的難分解性有機物，例如苯類、酚類或其他長碳鏈

的聚合物，光分解後的中間產物有可能比之前的化合物更具毒性、更難分解；此外，中間產物更可能會吸附在二氧化鈦的表面，且不易脫附去除，最後造成觸媒活性喪失、毒化觸媒。

塗佈固定技術會影響二氧化鈦的均勻度、堅硬度及耐久度，且並非每一種基材都可直接塗佈二氧化鈦。在日本已有廠商提供專門的塗佈技術，為客戶所需的環境或物品塗佈二氧化鈦。日本學者的研究著重於弱紫外光搭配二氧化鈦反應的影響。目前的研究目標則是開發以可見光為主要能量光源的二氧化鈦光觸媒，使光觸媒技術能更有效應用於日常生活上；在此方面也提及在醫療上的應用，如果能採用 450nm 或 500nm 的可見光能量搭配二氧化鈦滅菌，可使生物體在較安全的狀況下進行醫療的工作。此外，目前已開發許多光觸媒商品，但由於測試方法的不同，所表現出來的結果也不同，某些產品是否具有廠商說明的功效的確讓人質疑。因此本次會議特別提出標準檢驗方法之窠論，希望未來對光觸媒之活性鑑定有相同之準則。

四、攜回資料名稱及內容

1. 程序冊：介紹研討會各項活動名稱, 時間及地點。
2. 論文集壹冊

Treatment of Petrochemical Wastewater by Electro-Fenton Technology in a Pilot Reactor

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Abstract

The chemical wastewater for this study came from the petrochemical plant, which mainly produced aromatic compounds, organic acid, epoxidized soybean oil (ESBO), poly vinyl alcohol (PVA), hexamethylene tetramine (HEXA), etc., in Taiwan. The discharging quantity from the plant was about 3000 CMD. The electro-Fenton method was applied for treating the bioeffluent of petrochemical manufacturing wastewater. The major pollutant in the bioeffluent was identified as hexamine, which is nonbiodegradable and contributed 20% of COD to the wastewater. The goal of this study was to treat the biotreatment effluent with more than 50% of COD removal efficiency to meet the Effluent standard of 2003 in Taiwan.

Electro-Fenton and traditional Fenton were employed to treat this effluent for comparison. The onsite pilot reactor was operated at continuous mode for 800 hours. Results show that wastewater treated by traditional Fenton process could not meet the effluent standard in the range of operating conditions. However, more than 80% of COD was removed with the electro-Fenton process and the effluent quality can meet the standard; the consumed energy was 65 kWh/m³.

Keywords: Electro-Fenton process; electrolysis; petrochemical wastewater; pilot reactor

Introduction

Innovative technologies of wastewater treatment, advanced oxidation processes (AOPs), are developed to treat specific toxic and non-biodegradable organics. It is demonstrated that AOPs have been proven as an effective technology for treating hazardous organics in aqueous solution. Pignatello *et al.*, (2006) have already reviewed numerous AOPs investigation, including homogeneous Fenton and electro-Fenton reactions with various organic compounds. There is no study focusing on the treatment of petrochemical wastewater by Fenton or electro-Fenton processes.

Petrochemical wastewater often contains a high concentration of biodegradable compounds that possess either toxicity or activity inhibition to the biological unit. Numerous streams of wastewaters contain significant amounts of toxic organic compounds. While the wastewater contains toxic, inhibitory or refractory to biological cultures, chemical oxidation can pretreat the wastewater to produce biogenic intermediates. Conversely, biological pretreatment can initially remove the biodegradable fraction of

wastewater containing a mixture of refractory and biogenic compounds, and thereby conserve subsequent use of expensive chemical oxidant for the small remaining recalcitrant fraction. Consequently, there were used potential advantages of Fenton and electro-Fenton processes treating of petrochemical wastewater.

The Fenton process, one of the advanced oxidation processes (AOPs), is widely used as a suitable treatment method for highly concentrated wastewater due to its effectiveness in producing hydroxyl radical (Barbeni *et al.*, 1987; Kang *et al.*, 2002; Rivas *et al.*, 2001). It combines hydrogen peroxide and ferrous salt to produce hydroxyl radical with powerful oxidizing abilities to degradation certain toxic contaminants (Kitis *et al.*, 1999; Lu *et al.*, 2001; Yoon *et al.*, 2001). One of the drawbacks for Fenton method is the production of a significant amount of ferric hydroxide sludge that needs further separation and disposal.

Therefore, this paper presents a pilot scale electro-Fenton process, which is utilizing H_2O_2 and electrogenerated ferrous ion (Pratap and Lemley, 1994; Huang *et al.*, 1997). The bench and pilot scale Fenton processes were carried out for comparing the feasibility of traditional Fenton and electro-Fenton processes.

Materials and Methods

Site description

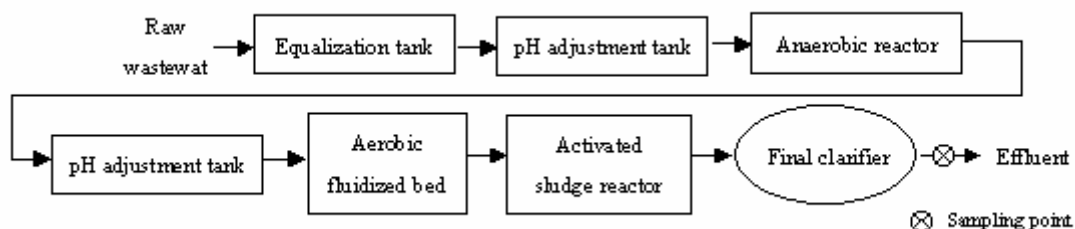


Figure 1. The flowchart of the biotreatment process in the petrochemical plant

Fig. 1 shows the unit of biotreatment process in this plant and sampling points. The raw wastewater was treated by two upflow anaerobic sludge beds (UASB), and then discharged in one adjustment tank for low strength wastewater. Subsequently, the mixing wastewater was treated through an aerobic fluidized bed reactor and an activated sludge reactor. The sampling points were located at the discharge of final clarifier for the aerobic biotreatment process. The average COD concentration of the bioeffluent was 250 ~ 400 mg/L.

Electro-Fenton and traditional Fenton methods

A batch-scale Fenton process and a pilot-scale electro-Fenton process were operated at room temperature.

The dimensions of electrolytic reactor was 10 cm (L) x 10 cm (W) x 10 cm (H). Both the anode and the

cathode were stainless steel. The initial COD concentrations of bench-scale trials were all controlled at 200 ~ 255 mg/L. The electro-Fenton method was performed by continuously feeding the wastewater, which was controlled at pH = 3.5 in the pH adjustment tank. H₂O₂ was continuously added to the electrolytic reactor for treating the wastewater at constant current mode.

Results and discussion

Characteristics of raw wastewater

Table 1. The composition of petrochemical wastewater treated in this study

| Stream | Composition |
|-------------------------------|--|
| PVB | N-butanal, PVB product, Anion |
| PVA | MeOH, Acetate, PVA, Aldehy |
| BUAC | Butanol, Solvent |
| Hexa | Formaldehyde, NH ₄ -N, Hexa methyltetramine |
| ESBO | Oil, Organic acid, Anion |
| Acrylic | Styrene, MMA |
| TMP | Ketone, Formaldehyde, N-butanal |
| H ₂ O ₂ | Aromatic solvent, H ₂ O ₂ |

Table 2. The qualities of bioeffluent

| pH | Cl ⁻ (mg/L) | COD _t (mg/L) | COD _s (mg/L) |
|-----------|------------------------|-------------------------|-------------------------|
| 7.32~8.20 | 103~128 | 226~435 | 231~398 |

The wastewater for this study came from the petrochemical plant in Taiwan, which mainly produced wastewater containing organic acid, epoxidized soybean oil (ESBO), poly vinyl alcohol (PVA), hexamethylene tetramine (HEXA), etc. The discharge quantity of treated wastewater from the plant was about 3000 CMD. Table 1 lists the composition of petrochemical wastewater. The characteristics of raw wastewater generally contained 3000 mg/L COD. The effluent qualities of the biotreatment process are shown in Table 2.

Treatment by traditional Fenton process

As mentioned above, COD concentration in the aerobic biotreatment process was about 220–400 mg/L. It should contain a large amount of recalcitrant organics in wastewater, and the effluent did not meet the effluent standard. Thus, the Fenton process was applied for promoting the COD removal ratio.

Fenton process was employed to treat bioeffluent by jar tests only. The reaction time was set at 30 minutes and the reaction pH was 3.5. Fig. 2 shows the effect of H₂O₂ dosage ranging from 0 to 600 mg/L COD removal. It was found that the maximum COD removal efficiency was 40 %, 600 mg/L of H₂O₂ and 1200

mg/L of Fe(II). Fig. 3 shows the effect of reaction time on the COD removal efficiency. Apparently, increasing the reaction time at optimum dosage still cannot meet the effluent standard. This result indicates that only applying Fenton process is not enough to comply with the regulation.

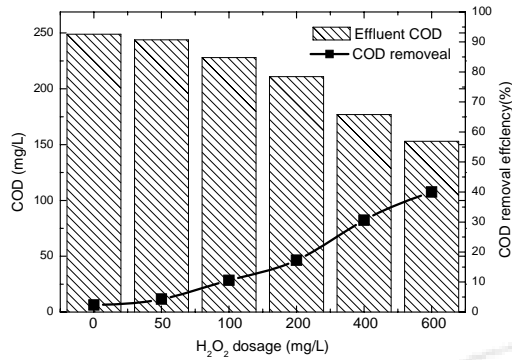


Figure 2. Effect of H₂O₂ dosage on the COD removal efficiency for Fenton process (COD_t=255 mg/L, COD_s=255 mg/L, pH=3.5, reaction time 30 min, [Fe²⁺]/[H₂O₂]=2)

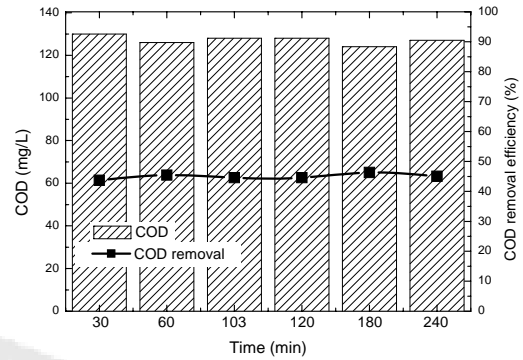
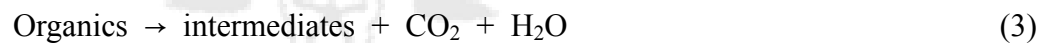


Figure 3. Effect of reaction time on the COD removal efficiency for Fenton process (COD_t=266 mg/L, COD_s=231 mg/L, pH=3.5, [Fe²⁺]=1200 mg/L, [H₂O₂]=600 mg/L)

Treatment by electro-Fenton process

Electro reactions on both anode and cathode are shown by equations (1) ~ (5).



In the solution phase, organic contaminants react with OH· produced according to Fenton's reaction and then are oxidized.

Table 3. The experimental conditions of the batch-scale electro-Fenton process

| pH | HRT (hr) | Current (A) | Voltage (V) | Influent COD (mg/L) |
|-----|----------|-------------|-------------|---------------------|
| 3.0 | 2 | 0.6 | 6 | 255 |

Feasibility and treatability studies using this electro-Fenton method to treat bioeffluent were performed in batch-scale and pilot-scale processes, respectively. Table 3 lists the experimental conditions of the batch-scale electro-Fenton process. This finding suggests that more than 80 % of COD was removed, where the theoretical H_2O_2 dosage (i.e. 600 mg/L) was used, as shown in Fig. 4. The above screening tests indicate that only the electro-Fenton process can meet the treatment goal. Fig. 5 indicates the changes of influent and effluent COD concentrations and COD removal efficiency of this process during the operation. The influent COD concentrations ranged from 307 mg/L to 420 mg/L. The applied average H_2O_2 dosage, current and average total voltage were 940 mg/L, 4.4 amperes and 9 volts, respectively. The final pH values of the effluent ranged from 6.0 to 7.0 after neutralization, while the pH of the electrochemic cell ranged from 2.1 to 3.2. The final effluent COD concentrations ranged from 86 mg/L to 214 mg/L with an average COD removal efficiency of 58 %.

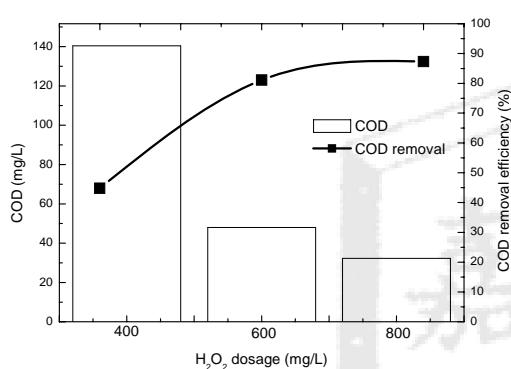


Figure 4. Effect of H_2O_2 dosage on the COD removal efficiency for Electro-Fenton process ($COD_t=254.4$ mg/L, $pH=3.5$, reaction time 180 min)

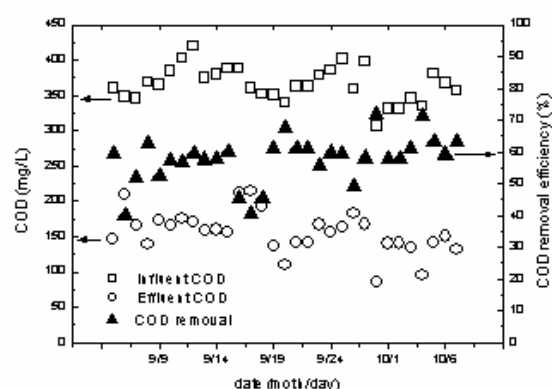


Figure 5. COD removal efficiency of the on-site electro-Fenton process ($COD_{avg}=366$ mg/L, $H_2O_{2,avg}=940$ mg/L, $pH_{avg}=3.02$)

Conclusions

The electrode can keep stable at continuous operation for 792 hours. Traditional Fenton process could not treat this biotreatment effluent of petrochemical wastewater with more than 50% of COD removal efficiency. Only the novel electro-Fenton method is effective in treating this wastewater. It is revealed that the electro-Fenton process could polish the effluent of the current biotreatment to meet the effluent standard in Taiwan.

Acknowledgement

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Application of Goethite/Hydrogen Peroxide on the Treatment of Chlorophenols

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Keywords: Goethite, Hydrogen Peroxide, AOPs, Chlorophenols

Abstract

The use of goethite and hydrogen peroxide was recently found that they could effectively oxidize organic compounds. This research was to investigate the effect of adsorption, pH, Fe^{2+} and Fe^{3+} on the 2-CP oxidation. Results indicated that 2-CP can be decomposed with hydrogen peroxide catalyzed by goethite and the oxidation rate increased with decreasing goethite particle size. The optimum oxidation rate was observed at the pH below 3.0. Addition of Fe^{2+} and Fe^{3+} can enhance the catalytic oxidation rate of 2-CP very efficiently. The main mechanism of goethite catalyzing hydrogen peroxide to oxidize 2-CP may be due to the catalysis of ferrous ions and goethite surface.

1. INTRODUCTION

Fenton process, a widely used and studied catalytic treatment system, has been applied to treat various wastes such as those found in the textile and chemical industries. It was first used to reduce odor in wastewater treatment plants, and from then on, hydrogen peroxide entered the realm of wastewater treatment. The Fenton system uses ferrous ions to react with hydrogen peroxide, subsequently producing hydroxyl radicals with a powerful oxidizing ability to degrade various toxic contaminants (Lipczynskakochany, Sprah et al. 1995; Spacek, Bauer et al. 1995; Miller, Valentine et al. 1996). Recent observations that various organic contaminants in water or soil can be oxidized by H_2O_2 in the presence of iron oxide minerals (Tyre, Watts et al. 1991; Watts, Udell et al. 1993; Ravikumar and Gurol 1994; Gates and Siegrist 1995; Lin and Gurol 1995) provided the motivation for this work. Furthermore, H_2O_2 and iron oxides are common constituents of natural and atmospheric waters (Moffett and Zika 1987; Cunningham, Goldberg et al. 1988).

Besides, contaminants may be oxidized into biologically degradable matter by just adding hydrogen peroxide, and oxygen produced from hydrogen peroxide enhances the decomposition abilities of microorganisms. It can also be used on soil remediation, because ferrous ions are often present in groundwater (Tyre, Watts et al. 1991; Kong, Watts et al. 1998). This study has focused on goethite (α -FeOOH) since it was found to be most reactive with H_2O_2 among the crystalline iron oxides tested (Gurol, Lin et al. 1997). Goethite, which has a very low solubility in water, is also the most abundant crystalline iron oxide mineral in nature (Bolt and van Riemsdijk 1987; Stumm and Morgan 1996). Recently, the use of goethite and hydrogen peroxide was found that they could effectively oxidize organic compounds due to the catalysis of goethite surface and ferrous ion generation. Gurol and Ravikumar (1994) pointed out that hydrogen peroxide can oxidize pentachlorophenol and trichloroethylene adsorbed on sand particles by interacting with the natural iron content of sand particles. Lin and Gurol (1997) also found that n-butyl chloride was oxidized by hydroxyl radicals generated from the interaction of hydrogen peroxide with goethite particles. In previous studies, ferrous ions and hydrogen peroxide have been used to oxidize dichlorvos with an attempt to explore the behavior of dichlorvos oxidation and how factors such as pH, $[H_2O_2]$ and $[Fe^{2+}]$ may influence the dichlorvos decomposition (Lu, Chen et al. 1997).

This study was to investigate the oxidation of 2-Chlorophenols (2-CP) with hydrogen peroxide in the presence of goethite. 2-CP was selected as the model compound to explore the effect of goethite particle size and pH on the oxidation efficiency. Fe^{2+} and Fe^{3+} were also added to study their effect on the 2-CP oxidation to provide insight into the mechanism of catalytic decomposition of H_2O_2 on goethite in aqueous medium.

2. MATERIAL AND METHODS

Goethite used in this study was purchased from Aldrich. Goethite particles have a diameter between 0.21 and 0.044 μm . The density of granular goethite were ranged from 3.99 to 4.58 g/cm^3 . The concentration of the replaceable surface hydroxyl groups of the goethite was determined to be 5×10^{-4} mol/g. All other chemicals were of reagent grade. Solutions containing goethite and 2-CP were prepared and then were poured into 250 ml flasks after the pH adjustment. In homogeneous solutions of hydrogen peroxide and iron salts, the pH was observed to have a significant effect on the decomposition of hydrogen peroxide and the oxidation efficiencies of organic chemicals. In this study, we therefore selected initial pH of 3 as the reaction condition using solution of $HClO_4$ but did not control a constant pH during the period of oxidation reaction. The pH variation during the reaction was $< \pm 0.1$ pH unit. A

thermal oscillator tank was used to maintain completely mixed at 30°C with a constant speed. The oxidation reaction was initiated after adding hydrogen peroxide. Samples were regularly taken to be filtered through Whitman filter papers upon withdrawal to separate goethite from the solutions, and the residual quantities of 2-CP were measured by an HPLC (Waters LC module 1). The total dissolved Fe was measured by an AA (Hitachi, z-8100) and ferric and ferrous ions was measured by colorimetric procedure. Hydrogen peroxide was analyzed by was analyzed by an iodometric titration with Na₂S₂O₃ solution (17). A DO meter (MTW Microprocessor Oximeter OXI 196) was used to monitor the concentration of dissolved oxygen.

3. RESULTS AND DISCUSSION

The effect of goethite adsorption

In our previous studies, 2-CP can be decomposed with hydrogen peroxide catalyzed by goethite before 500 min and oxidation rate increased with decreasing goethite particle size. Based on the results, it is three-stage reaction; the initial decomposition rate 2-CP was slow, and then it slightly increased after 90min. After the transition step, a rapid oxidation rate of 2-CP was observed. The amount of 2-CP adsorbed onto goethite surface was less than 10% under various particle size of goethite at initial pH 3.0 as shown in Fig. 1. It is clear that the removal of 2-CP from solution is not due to the adsorption.

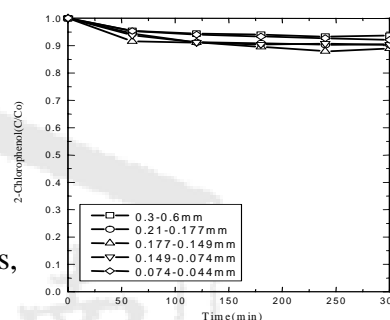


Figure 1: Effect of particle size for the 2-CP sorption on the goethite. Experimental conditions: [2-CP]= 3.9×10^{-4} M; [α -FeOOH]=0.2 g/L; [NaClO₄]=0.1 M; pH_i=3.0; Temp.=30°C

The effect of pH

The effect of pH on catalytic action of goethite in the oxidation of 2-CP with hydrogen peroxide was examined in a set experiment, the pH slight increased with time of reaction. Only the effect of initial pH on 2-CP decomposition will be discussed here. Typical changes in 2-CP concentration over time are shown in Fig. 2 for the range of pH, i.e. 2.0 to 5.0. The optimum oxidation rate was observed at the pH below 3.0. According to the findings of Sedlak

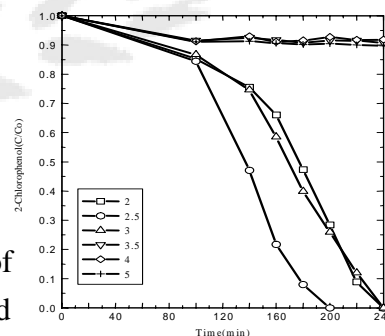


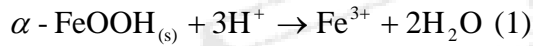
Figure 2: Effect of pH for the 2-CP oxidation. Experimental conditions: [2-CP]= 3.9×10^{-4} M; [α -FeOOH]=0.2 g/L; [NaClO₄]=0.1 M; pH_i=3.0; Temp.=30°C; particle size=0.074 – 0.149 mm.

and Andren (Sedlak and Andren 1991), the most ideal pH for chlorodiphenyl and chlorobenzene is between 2 and 3. Sudouh found the optimum pH of phenol decomposition using Fenton's reagent is between 2 and 3. At high pH, the degradation of 2-CP decreased because ferric ions will form Fe(OH)₃. It has low activity and will not react with hydrogen peroxide (Pignatello 1992). When the pH is too low, the

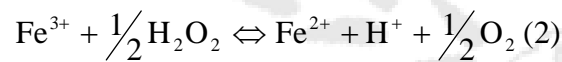
hydrogen ion will cause the formation of FeOOH^{2+} to slow down the reaction, which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well.

The dissolution behavior of goethite

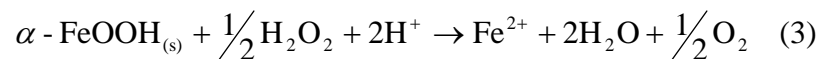
The dissolution of goethite under acidic conditions requires protons which may bind to the surface and weaken critical bonds, resulting in the detachment of the metal species into solution (Stumm 1992). In addition, the dissolution rate increases with decrease of pH and increase of goethite dosage. The phenomenon is known as the proton-promoted dissolution reaction as described below:



Hydrogen peroxide was used as the oxidant in the system. Although there were ferrous ions generated in solution, the total amount of soluble iron did not significantly change with the various H_2O_2 concentration added in the solution without 2-CP (data not shown). Lin and Guro (1998) demonstrated that a low concentration of H_2O_2 does not affect the surface reactivity and the structure of the goethite particle. Ferric ions detached from the surface in acidic solution Eq. (1), and subsequently followed by a homogeneous redox reaction Eq.(2).



Combining Eq. (1) and (2), the following equation is obtained:



To investigate the effect of goethite dissolution on the oxidation rate of 2-CP, ferrous iron were monitored at initial pH 3.0. as shown in Fig. 3. Based on the results, iron ions in the solution were mostly ferrous ions (>90%) during the experiment. Within the 90 min, the ferrous ions were negligible, and then the amount of dissolved ferrous ions slightly increased in the following transition region. The appearance of ferrous ions could be attributed to (1) the interaction between ferric ions and H_2O_2 (Eq.(2)), (2) Organic reductant (2-CP) can react with ferric ion to form a complex and then produce ferrous ions due to electron transformation (Eq.(4))(Dong 1993), and (3) the reductant bind to the surface of goethite to release ferrous ions (Eq. (5-7))(Zinder, Furrer et al. 1986).

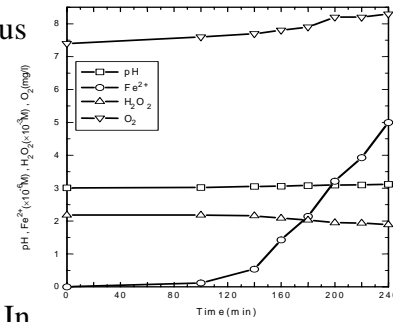
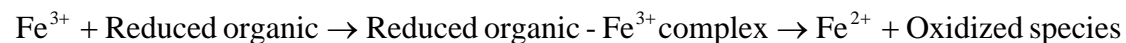
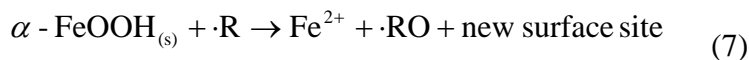
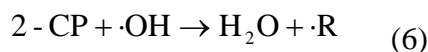
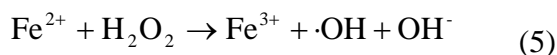


Figure 3: Changes in the concentration of ferrous/ferric ion, hydrogen peroxide, dissolved oxygen and pH. Experimental conditions: [2-CP]= 3.9×10^{-4} M; [α -FeOOH]=0.2 g/L; [H_2O_2]_i= 2.2×10^{-3} M, [NaClO_4]=0.1 M; pH_i=3.0; Temp.=30°C; particle size=0.074 – 0.149 mm.

(4)



The reaction mechanism

The mechanism of goethite catalyzing hydrogen peroxide to oxidize 2-CP are: (1) the surface of goethite catalyzing hydrogen peroxide to produce hydroxyl radicals; (2) the ferrous ions generated from goethite combined with hydrogen peroxide and (3) the ferric ions generated from goethite combined with hydrogen peroxide. Therefore, it was compared the goethite/H₂O₂

process with other systems such as Fe²⁺/H₂O₂, Fe³⁺/H₂O₂, goethite/Fe³⁺/H₂O₂ and goethite/Fe²⁺/H₂O₂ processes. As shown in Fig. 4, the rate of 2-CP degradation using Fe³⁺ is almost zero, and goethite

as the catalyst is lower than that using Fe²⁺. Based on the results, the dissolution should be the main mechanism of goethite catalyzing H₂O₂ to oxidize 2-CP in this study. The proton-promoted dissolution is the initial rate-determining step. After a transition stage, the reductive dissolution of ferrous ions initiates Fenton's reaction, thereby becoming the overall oxidation rate-determining step for the oxidation of 2-CP.

Conclusion

Particle size of goethite and the pH of solution are important factors affecting the oxidation rate of 2-CP, because both of them can influence the concentration of ferrous ions due to goethite dissolution. Smaller size of goethite and acid condition will enhance the degradation of 2-CP with hydrogen peroxide. The main mechanism of goethite catalyzing hydrogen peroxide to oxidize 2-CP may be considered to be the mixture of ferrous salts and hydrogen peroxide, known as Fenton's reagent, producing hydroxyl radicals with powerful oxidizing abilities to degrade 2-CP.

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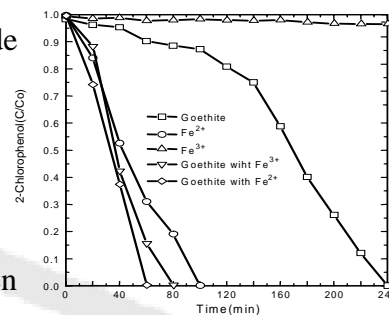


Figure 4: Effect of Catalyst on the 2-CP oxidation. Experimental conditions: [2-CP]=3.9×10⁻⁴ M; [α-FeOOH]=0.2 g/L; [Fe²⁺]=[Fe³⁺]=8.2×10⁻⁶ M, [NaClO₄]=0.1 M; pH=3.0; Temp.=30°C; particle size=0.074 – 0.149 μm.

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