國立交通大學

環境工程研究所

碩士論文

利用 Fenton 處理法降解水中加保扶之研究

Application of Fenton process in the degradation of carbofuran contaminated water

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摘要

加保扶 (carbofuran) 為一種普遍且被廣泛使用的殺蟲劑，主要用途為殺死土壤中昆蟲及害蟲，其使用量約占每年台灣總殺蟲劑使用量 (15,478 噸) 的百分之七，由於加保扶具有高致毒性與高水溶解性 (25^{o}C, 700 mg/L)，因此加保扶的存在與處理問題必須重視。利用 Fenton 法處理廢水中的毒性有機污染物為一高效率且省時、常見的方法，本研究即利用 Fenton 法具備之特性，處理水中不同濃度之加保扶 (10 mg/L 與 50 mg/L)；由於文獻指出 pH 值為 3 的條件下，Fenton 試劑對於有機物的降解效果為最佳，因此本研究透過中央合成設計搭配反應曲面法，進行實驗組數之規劃與結果分析，於固定初始 pH 值為 3 的條件下，分別探討初始加保扶濃度為 10 mg/L 與 50 mg/L 時，亞鐵離子 (0-10 mg/L) 和過氧化氫 (0-200 mg/L) 濃度對於加保扶降解率之影響，目的為決定其最佳化之操作條件。除此之外，本研究亦選擇加保扶降解效率最佳之實驗組，利用 GC-MS 分析其可能之中間產物，並推導其降解過程之反應途徑 (pathway)。

研究結果顯示，加保扶的降解率隨著亞鐵離子和過氧化氫濃度的增加而提升，當添加的亞鐵離子和過氧化氫濃度分別在 5 mg/L 和 100 mg/L 以上時，90% 以上的加保扶可在 5 分鐘內被有效降解。相反地，當水中並無添加過氧化氫或是亞鐵離子的條件下，此時加保扶則無任何被降解的現象。當加保扶的初始濃度為 10 mg/L 時，其最佳的 Fenton 試劑加藥量分別為亞鐵離子 7.4 mg/L 與過氧化氫 143 mg/L，最佳降解率與最佳 Fenton 試劑添加量之關係可由 (方程式) 計

算而得。根據 GC-MS 分析結果可知 7-benzofuranol,2,3,-dihydro-2,2-dimethyl (分子量 164)、7-hydroxy-2,2-dimethyl-benzofuran-3-one (分子量 178) 與 1,4-Benzene-di- carboxaldehyde (分子量 134) 為加保扶被 Fenton 試劑降解之主要中間產物，根據中間產物分析之結果即可推導並獲得加保扶之反應降解途徑。

關鍵字：加保扶、殺蟲劑、Fenton 法、中央合成設計、反應曲面法、反應途徑

Application of Fenton process in the degradation of carbofuran contaminated water

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Abstract

Carbofuran ($C_{12}H_{15}NO_3$) is a broad spectrum, carbamates insecticide widely used to control certain soil-borne insects and nematodes. In Taiwan, carbofuran accounts for about 7% of the 15478 tons of insecticides produced per year. Carbofuran usage has received intensive concern not only due to its heavy use but also due to its high oral toxicity. The wastewater treatment processes using the Fenton reaction are known to be very effective in the removal of many hazardous organic pollutants from water. In this study, Fenton process was applied to remove carbofuran from aqueous system. Fenton experiments were conducted in batch mode at two different carbofuran concentrations i.e. 10 and 50 mg/L and at fixed initial pH of the system i.e. pH 3. Batch experiments at each carbofuran concentrations were designed by central composite design (CCD) with two independent variables i.e. Fe^{2+} and H_2O_2. The efficiency of the experiments was determined based on the percentage removal of carbofuran. Finally, a statistical experimental design and the response surface methodology were used to optimize the Fe^{2+} and H_2O_2 concentrations for maximum percentage removal of carbofuran.

More than 90% of carbofuran removal was observed within 5 min of Fenton reaction with Fe^{2+} concentration above 5 mg/L and H_2O_2 concentration above 100 mg/L. The increase in Fe^{2+} and/or H_2O_2 concentrations beyond 5 and 100 mg/L, respectively, produced 100% carbofuran removal in the Fenton process. No carbofuran removal was observed when either Fe^{2+} or H_2O_2 was absent in the system. Based on the experimental observations, the optimal Fe^{2+} and H_2O_2 dosages required for 10 mg/L of aqueous carbofuran removal were estimated as 7.4 and 143 mg/L, respectively. Carbofuran degradation experiments were repeated at optimal Fe^{2+} and H_2O_2 concentrations and the samples were collected at various time intervals. The collected samples were analyzed in gas chromatography-mass spectrometry (GC-MS) for the determination of carbofuran degradation pathway. The GC-MS analysis indicated that carbofuran was oxidized to 7-benzofuranol,2,3,-dihydro-2,2-dimethyl (m/z 164), 7-hydroxy-2,2-dimethyl-benzofuran-3-one (m/z 178) and 1,4-Benzene-di-carboxaldehyde (m/z 134).

Keywords: Carbofuran; Fenton process; pesticide; degradation pathway

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Chapter 1

Introduction

1.1 Research background

Carbofuran (2,3-dihydro-2,2-dimethylbenzofurarn-7-yl methylcarbamate) is a broad spectrum, carbamates insecticide widely used to control certain soil-borne insects and nematodes. It is used against foliar pests found in fruits, vegetables and forest crops. Residues of the substance, even in small quantities, may accumulate in the surrounding soil and groundwater, becoming the potential source of human contact with these toxic chemicals. The use of carbofuran has received intensive concern not only due to its heavy use but also due to its high oral toxicity. In comparison to parathion an extremely toxic organophosphorus pesticide with a lethal dose for 50% of target species on long term exposure (LD50) of 8 mg kg^{-1}, the LD50 for carbofuran is 11 mg kg^{-1} (Wang *et al.*, 2003).

In Taiwan, carbofuran accounts for about 7% of the 15478 tons of insecticides produced per year (Executive Yuan, ROC, 2006). Carbofuran has been used to control insects of rice, sugarcane, tobacco, maize, potatoes, soybeans and vegetables in Taiwan since its introduction in 1969. It is either applied as a foliar spray or in its granular form. Carbofuran is known to be a more persistent insecticide than the other carbamates or organophosphorus insecticides. However, carbofuran has been found to dissipate easily into the environment. Several physical and chemical treatments are employed for the destruction of aqueous pesticides. Many approaches have been used including chemical oxidation, photo degradation, biological degradation, coagulation, incineration and adsorption, (either independently or jointly) only a few are sufficiently broad-based and convenient to the user (Gupta *et al.*, 2006). Compound specificity slows down the rates of degradation and results in the incomplete metabolism due to the number of pesticides normally observed in the field. Incineration, currently the only practical option in many localities, however, is not economical and requires long-distance transport to a central facility, a key point strongly resisted by the public (Steverson, 1991). Studies have been performed on carbofuran degradation with ozone, ultraviolet (UV) irradiation, hydrogen peroxide (H_2O_2) (Bachman and Patterson, 1999) and sonochemical destruction (Hua and Thompson, 2001). The long residence times of microorganisms to degrade the pollutant in biological treatment, and the secondary emissions of hazardous compounds during thermal treatment make oxidative reactions a promising method to destroy pollutants (Cravotto *et al.*, 2007). Fenton treatment has been investigated in the transformation of various environmentally-important organic compounds, including 2,4-dichlorophenol (Oliveria *et al.*, 2006), aniline (Gunale and Mahajani, 2007), herbicide tebuthiuron (Silva *et al.*, 2007), atrazine (Aronld *et al.*, 1995) and 4-chlorophenoxyacetic acid (Boye *et al.*, 2002). However, thus far, there have only been a few papers on the Fenton application to treat carbofuran.

1.2 Research goals

The primary goal of this study is to assess the efficacy of Fenton process for the treatment of carbofuran contaminated water. In addition, the study was extended to investigate the influences of Fe^{2+} and H_2O_2 in the removal of carbofuran by Fenton process. The key research objectives of the present study are listed below:

- Determination of the optimal Fe^{2+} and H_2O_2 dosages for maximum carbofuran removal in Fenton process at different initial carbofuran concentrations.

- Enumeration of carbofuran degradation pathway in the Fenton process at the optimal conditions.

Chapter 2

Literature review

2.1 Pesticides

Pesticide is a common term used for the chemicals employed for the pest control. Pesticides can be classified into several groups i.e. insecticides, herbicides, fungicides, wood preservatives and disinfectants. The contamination of surface water and wastewater with pesticides is increasing day by day, and presently, it constitutes as a major problem owing to its extensive use in agriculture (Varshney *et al.*, 1995; Hsieh and Kao, 1998; Huston and Pignatello, 1999; Benitez *et al.*, 2002). In addition to the toxic character of the pesticides, the hazardous potential is increased by the possibility of generating organohalogen compounds through their reactions with chloro derivatives, (Benitez *et al.*, 2002). Hence, to meet the worldwide problem of environmental protection and pollution control, it is necessary to detect, separate, identify and determine pesticide residues in the ecosystem. The disposal of pesticide wastes including equipment rinsates is a major concern and the improper disposal of such wastes can lead to the contaminations of soil, groundwater and surface water. Pesticide contamination at farm mixing and loading sites (Habecker, 1989), agrichemical dealer sites (Norwood, 1990) and landfills were reported in the past. Pesticide waste treatment technologies are desired to prevent water pollution and to comply with increasing regulatory pressure (Houston and Pignatello, 1999).

2.1.1 Insecticides

Insecticides are used to kill insect pests by disruption of their vital processes through chemical action. Insecticides may be inorganic or organic molecules and can be classified according to their mode of entry into the insect: stomach poison, contact poison and fumigation. In another way, insecticides can be classified by their mode of action. Pyrethroid, organophosphorus and carbamates insecticides all adversely affect the nervous system. However, based on their chemical composition, synthetic organic insecticides are classified in various ways, namely chlorinated hydrocarbons, cyclodine compounds, carbamates, organophosphates, etc. The target compound selected for the present study i.e. carbofuran, falls under the category of the carbamates group of insecticides.

2.2 Carbofuran

Carbofuran is one of the most toxic carbamates pesticides. It is used to control insects in a wide variety of field crops including potatoes, corn and soybeans. It is a systemic insecticide, which means that initially the plant absorbs it through the roots and later distributes it throughout its organs (mainly vessels, stems and leaves; not the fruit), where insecticidal concentrations are attained. Carbofuran also has contact activity against pests (Wang *et al.*, 2003).

The persistence of carbofuran in water is directly related to the pH of water. Carbofuran is stable in acidic water, but subject to increasing chemical hydrolysis as water becomes more alkaline. Microbial populations in water, sediments and flooded soils also reduce the persistence of carbofuran. Carbofuran is very toxic to fish and its reported LD50 to fish is below 1 mg/L. While accidental spraying of carbofuran poses a threat to the aquatic environment, carbofuran poses a more serious threat in runoff water from fields or orchards immediately after treatment. Killing of localized fish has been reported in such instances (Wang *et al.*, 2003).

The molecular structure of carbofuran is shown in Figure 2-1. Carbofuran is highly soluble in water (700 mg/L at 25 °C) (Worthing, 1991) as well as in other solvents like acetone (150 g/kg) and acetonitrile (140 g/kg). The detailed physical and chemical characteristics of carbofuran are listed in Table 2-1. Risks from exposure to carbofuran are especially high for persons with asthma, diabetes, cardiovascular disease, mechanical obstruction of the gastrointestinal or urogenital tracts, or those with vagotonic conditions (U.S. Department of Agriculture, 1995). As with other carbamates pesticides, carbofuran's cholinesterase-inhibiting effect is short-term and reversible. Several reports showed the chronic toxicity of carbofuran on various test organisms (Kearney and Kaufman, 1975; Hayes and Wayland Jr., 1982). Prolonged or repeated exposure to carbofuran may cause the same symptoms as an acute exposure (U.S. Department of Agriculture, 1995).

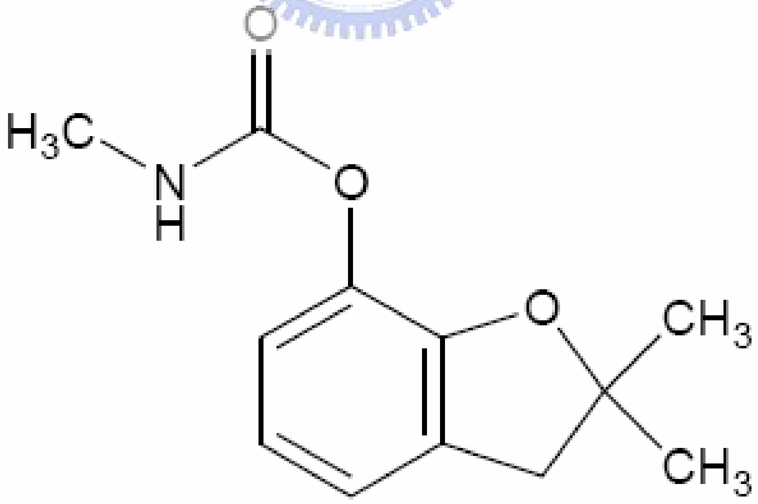

Figure 2-1 Molecular structure of carbofuran

Table 2-1 Physical and chemical properties of carbofuran

Parameters	**Description**
Common name	Carbofuran
IUPAC name	2,3-dihydro-2,2-dimethyl-benzofuran-7-yl methylcarbamate
Molecular weight	221.3 g/mol
Molecular formulae	$C_{12}H_{15}NO_3$
Form	Colorless (white) crystalline solid
Melting point	153-154°C
Vapor pressure	3.4×10^{-6} mm Hg (25°C)
Octanol /Water partition coefficient (Kow) Log Kow	2.32
Solubility	In water 700 mg/L and in acetone 150, acetonitrile 140, benzene 40, cyclohexone 90, dimethylformade 270 and dimethyl sulfoxide 250 (all in g/kg at 25°C).
Stability	It is stable under neutral or acidic conditions but unstable in alkaline media
Henry's constant	3.9×10^{-9} atm m^3/mol
Hydrolysis half-lives	27.7 d (pH 8, 25°C) 0.54 d (pH 9, 25°C)
Aqueous photolysis half-life	7.95×10^3 d (pH 7, 28°C)

(Source: HSDB, 1998; U.S. EPA, 1995)

2.3 Transport and fate of carbofuran in water and soil

Carbofuran is moderately soluble in water. The migration of carbofuran with runoff and its presence in surface water and groundwater have been discussed by many researchers (Nicosia *et al.*, 1991; McCall *et al.,* 1980; Lee *et al.,* 1990). Direct photolysis and photooxidation (via hydroxyl radicals) are thought to be the major pathways of carbofuran degradation in water. The hydrolysis half-lives of carbofuran in water were found to be 5.1 weeks at pH 7.0 and 1.2 h at pH 10. Carbofuran can be degraded to 2-hydroxyfuradan and furadan phenol when exposed to sunlight (HSDB, 1998). When compared with other insecticides, carbofuran is less persistent than organochlorine and most organophosphorus pesticides.

Lee *et al.* (1990) reported that carbofuran is the most mobile of eight major pesticides applied to the soils in Taiwan. Nicosia *et al.* (1991) estimated that more than 11% of soil-applied (around 1 to 5 cm depth) carbofuran was transported with runoff. Carbofuran has a varied persistence rate in different soils with observed half-lives of several days to over three months. The environmental fate of carbofuran depends on the organic content, moisture content and pH of the soil. Rapid carbofuran biodegradation rate was observed in the soil with high organic content. A residue of carbofuran and its breakdown product, 3-hydroxyfuran, have been detected in raw and finished agricultural products. Tolerances have been established for carbofuran and its metabolites in various agricultural commodities and meat products (HSDB, 1998).

2.4 Carbofuran removal methods

A variety of effective treatment techniques such as irradiation, direct photolysis, UV irradiation in the presence of ozone or Fenton reagent, anodic Fenton treatment (AFT) and TiO_2 as a photocatalyst have been proposed for carbofuran removal from drinking water. Table 2-2 summarizes the experimental conditions and the outcomes of above stated methods in aqueous carbofuran removal.

The photodegradation of carbofuran by excitation of Fe^{3+} aquacomplexes under UV irradiation has received considerable attention in the past. Katsumata *et al.* (2004) reported that an initial carbofuran concentration of 10 mg/L was completely degraded within 50 min at pH 2.8 with original Fe^{3+} concentration of 8×10^{-4} mol/L. This reaction was found to follow the first-order kinetics and the rate constant of $1.60 \times 10^{-3}\ s^{-1}$ was observed. The degradation rate was strongly influenced by the pH and the initial concentration of Fe^{3+}. Moreover, the variation of carbofuran removal efficiency at different pH was in good proportion with the initial Fe^{3+} concentration. The decrease of TOC content was observed during the photocatalytic process and the removal percentage obtained was about 70% after 25 h (Katsumata *et al.*, 2004).

Purification of water using TiO_2 as a photocatalyst has attracted a great deal of attention. It has been found that TiO_2 microcystallites can become firmly affixed to the glass plates without any deactivation. As an example, mineralization of 222 mg/L carbofuran was tested by Tennakone *et al.* (1997) and they reported that complete mineralization of carbofuran can be achieved after 15 h of 400 W irradiation at pH 2.8. This method is a low-cost process and plates can be reused without any deactivation. However, the technical limitation of using the powder form of TiO_2 is its separation from the system. AFT is a new Fenton technology for the treatment of pesticide wastewater. The substitution of an ion exchange membrane for the salt-bridge, an improvement to the practicality of the AFT without sacrificing treatment efficiency, has also been reported (Wang *et al.*, 2003). The results showed that the degradation kinetics of carbofuran with different initial concentrations from 6 to 43 mg/L followed the first-order kinetics, and the treatment efficiency increased with increasing initial concentration. The increase in treatment temperature enhanced the degradation of carbofuran in solution. The pseudo-activation energy of carbofuran by membrane AFT was estimated to be 7.66 kJ mol^{-1}. The results also showed that AFT could effectively remove COD and dramatically improve the degradability of carbofuran in solution (Wang *et al.*, 2003).

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Table 2-2 Carbofuran degradation treatment techniques

Reference	**Method**	**Carbofuran conc. (mg/L)**	**Condition**	**Reaction time**	**Carbofuran removal (%)**
Hua and Thompson (2001)	Ultrasonic	30	1800 W, 20 kHz Argon:Oxygen (4:1)	30-60 min	>90
Wang *et al.* (2003)	Anodic Fenton	22	Temp. 25°C	5 min	100
Katsumata *et al.* (2004)	UV + Fe(III)	10	pH 2.8	50 min	>90
Tennakone *et al.* (1997)	TiO_2 + UV	222	Temp. 26°C, pH 2.8, 400 W	6 h	90
Benitez *et al.* (2002)	Ozone + UV	100	Temp. 20°C, pH 2	50 min	>90
Bano and Musarrat (2004)	Pseudomonas sp.	100	Temp. 30°C	40 d	100

2.5 Carbofuran degradation by physico-chemical processes

2.5.1 Carbofuran degradation pathway under AFT

Wang *et al.* (2003) analyzed the degradation products generated after 2 min of membrane AFT in a GC-MS. The results indicated the formation of 2,3-dihydro-2,2-dimethylbenzofuran-7-ol, which is the product formed by the cleavage of the carbamates group from the parent compound. Further, it was oxidized to 2,3-dihydro-2,2-dimethylbenzofuran-7-yl formate and then to 2,3-dihydro-3-oxo-2,2-dimethylbenzofuran-7-ol and 2,3-dihydro-3-hydroxyl-2,2-dimethylbenzofuran-7-ol. In addition to these four compounds, other degradation products still possibly exist in the oxidation system but were not detected because of their low concentration, low extraction efficiency and/or limited sensitivity in GC-MS. With these identified products, a suggested oxidation pathway of carbofuran by membrane AFT is shown in Figure 2-2.

The degradation products of carbofuran i.e. intermediates, stated above were also detected during the hydrolysis (Wei *et al.*, 2001), photolysis (Bachman and Patterson, 1999) and TiO_2 catalyzed photolysis (Kuo and Lin, 2000) of carbofuran. It can be observed from the literatures that carbamates group appears to be the primary attack site by the OH radical and it is also the first group removed during the AFT. After the removal of carbamates group, the OH radical continues to attack by substituting an OH group for one of the H atoms at 3-C of the furan ring. Further oxidation eliminates another H atom at 3-C and a carbonyl group is formed. Based on the decrease of COD during the AFT, it can be anticipated that the furan ring and/or benzene ring is opened and further oxidative products are formed in AFT.

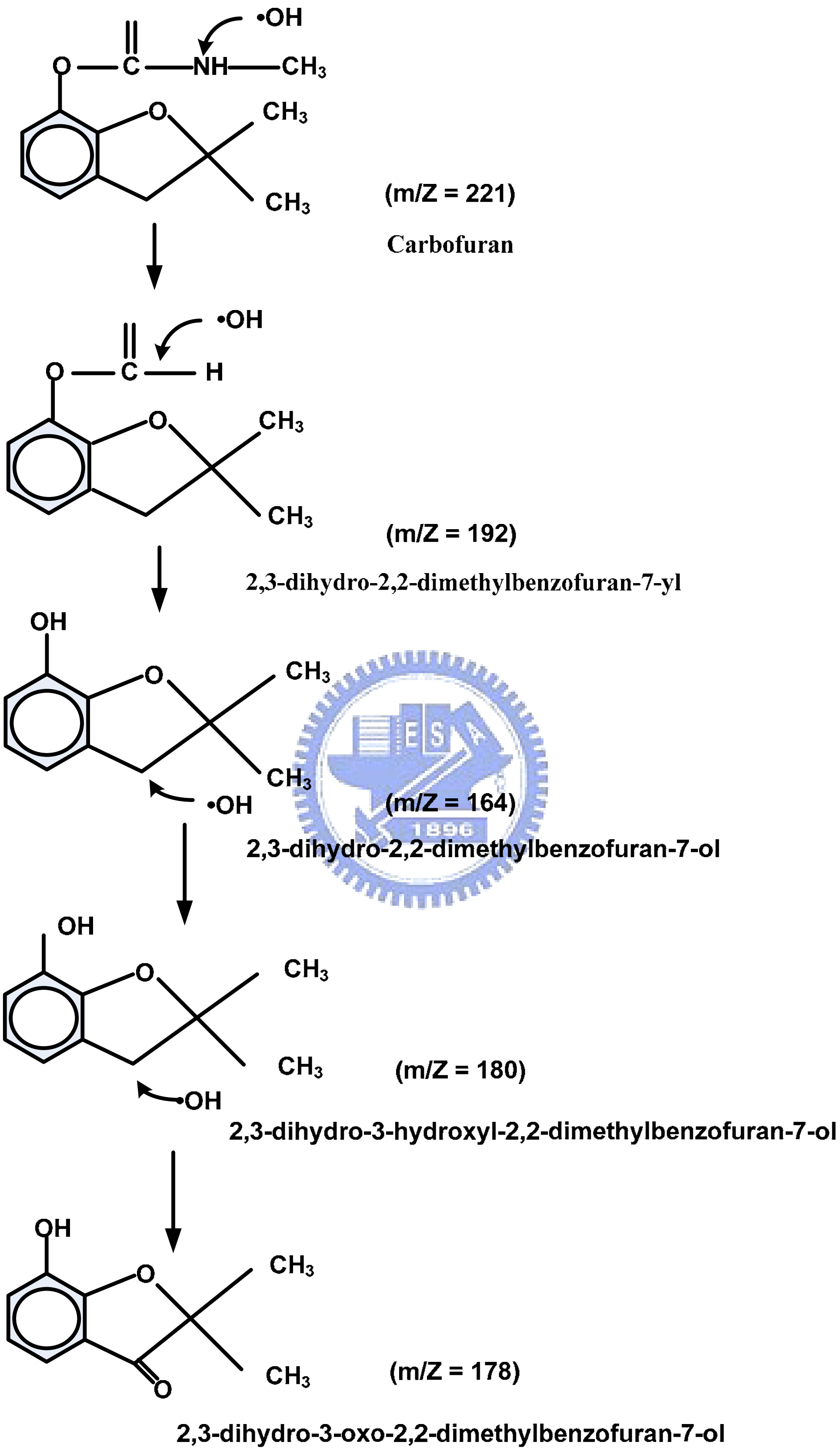

Figure 2-2 Carbofuran degradation pathway under AFT

2.5.2 Carbofuran degradation pathway under photocatalytic process

Katsumata *et al.* (2004) used GC-MS to investigate the photoproducts formed in the photocatalytic degradation of carbofuran in the aqueous solution after 20 min. By interpreting the mass spectrum, the photo-products of carbofuran were assigned as 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol, 7-hydroxy-2,2-dimethyl-benzofuran-3-one, 2,2-dimethyl-2,3-dihydro-benzofuran-3,7-diol and 3-hydroxy-2-methoxy-benzaldehyde. The possible degradation pathway of carbofuran under photocatalytic process is shown in Figure 2-3 (Bachman and Patterson, 1999).

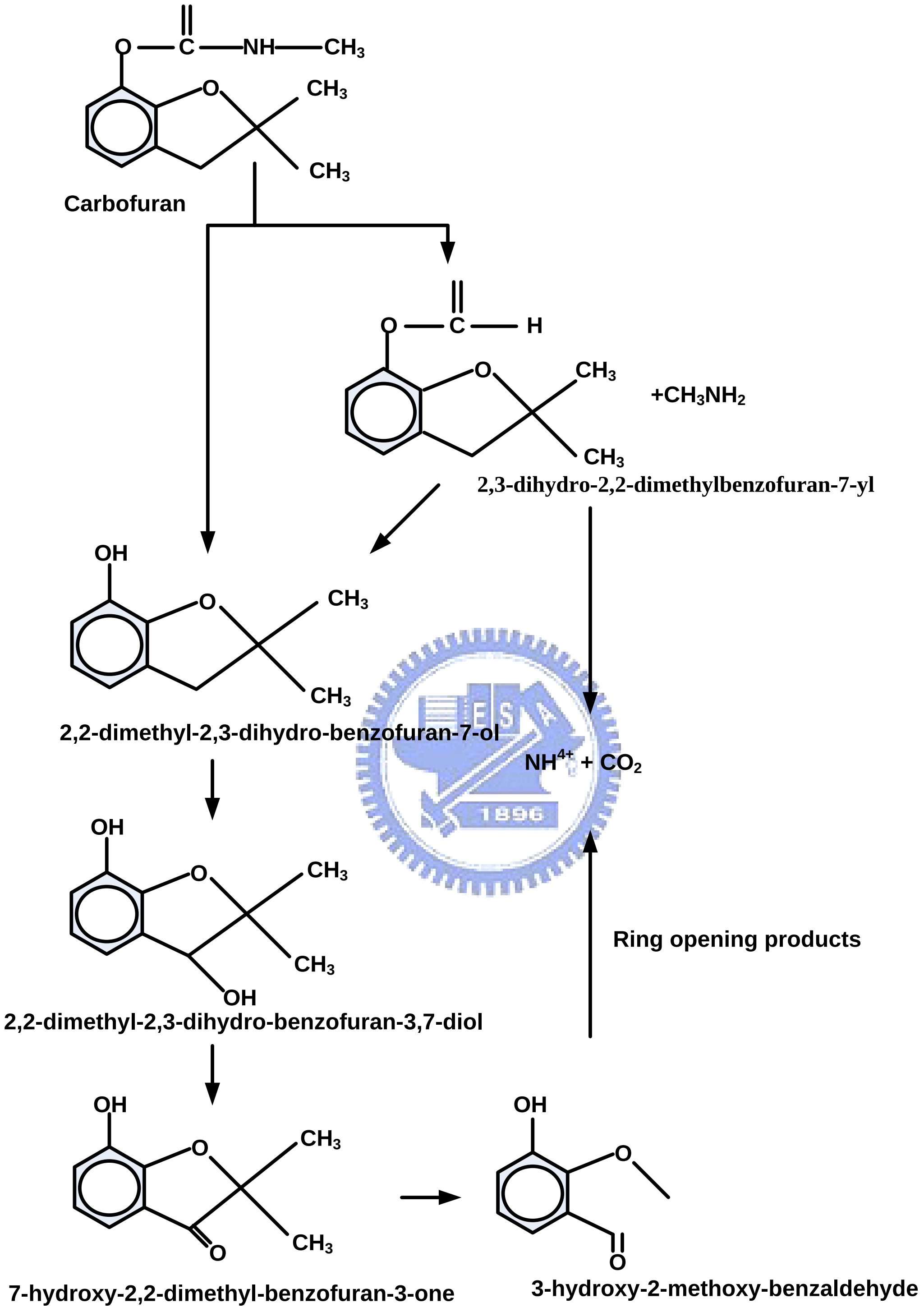

Figure 2-3 Carbofuran degradation pathway under photocatalytic process

2.6 Fenton process

Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Huang *et al.*, 1993). The wastewater treatment processes using the Fenton reaction are known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants (Neyens and Baeyens, 2003).

Fenton's reagent is a mixture of H_2O_2 and ferrous iron (Fe^{2+}), which generates hydroxyl radicals according to the reaction in Eq. 2-1 (Kitis *et al.*, 1999). The ferrous iron initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution.

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

One of the advantages of Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost-effective source of OH radicals. Furthermore, it commonly requires a relatively short reaction time compared with other advanced oxidation processes (AOPs). The Fenton process has been employed successfully to treat different industrial wastewaters, including textile (Fang *et al.*, 2002), paper pulp (P´erez *et al.*, 2002), pharmaceutical (H¨ofl *et al.*, 1997), dyes (Szpyrkowicz *et al.*, 2001), olive oil (Rivas *et al.*, 2001) and petroleum industrial wastewaters (Gao *et al.*, 2004).

2.6.1 Factors affecting Fenton process

The key features of the Fenton process are believed to be its reagent condition, i.e. [Fe^{2+}], [Fe^{3+}], [H_2O_2] and the reaction characteristics (pH, temperature and the quantity of organic and inorganic constituents). Because these parameters determine the overall reaction efficiency, it is important to understand the mutual relationships between these parameters in terms of hydroxyl radical production and consumption (Neyens and Baeyens, 2003).

H_2O_2 concentration

As the concentration of H_2O_2 increases, the degradation of organic compounds also increases because the amount of oxidant present in the reaction system is higher. This finding is in agreement with the results found in other studies (Catalkaya and Kargi, 2007; Bautista *et al.,* 2007; Oliveria *et al*., 2006). However, for higher H_2O_2 loads the degradation efficiency decays. This detrimental effect at high H_2O_2 concentrations can be explained by the fact that hydrogen peroxide competes with the organic matter for the OH radicals, and in this way it reduces the amount of these highly oxidative radicals present in the system (Oliveria *et al.*, 2006). Thus, an increase of H_2O_2 concentration will result in an increase in the rate of radical scavenging, leading to the reduction in treatment efficiency. Glaze *et al.* (1995) and Beltran *et al.* (1996) reported a reduction in pesticide removal at high H_2O_2 concentrations indicating the adverse effects of excess H_2O_2.

Fe^{2+} concentration

The increase in the initial concentration of Fe^{2+} considerably improved the degradation efficiency of herbicide tebuthiuron (Silva *et al.*, 2007). These results can be explained by an increase in the reaction kinetics due to the higher iron concentration.

Characteristics of the target compound

Ruppert and Bauer (1993) studied the influence of the structure of several organic pollutants as they were mineralized by OH radicals. All of the aromatic substances studied were strongly degraded after several hours, while the organic carbon of cyclohexanol and cyclohexanone was hardly attacked. In alicyclic compounds the attack of the electrophilic OH radicals cannot occur at conjugated C = C double bonds in contrast to aromatic compounds where ring opening and further degradation takes place. The ordered H_2O_2 decrease during reaction was in good correlation with the total organic carbon (TOC) degradation. For all aromatic substances studied, degradation curves became linear after the first 30 min, until H_2O_2 was completely exhausted. During degradation of cyclohexanol and cyclohexanone only a slight decrease of the oxidant could be observed. The continued destruction of nitroaniline after exhaustion of H_2O_2 was attributed to photo-Fenton reactions (Ruppert and Bauer, 1993).

Initial concentration of the target compound

Initial pesticide concentration was the most important parameter affecting the efficiency of pesticide removal in the Fenton reaction. Mineralization efficiencies obtained at low pesticide concentrations were higher than those obtained at high pesticide concentrations. Increases in initial pesticide concentrations yielded decreasing pesticide removal at all Fe^{2+} concentrations indicating limitations of H_2O_2 concentration at high initial pesticide concentrations. The percentage pesticide removals were 35%, 48% and 72% with an initial pesticide doses of 15, 10 and 1 mg/L, respectively, at a constant Fe^{2+}/H_2O_2 dose of 15/170 mg/L (Catalkaya and Kargi, 2007).

Initial pH

Walling *et al.* (1975) simplified the overall chemistry of Fenton process by accounting the dissociation of water, as seen in Eq. 2-2.

$$Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(2-2)}$$

This equation suggests that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acidic environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for the Fenton reactions (Hickey *et al.*, 1995). In the presence of organic substrates (RH), excess Fe^{2+} and at low pH, hydroxyl radicals can add to the aromatic or heterocyclic rings.

At low pH, H_2O_2 is stabilized as H_3O^{2+} (Kwon *et al.*, 1999) and moreover, the regeneration of Fe^{2+} by reaction of Fe^{3+} with H_2O_2 is inhibited and the reaction between $^{\bullet}OH$ and H^+ becomes important. On the other hand, the decrease of oxidation yield of the process at higher pH values (pH>3) is due to the precipitation of Fe^{3+} as $Fe(OH)_3$, hindering the reaction between Fe^{3+} and H_2O_2. Besides, $Fe(OH)_3$ catalyzes the decomposition of H_2O_2 to O_2 and H_2O, thus decreasing the production of $^{\bullet}OH$ (H¨ofl *et al.*, 1997). Moreover, at higher pH values it is possible that highly stable Fe^{2+} complexes are formed (Tang and Huang, 1996). Therefore, in the present investigation all the experiments were carried out at an initial pH value of 3.

2.7 Application of Fenton process for water and wastewater treatment

Over the last years, a great number of studies on the Fenton degradation of organic compounds have been reported (Table 2-3). The advanced oxidation of diuron in aqueous solution by Fenton's reagent using $FeSO_4$ as the source of Fe^{2+} was investigated in the absence of light. The effect of operating parameters such as concentrations of pesticide (diuron), H_2O_2 and Fe^{2+} on oxidation of diuron was investigated using the Box-Behnken statistical experiment design and the surface response analysis. Diuron removal increased with increasing H_2O_2 and Fe^{2+} concentrations up to a certain level. Around 98.5% diuron removal was achieved after 15 min reaction period. However, only 58% of diuron was mineralized after 240 min under optimal operating conditions indicating the formation of some intermediate products. The optimal H_2O_2/Fe^{2+}/diuron concentration resulting in the maximum diuron removal (98.5%) was found to be 302/38/20 mg/L (Catalkaya and Kargi, 2007)

Bautista *et al.* (2007) evaluated the removal of organic matter (TOC and COD) from a cosmetic wastewater by the Fenton process. With the operating conditions of initial pH equal to 3.0, Fe^{2+} concentration of 200 mg/L, and H_2O_2 concentration to COD initial weight ratio corresponding to the theoretical stoichiometric value (2.12), TOC conversions higher than 45% at 25°C and 60% at 50°C were achieved. A simple kinetics analysis based on TOC was also studied. The second-order kinetics well described the overall process within a wide TOC conversion range covering up to 80 to 90% of the maximum achievable conversion.

The degradation of wheat straw black liquor (WSBL) by Fenton's reagent was investigated by Torrades *et al.* (2007). The use of irradiation providing the conditions needed for the occurrence of photo-Fenton reaction along with the main parameters that govern the complex reactive system have been studied. Concentrations of Fe^{2+} (20-1000 mg/L) and H_2O_2 (500-2000 mg/L) were chosen for the experiments. The best results were obtained when using 1500 mg/L H_2O_2 and 200 mg/L Fe^{2+} (12:1 molar ratio of H_2O_2/Fe^{2+}). The use of Fenton and photo-Fenton reactions have been proven to be highly effective in the treatment of WSBL. Also, the high levels of COD, aromatic and lignin removals were observed in the system.

Oliveria *et al.* (2006) used an experimental design methodology for designing 2,4-dichlorophenol (2,4-DCP) oxidation experiments using Fenton's reagent. The multivariable and multilevel approaches of the experimental design methodology were useful to quantify the effects between the experimental variables (temperature, Fe^{2+}, and H_2O_2 concentrations) in the process performance, with the minimum number of experiments. Response factors considered were 2,4-DCP degradation after 5, 10, and 20 min of reaction time, for an initial 2,4-DCP concentration of 100 mg/L. It was found that the Fe^{2+} concentration had a positive effect on the oxidation performance. Besides, the optimal conditions depend on the response considered, with it being advisable to use less-aggressive conditions if responses are taken at longer reaction times. Finally, the kinetic model proposed was useful for predicting the evolution of 2,4-DCP concentration within the batch reactor over time.

Table 2-3 Literature review of Fenton process

Reference	Method	Compound	Condition	Reaction time	Degradation (%)
Silva *et al.* (2007)	Photo-Fenton	Tebuthiuron 5×10^{-3} M	pH 2.5-7.5 H_2O_2 340 mg/L 1.9-16.2 J/cm^2	15 min	>90
Gunale et al. (2007)	Fenton and wet oxidation	Aniline 500 mg/L	5:1 (w/w) H_2O_2 to catalyst ratio pH = 4	120 min	100
Catalkaya and Kargi (2007)	Fenton	Diuron 25mg/L	H_2O_2 1.5-340 mg/L Fe^{2+} 0.25-56 mg/L pH 4.2	15 min	82
Bautista *et al.* (2007)	Fenton	Cosmetic wastewater COD=2720 mg/L	H_2O_2 9040 mg/L Fe^{2+} 200 mg/L pH 3	250 min	70
Torrades *et al.* (2007)	Photo-Fenton	WSBL* COD=50000 mg/L	H_2O_2 500-2000 mg/L Fe^{2+} 20-1000 mg/L pH 3	90 min	80
Oliveria et al. (2006)	Fenton	2,4-dichlorphenol 100 mg/L	H_2O_2 = 212 mg/L Fe^{2+}= 6.5 mg/L	120 min	>90
Arnold *et al.* (1995)	Fenton	Atrazine 140 µM	H_2O_2 170 mg/L Fe^{2+} 156 mg/L pH 3-9	60 min	100

*Wheat straw black liquor

Chapter 3

Materials and Methods

3.1 Chemicals

Carbofuran was obtained from Shida Chemical Industries (Taoyuan, Taiwan) and was used as received (HPLC grade＞98%). Fe^{2+} solution was prepared by dissolving $FeSO_4 \cdot 7H_2O$ (Panreac, E.U.) in ultra pure water. Hydrogen peroxide (30%, w/w in water) was supplied by Panreac, E.U. All other chemicals and solvents were of the purest grade commercially available and were used without further purification.

3.2 Experimental procedure

The schematic diagram of the Fenton process experimental set-up is shown in Figure 3-1. The stock carbofuran solution (100 mg/L) was prepared in ultrapure water just prior to the experiments. The Fenton degradation experiments were conducted at two carbofuran concentrations i.e. 10 and 50 mg/L with a working volume of one litre. The H_2O_2 and Fe^{2+} concentrations in the range of 0 to 200 mg/L and 0 to 10 mg/L, respectively (as per CCD) were added to 50 and 10 mg/L carbofuran solutions separately under continuous stirring. The initial pH of the reaction mixture was adjusted to 3 with the addition of HCl (0.01 M). Fenton experiments were carried out at room temperature and the changes in temperature throughout the study were negligible. The complete experimental flowchart of the present study is shown in Figure 3-2. Fenton experiments were conducted for 20 min and at the end of 0, 1, 2, 5, 10 and 20 min, 40 mL of sample was collected from each reactor and preserved in refrigerator at $4^{o}C$ in dark. The collected samples were analyzed for carbofuran and

H_2O_2 concentrations, TOC, nitrate and nitrite. In addition, the pH and ORP of the system were measured online using pH (Suntex sp-2200, Taiwan) and ORP meters (Suntex pc-3200, Taiwan), respectively.

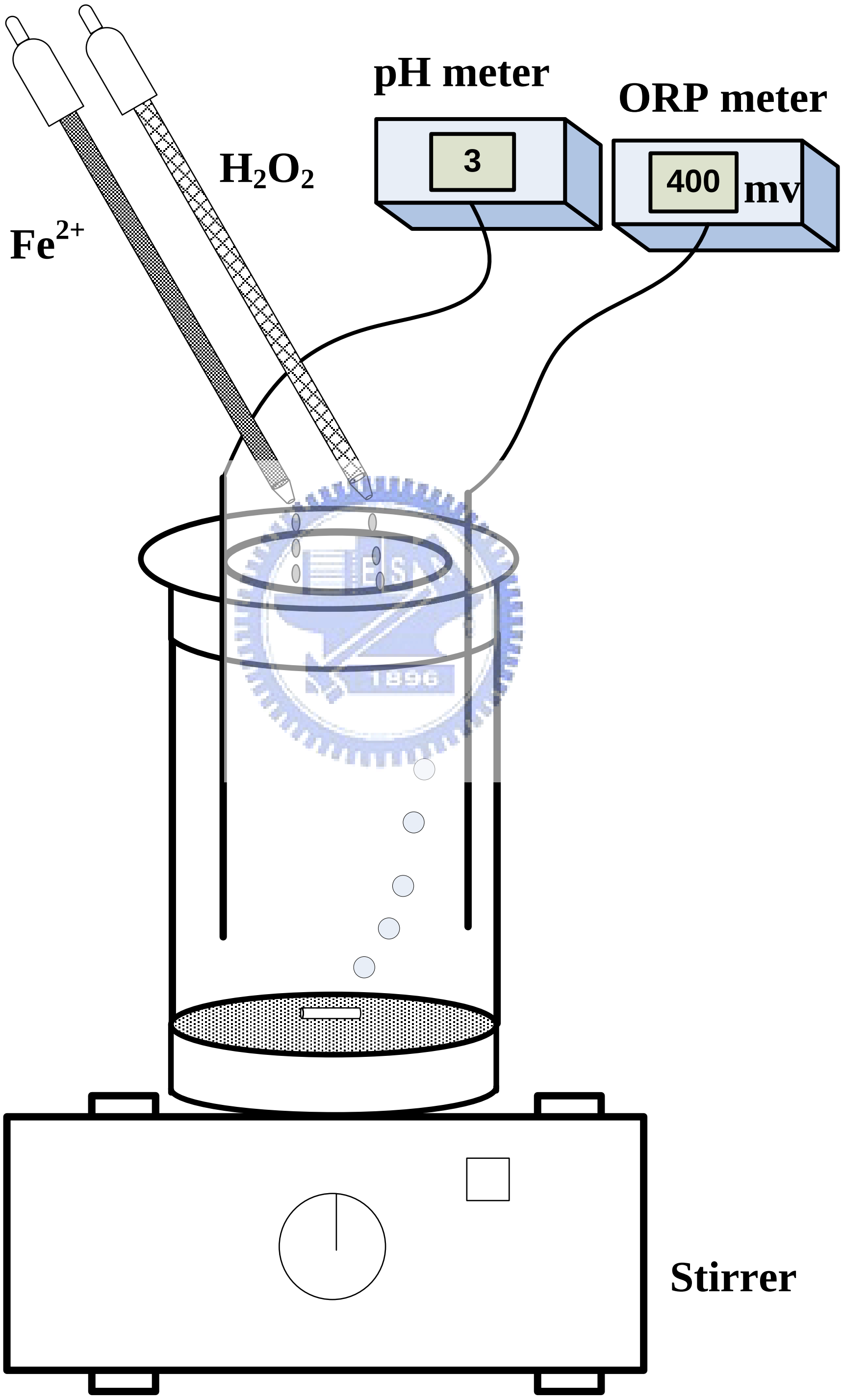

Figure 3-1 Schematic diagram of the Fenton process experimental set-up

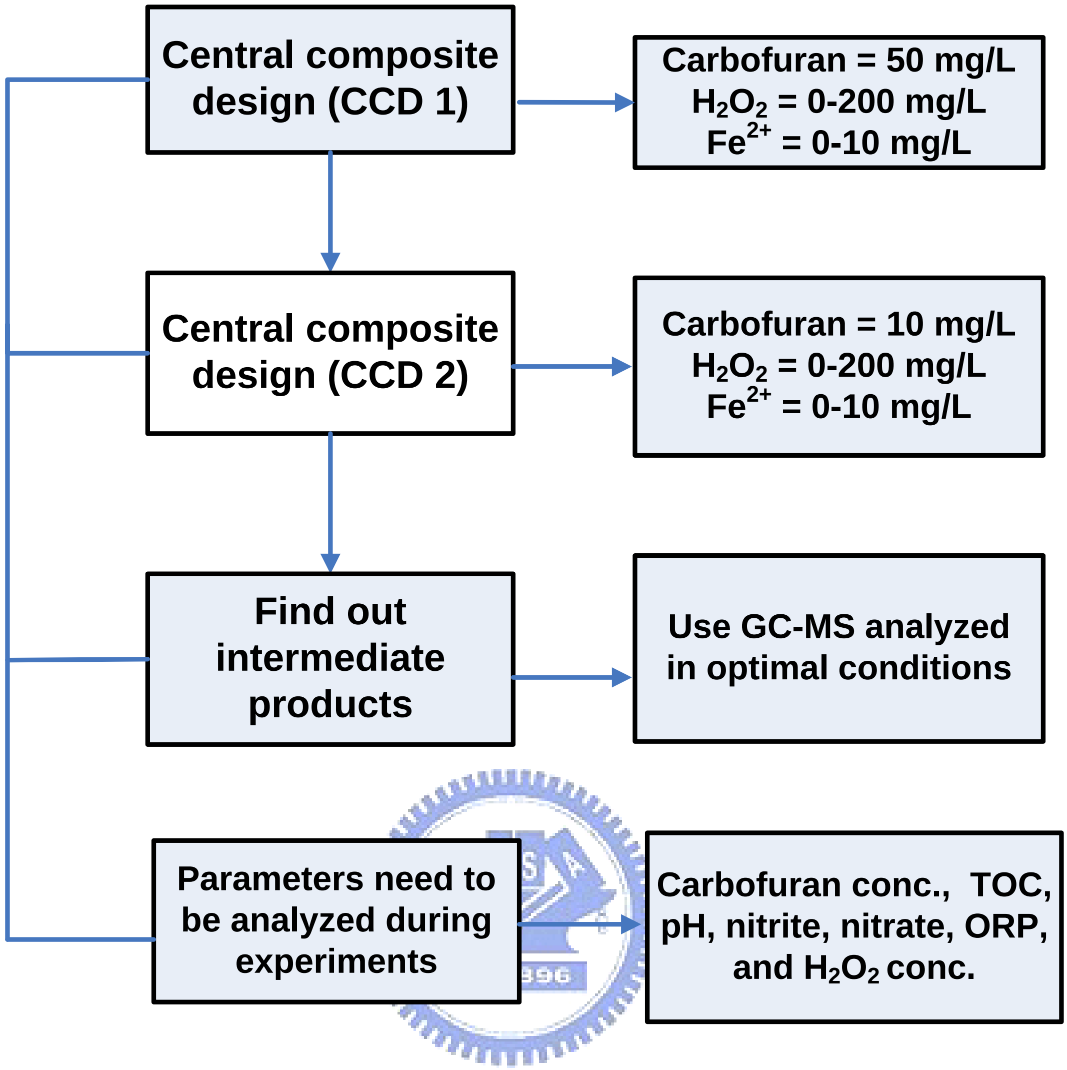

Figure 3-2 Flowchart of the Fenton experiments

3.3 Central composite design (CCD)

A central composite design (CCD) with two factors was used to relate the dependent and independent variables as well as to minimize the number of experiments. Moreover, CCD was utilized to construct a second-order polynomial with independent variables and identification of statistical significance in the variables (Diaz *et al.*, 2003).

CCD contains an imbedded factorial or fractional factorial matrix with center points and “star points” around the center point that allow estimation of the curvature.

Assuming that the distance between the center point and each factorial point is ±1 unit, and the distance between the center point and star point is ±α, where $|\alpha|$ is greater than 1. In order to maintain rotatability, the value of α is related to the number of experiments in the fractional portion of the CCD. Therefore, the values of α (when the factional is full factional) and number of experiments (N) can be determined using the Eqs. 3-1 and 3-2, respectively (Techapun *et al.*, 2002). Figure 3-3 shows a typical CCD and Figure 3-4 shows the 2-factors CCD.

$$\alpha = [2^{K}]^{1/4} \qquad \text{……(3-1)}$$

$$N = 2^{K}+2K+1 \qquad \text{……(3-2)}$$

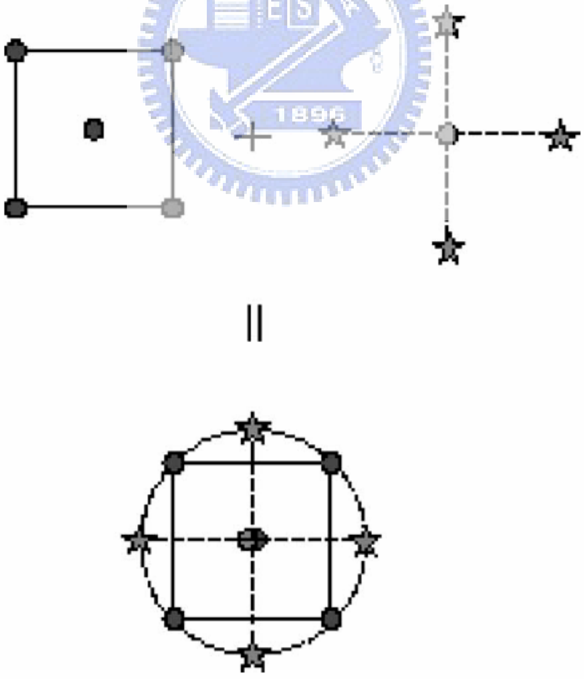

Figure 3-3 Diagram of central composite design

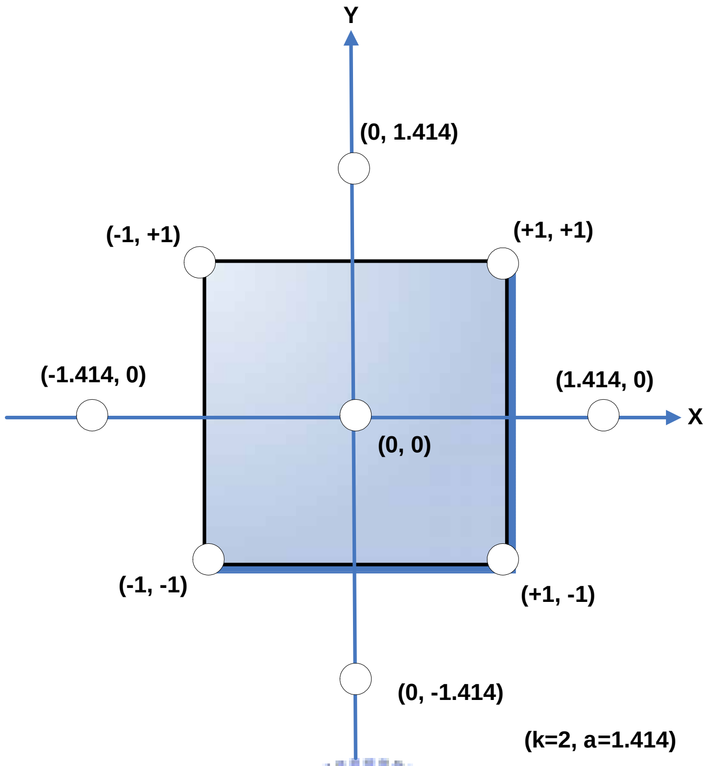

Figure 3-4 Schematic representation of 2-factors CCD

In order to facilitate the comparison of the coefficients and visualization of the individual independent variable on the response variables, the values of the independent variables (X_n) were normalized from -1.414 to 1.414 by Eq. 3-3. Normalization not only makes it more accurate to estimate the regression coefficients but also reduces the interrelationship between linear and quadratic terms (Diaz *et al.*, 2003).

$$X_n = \frac{X - \overline{X}}{\left(X_{\max} - X_{\min}\right)/2} \qquad \text{..(3-3)}$$

Where, X is absolute value of the independent variable, $\overline{X}$ is the average value of variable and X_{max} and X_{min} are the maximum and minimum values of independent variable, respectively.

3.3.1 Response surface methodology

The response surface methodology can more effectively attain the optimization of the response and the values of variable. Assuming the carbofuran degradation rate is Y, and the operating factors of the initial carbofuran and H_2O_2 concentrations are X_1 and X_2, respectively, the carbofuran degradation rate is a function of X_1 and X_2 (Eq. 3-4).

$$Y = f\left(X_1, X_2\right) + \varepsilon \quad \text{……………………………………………………………(3-4)}$$

Where, ε is the error in the response Y. The equation can be simplified to $Y = f\left(X_1, X_2\right)$. Consequently, the curved surface of this equation is called response surface. Applying response surface method with the contour map can determine the optimized conditions or range of the operation factors.

3.3.2 Experimental design

In order to maintain the credibility of the experiment and decrease the total number of experiments, a CCD was applied to conduct the experiments with two main factors, Fe^{2+} concentration (Fe^{2+}) and H_2O_2 concentration (H_2O_2). Subsequently, the optimal operating conditions were obtained by the response surface method. The CCD matrix generated for random experimental design is tabulated in Tables 3-1 and 3-2. The experimental 2-factor CCD design is shown in Figure 3-5.

Table 3-1 CCD-generated levels for two experimental factors

Factor	Level				
	-1.414	**-1**	**0**	**1**	**1.414**
X_1: Fe^{2+} (mg/L)	0	1.46	5	8.54	10
X_2: H_2O_2 (mg/L)	0	29.28	100	170.72	200

Table 3-2 Experimental conditions of carbofuran investigation

Run No.	Coded value		Natural value	
	Fe^{2+} conc. (X_1)	H_2O_2 conc. (X_2)	Fe^{2+} conc. (X_1) (mg/L)	H_2O_2 conc. (X_2) (mg/L)
1	0	0	5	100
2	1	-1	8.54	29.28
3	-1.41421	0	0	100
4	-1	1	1.46	170.72
5	1.41421	0	10	100
6	0	1.41421	5	200
7	0	-1.41421	5	0
8	0	0	5	100
9	1	1	8.54	170.72
10	0	0	5	100
11	-1	-1	1.46	29.28

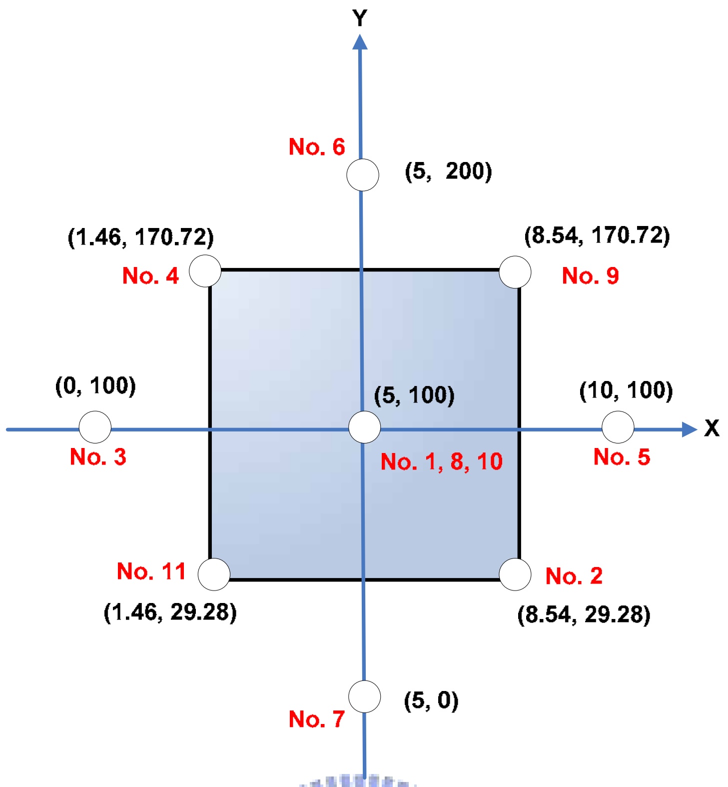

Figure 3-5 Schematic representation of the CCD adopted in the present study

3.4 Analytical measurements

The analysis included measurements of ORP, pH, carbofuran concentration, H_2O_2 concentration, total organic carbon (TOC), nitrite and nitrate. The analytical properties, methods and instruments used are listed in Table 3-3. The flow chart of the sample analysis for the study is displayed in Figure 3-6. The concentration of carbofuran was analyzed by a Hitachi L-2130 HPLC equipped with a UV-detector and a C18 column. The mobile phase was composed of methanol and water with a volume ratio of 50/50. A 250 mm × 4.6 mm (i.d.) with 5 μm film thickness (C18, PRISM RP) column was used for separation. The UV-detector wavelength was set at 280 nm and methanol was pumped at a flow rate of 1.0 mL/min. Under these conditions, the retention time of carbofuran was 12.3 min. Prior to sample analysis, a calibration curve was plotted with known concentrations of carbofuran (between 20 and 160 mg/L) and area response (R^2 of 0.99).

The hydrogen peroxide concentration was determined iodometrically via its ammonium molybdate decomposition reaction in a 10% potassium iodide solution. A pH meter was used to monitor pH and an ORP meter was used to determine the conductivity. The progress of the mineralization of carbofuran was monitored by measuring the TOC. An OI Analytic Model 1010 TOC Analyzer was used to determine the total TOC content of the samples. For the TOC measurements, potassium phthalate solutions were used as the calibration standard with concentrations of 0, 10, 20, 30, 40 and 50 mg/L. Similarly, nitrite and nitrate ion formations were analyzed by spectrophotometer using a UV-vis Detector L-2420.

The intermediate products of carbofuran during the Fenton process were extracted by liquid-phase extraction. A mixture of dichloromethane and ethyl acetate (1/1, v/v) was used to elute the intermediate products. A HP6890 GC coupled with a 5973 mass selective detector was used for separation and detection of the intermediate products. The GC was equipped with a HP-5 capillary column (30 m × 0.25 mm i.d.) in helium carrier gas (1.5 mL/min) and with a splitless injection system. The GC oven temperature was programmed as follows: initially held at 80°C for 2 min, increased to 210°C at a rate of 10°C min^{-1} and from 210 to 300°C at a rate of 30°C min^{-1} and finally held at 310°C for 2 min. The injector and detector temperatures were maintained at 220 and 250°C, respectively. The mass spectra was obtained by the electron-impact (EI) mode at 70 eV using the full-scan mode.

Table 3-3 Methods and instruments used for analytic measurements

Analytical parameter	Method	Instrument	Model
pH	NIEA R208, 00T	pH meter	Suntex sp-2200
ORP	NIEA W203.51B	ORP meter	Suntex pc-3200
TOC_W	NIEA W532, 51C	TOC analyzer	OI analytical 1010
Nitrite	NIEA W418, 51C	Spectrophotometer (OD 543)	UV-vis Detector L-2420
Nitrate	NIEA W419, 51A	Spectrophotometer (OD 220 and 275)	UV-vis Detector L-2420
Weight		Platform scales	Jaever JPC-150
Intermediate products		GC/MS	HP 6890
Carbofuran		HPLC	Hitachi L-2130

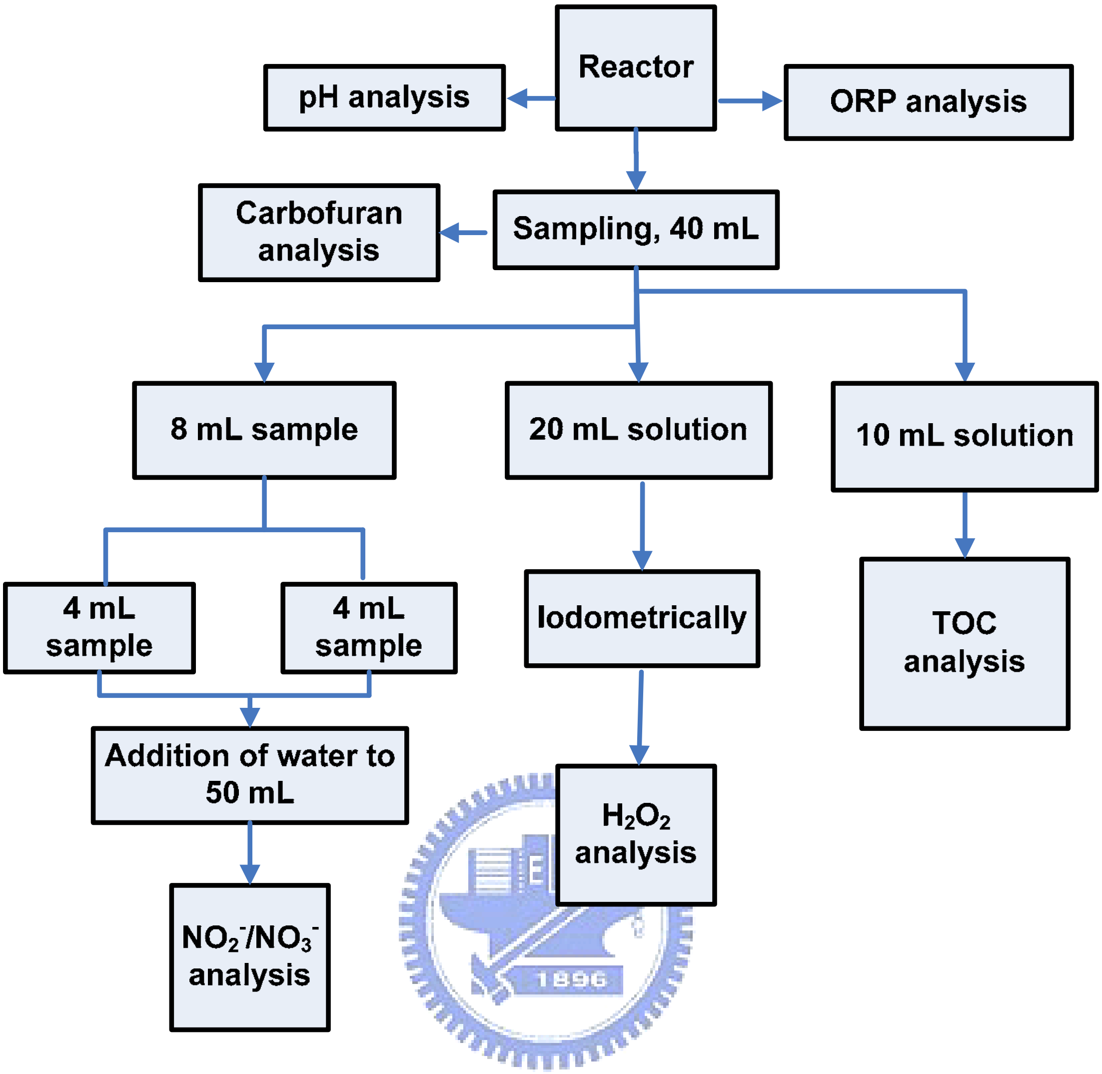

Figure 3-6 Flowchart of sample analysis

Chapter 4

Results and discussion

4.1 Fenton experiments at 50 mg/L of carbofuran

A statistical experimental design and the response surface methodology were used to investigate the effect of two independent variables (i.e. Fe^{2+} and H_2O_2) on the response function and to determine the optimal conditions for maximum carbofuran removal. The optimization procedure involved studying the following four steps: (a) studying response of statistically-designed combinations, (b) estimating the coefficients by fitting the experimental data to the response functions, (c) predicting the response of the fitted model, and (d) checking the adequacy of the model. The independent variables were the concentrations of Fe^{2+} (X_1) and H_2O_2 (X_2). The low, center and high levels of each variable were designed as -1.414, -1, 0, 1, and 1.414, respectively. The dependent variable (or objective function) was the carbofuran (Y) removal. The center point (0, 0) was repeated three times and the same results were obtained indicating reproducibility of the data. The experimental conditions of the Fenton experiments at 50 mg/L of carbofuran (later referred as CCD-1) are shown in Table 4-1. The observed and calculated percentage removals of carbofuran and TOC are also summarized in Table 4-1. It can be observed that the combined interaction of Fe^{2+} concentration with the H_2O_2 concentration had a strong interaction on the carbofuran removal percentage. The accumulated carbofuran removal percentages in each run are shown in Figure 4-1. In some experiments a significant decrease in the carbofuran concentration is noticed after few seconds. This is a consequence of the whole reaction mechanism of Fenton process wherein Fe^{2+} reacts very quickly with H_2O_2 (rate constant 53 /mol. dm^3/s, at 20 to 25°C) to produce OH radicals, which can further react rapidly with carbofuran (Dutta *et al.*, 2001). The results show that the highest carbofuran removal of 57% was observed when the initial Fe^{2+} and H_2O_2 concentrations were kept at 5 and 200 mg/L (run 6), respectively.

4.1.1 Profiles of pH, ORP and H_2O_2 in CCD-1

The variations of pH, ORP and H_2O_2 in CCD-1 are shown in Figures 4-2, 4-3 and 4-4. The pH remained at 3 during the Fenton process in all eleven runs. ORP increased after the additions of Fe^{2+} and H_2O_2 solutions into the reactor and then decreased slightly with time. In Run 1, the ORP was initially 475 mv and it increased to 523 mv after the additions of Fe^{2+} and H_2O_2 solutions into the reactor. After 20 minutes of reaction the ORP value decreased to 517 mv. Similar profile was observed in all other runs (Figure 4-2). The ORP value was influenced by the H_2O_2 concentration in the reactor. The H_2O_2 concentration barely decreased with time as observed in Figure 4-4, thus causing ORP to decrease. Experimental results indicate that the additions of Fe^{2+} and H_2O_2 increased the oxidation power of the system.

Table 4-1 CCD-1 matrix and the experimental results

Run No.	Fe^{2+} conc. (mg/L)	H_2O_2 conc. (mg/L)	Final carbofuran conc. (mg/L)	Initial TOC (mg/L)	Final TOC (mg/L)	Carbofuran removal (%)	TOC removal (%)
1	5	100	36	31	29	28	6
2	8.54	29.28	42	30	29	13	3
3	0	100	56	38	38	0	0
4	1.46	170.72	45	31	30	13	3
5	10	100	33	31	27	39	13
6	5	200	23	31	28	57	10
7	5	0	49	30	30	0	0
8	5	100	36	29	28	28	3
9	8.54	170.72	31	28	28	37	0
10	5	100	36	29	28	25	3
11	1.46	29.28	46	28	28	2	3

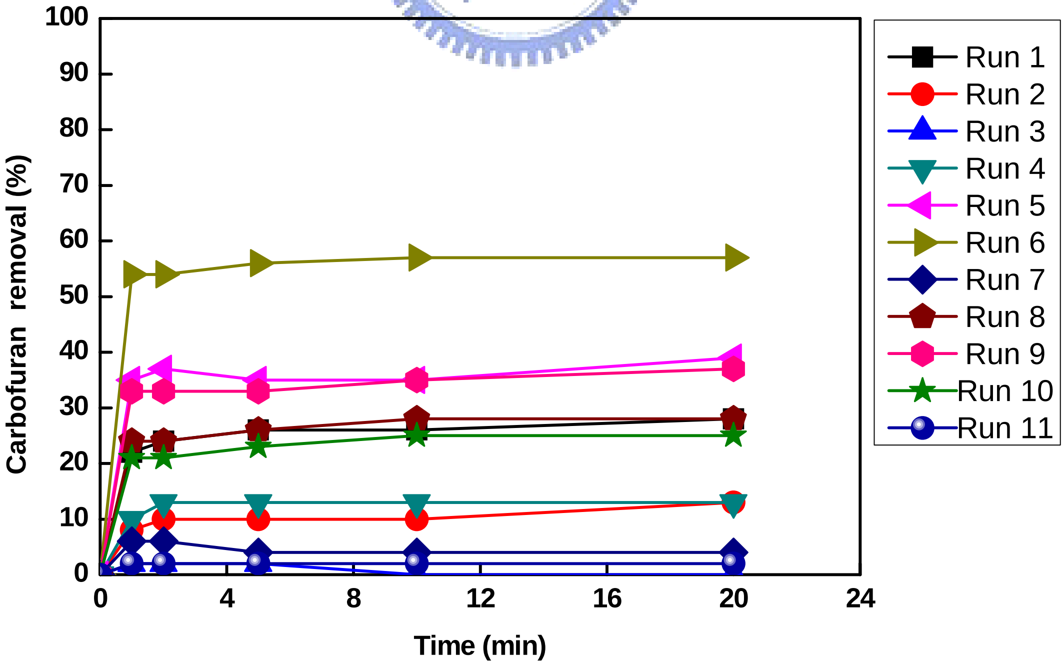

Figure 4-1 Carbofuran removal in CCD-1

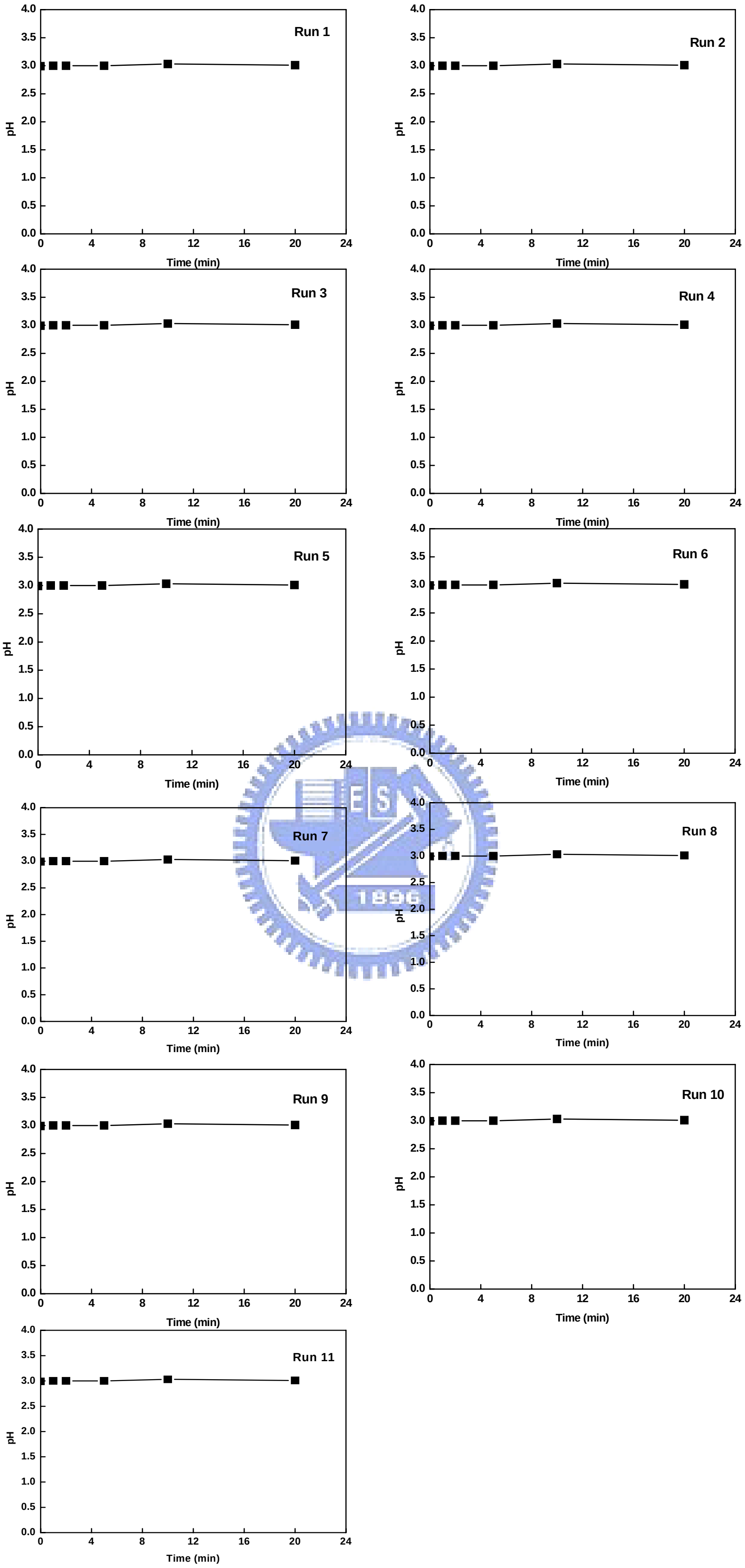

Figure 4-2 The variations of pH in CCD-1

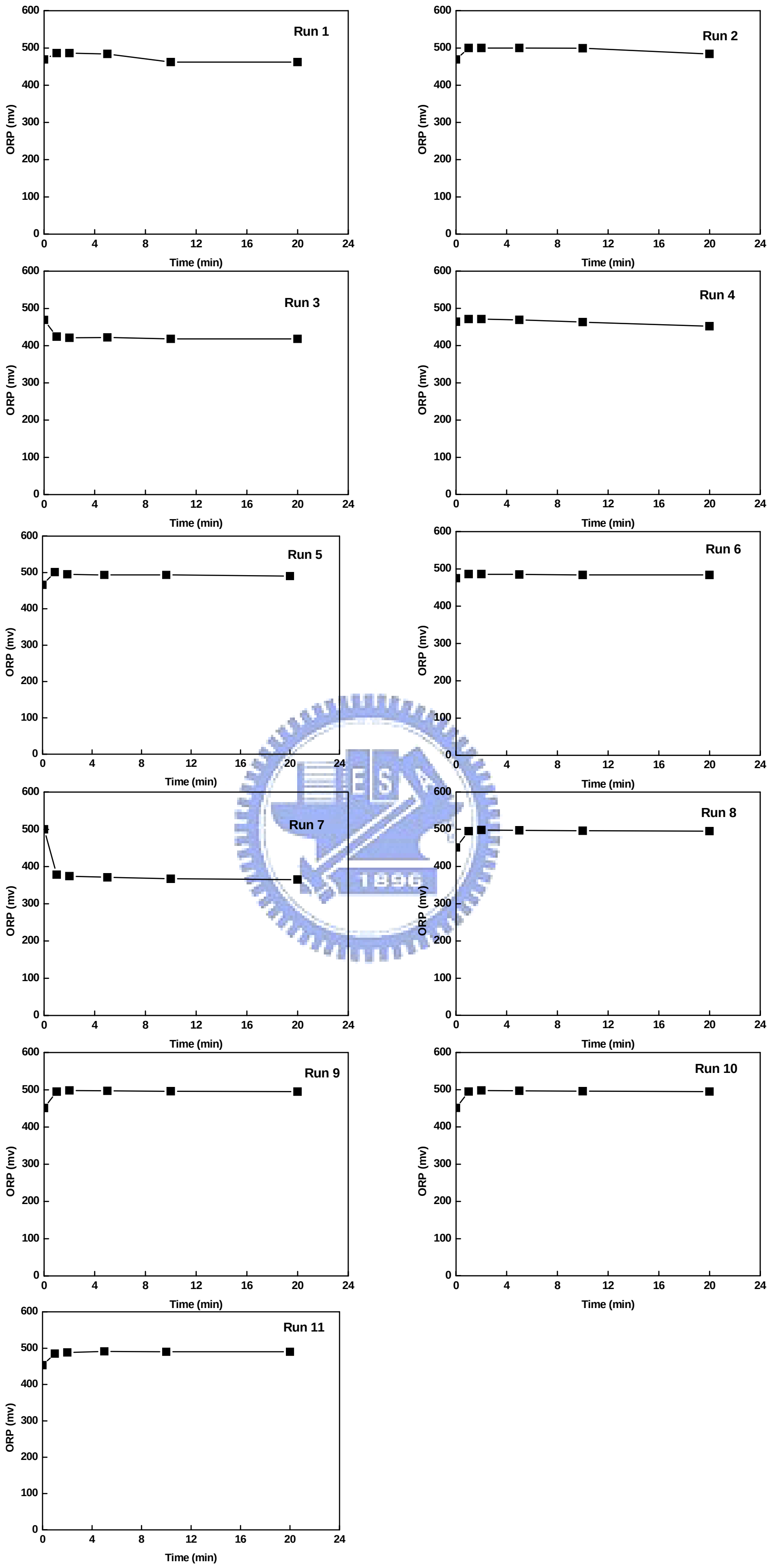

Figure 4-3 The variations of ORP in CCD-1

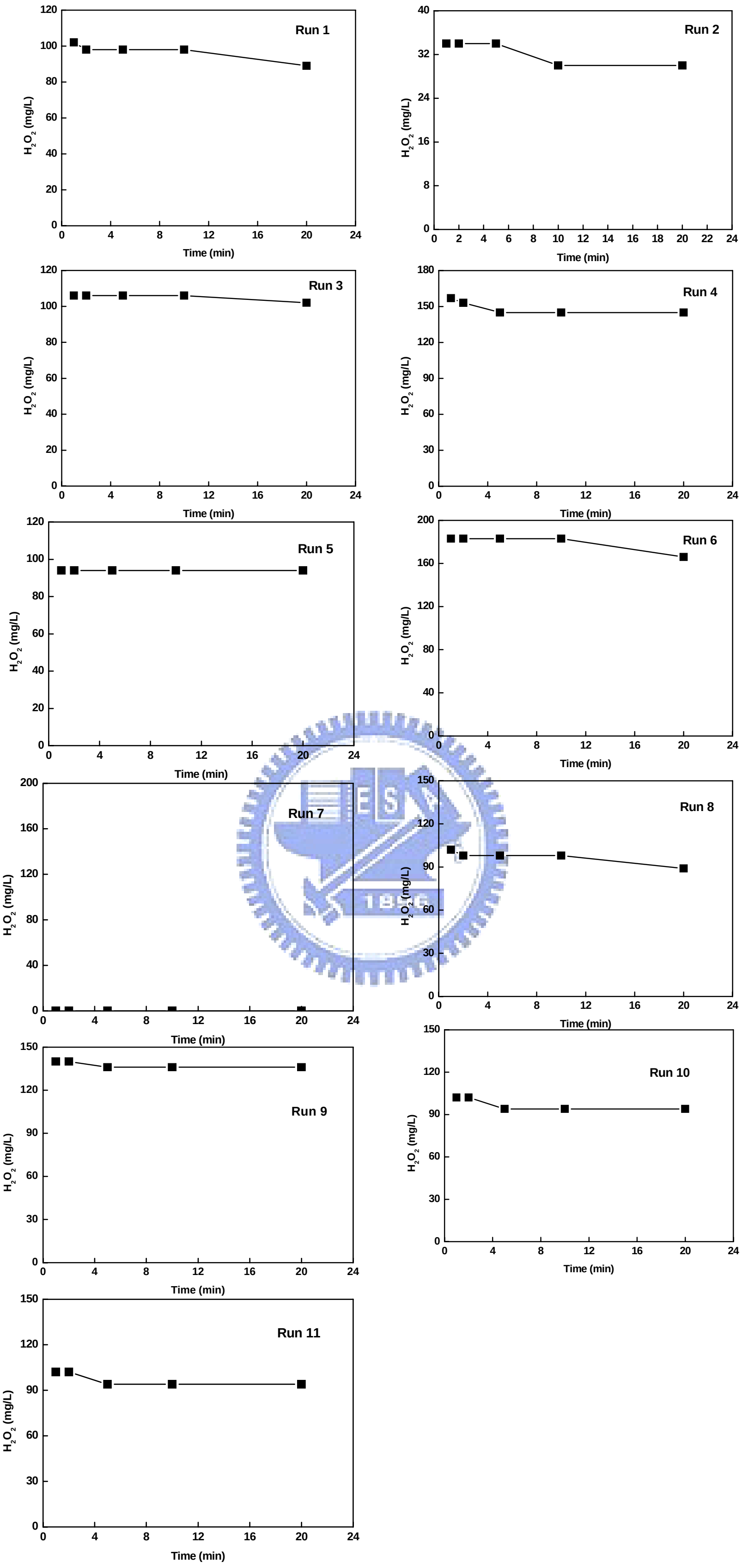

Figure 4-4 The variations of H_2O_2 concentration in CCD-1

Using the experimental data, the response surface and contour plot were prepared by Minitab®14.1 and the results are shown in Figures 4-5 and 4-6, respectively. It can be seen from Figure 4-5 that the percentage carbofuran degradation increased with increasing H_2O_2 concentration. Dutta *et al.* (2001) also stated that higher H_2O_2 dosage increased the production of OH radicals and finally resulted in the increase in percentage removal of carbofuran. The effects of Fe^{2+} concentration and percentage carbofuran degradation in the Fenton process are depicted in Figure 4-5. Carbofuran removal was increased with increasing Fe^{2+} concentration. These results are in agreement with previous literature, where a beneficial effect of increasing Fe^{2+} was observed in degrading pesticides (Bautista *et al.*, 2007; Catalkaya and Kargi, 2007; Oliveria *et al.*, 2006).

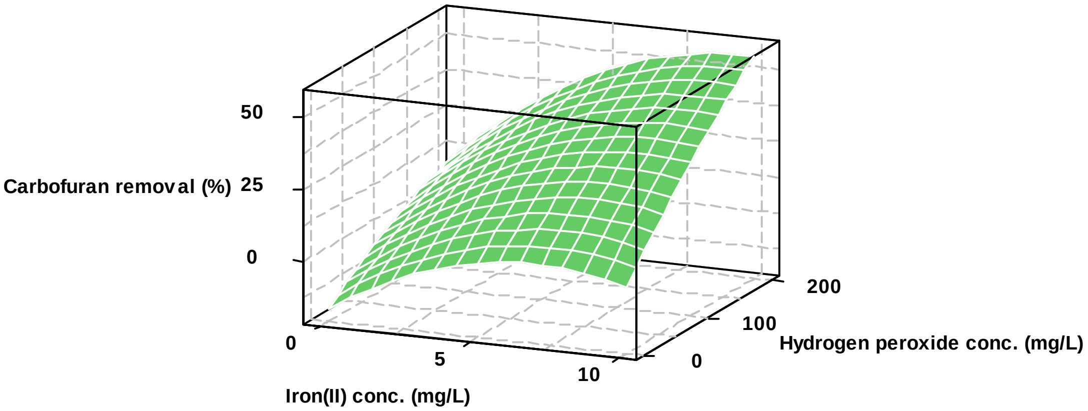

Figure 4-5 Response surface depicts the carbofuran removal in CCD-1

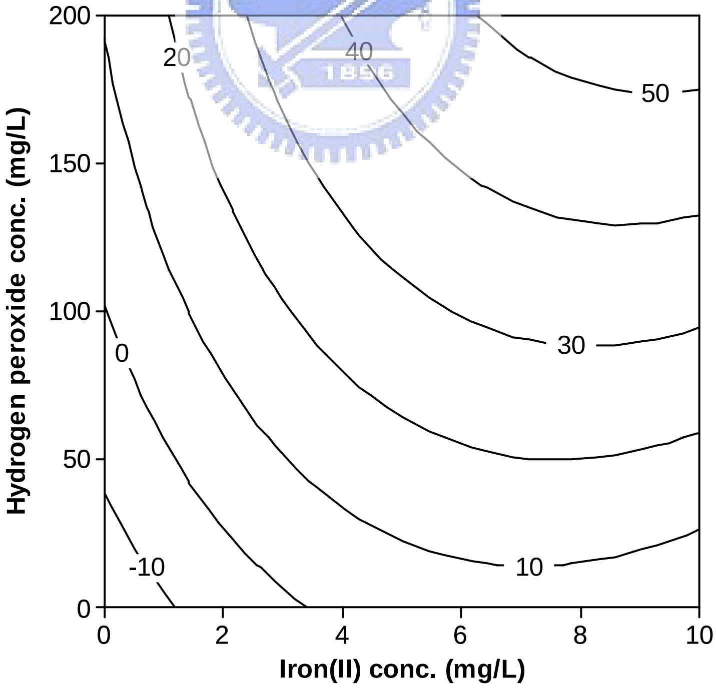

Figure 4-6 Contour plot of carbofuran removal in CCD-1

4.1.2 Modeling the optimal conditions for Fenton process

The application of response surface method offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function (Y) and the independent variables (X) can be approximated by a quadratic polynomial equation. This approach was selected because relatively fewer combinations of the variables were used to estimate a potentially complex response function. The analysis of variance (ANOVA) for CCD-1 experiments carried out using Minitab®14.1 is shown in Table 4-2. The P-value of ANOVA being the probability of obtaining a result at least as extreme as a given data point, under the null hypothesis, was used to determine the significance of the variances. If the P-value is smaller than or equal to the significance level α, it can be rejected as a null hypothesis. When α is equal to 0.05, it represents that the results are only 5% likely to be as extraordinary given that the null hypothesis is true. The P-value for Fe^{2+} of 0.149 obtained from ANOVA in Table 4-2 is smaller than that of H_2O_2 (0.368), which indicates that the result of the carbofuran removal is more significantly influenced by the Fe^{2+} concentration than the H_2O_2 concentration. The second-order model for the CCD-1 experimental design is shown in Eq. 4-1, and the correlation R^2 and adjusted R^2 values (ignoring the insignificant terms) of Eq. 4-1 are shown in Table 4-2. The R^2 value is 87% (greater than 80%) and the regression P value is 0.029 (smaller than 0.05), which indicates that the second-order model fits well with the experimental results.

$$Y = -16.171 + 6.4396X_1 + 0.1869X_2 - 0.4553X_1^2 - 0.002X_2^2 + 0.013X_1X_2 \quad \text{.................} (4\text{-}1)$$

Where, Y is the carbofuran removal rate (%), and X_1 and X_2 are the Fe^{2+} and H_2O_2 concentrations (mg/L), respectively.

Table 4-2 Analysis of variance for carbofuran removal in CCD-1

Central Composite Design-1

Central Composite Design

Factors: 2 Blocks: none Center points: 3

Runs: 11 Alpha: 1.414

Response Surface Regression

The analysis was done using coded units.

Estimated regression coefficients for carbofuran removal

Term	Coefficient	Standard deviation	T	P
Constant	-16.171	14.2673	-1.165	0.297
Fe^{2+}	6.4396	3.7445	1.706	0.149
H_2O_2	0.1869	0.1888	0.990	0.368
$Fe^{2+} * Fe^{2+}$	-0.4553	0.3145	-1.448	0.207
$H_2O_2 * H_2O_2$	-0.0002	0.0008	-0.302	0.775
$Fe^{2+} * H_2O_2$	0.0130	0.0187	0.695	0.518

S = 9.347 R-square = 87% R-square (adj) = 74%

Analysis of variance for carbofuran removal

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	2913.15	2913.145	582.629	6.67	0.029
Linear	2	2686.32	259.856	129.928	1.49	0.311
Square	2	184.58	184.580	92.290	1.06	0.414
Interaction	1	42.25	42.250	42.250	0.48	0.518
Residual Error	5	436.85	436.855	87.371		
Lack-of-Fit	3	430.85	430.855	143.618	47.87	0.021
Pure Error	2	6	6	3		
Total	10	3350				

Calculated by Minitab®14.1

Minitab®14.1 also calculated a residual versus fitted value plot to test the accuracy of the second-order model shown in Eq. 4-1. The fitted values of the residuals should be shapeless and should not have relation to other variables if the model is correct and the hypotheses are true. The residual versus fitted value plot for the carbofuran removal shown in Figure 4-7 does not indicate any typical shapes such as a funnel or bell shape. This indicates that the model given in Eq. 4-1 is correct and the hypotheses are valid.

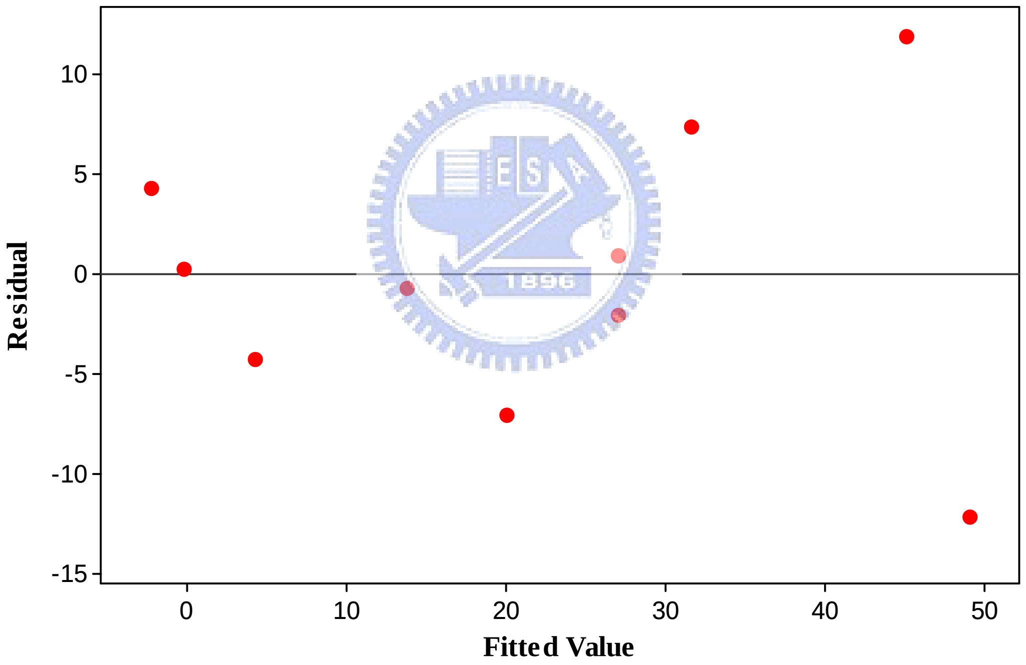

Figure 4-7 Residual versus fitted value plot for carbofuran removal in CCD-1

A normal probability plot was used in order to test the normality of the error distribution (Figure 4-8). The linear profile shown in Figure 4-8 represents that the error distribution is normal and the experimental data fit in good proportion with the normal distribution.

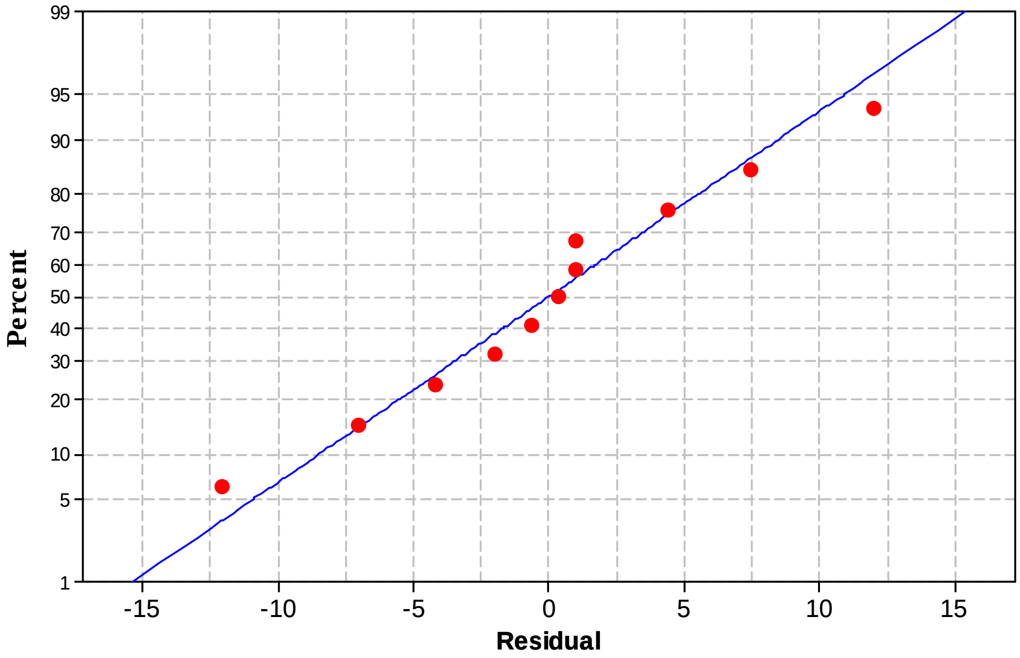

Figure 4-8 Normal probability plot of residuals for carbofuran removal in CCD-1

4.1.3 Determination of optimal conditions

From Figure 4-6, the optimal Fe^{2+} and H_2O_2 concentrations for maximum percentage carbofuran removal were found as 9 to 10 mg/L, and above 200 mg/L, respectively. An equation shown below (Eq. 4-2) can be used to find the highest carbofuran removal percentage from Figure 4-6.

$$X_S = -\frac{1}{2}B^{-1}b \quad \text{………………………………………………. …………………(4-2)}$$

Where, from Eq. 4-1, $b = \begin{bmatrix} 6.44 \\ 0.187 \end{bmatrix}$, and $B = \begin{bmatrix} -0.455 & 0.0065 \\ 0.0065 & -0.0002 \end{bmatrix}$.

Substituting these values into Eq. 4-2 yields

$$X_S = -\frac{1}{2}B^{-1}b \quad = \frac{1}{2}\begin{bmatrix} 6.81 & -133 \\ -133 & 6366 \end{bmatrix}\begin{bmatrix} 6.44 \\ 0.187 \end{bmatrix} = \begin{bmatrix} 9.5 \\ 217 \end{bmatrix}$$

The result shows the optimal Fe^{2+} and H_2O_2 concentrations, respectively i.e. $X_1 = 9.5$ mg/L and $X_2 = 217$ mg/L.

4.2 Fenton experiments at 10 mg/L of carbofuran

Fenton experiments were carried out at similar Fe^{2+} and H_2O_2 concentrations as CCD-1 at an initial carbofuran concentration of 10 mg/L (later referred as CCD-2). Table 4-3 summarizes the experimental conditions and the outcomes of the Fenton experiments. The results show that carbofuran was completely removed (100%) in runs 5, 6 and 9. Figure 4-9 shows the carbofuran degradation profiles in CCD-2 experiments. No carbofuran removal (0%) was observed in runs 3 and 7 where Fe^{2+} and H_2O_2 were absent in the experiments, respectively. The initial carbofuran concentration (50 mg/L) in CCD-1 was higher than in CCD-2 and the highest removal was only 57% in CCD-1. The lower initial carbofuran concentration was more effectively removed by the Fenton process. The TOC degradation was the highest at 43% with Fe^{2+} concentration of 8.54 mg/L and H_2O_2 concentration of 170.72 mg/L (run 9). The experimental outcomes infer that the Fe^{2+} concentration and its interaction with H_2O_2 concentration have strong effect in carbofuran removal.

Table 4-3 CCD-2 matrix and the experimental results

Run No.	Fe^{2+} conc. (mg/L)	H_2O_2 conc. (mg/L)	Final carbofuran conc. (mg/L)	Initial TOC (mg/L)	Final TOC (mg/L)	Carbofuran removal (%)	TOC removal (%)
1	5	100	0.5	6.7	5.2	97	22
2	8.54	29.28	2.2	6.3	5.7	77	10
3	0	100	9.5	6.2	6.4	0	0
4	1.46	170.72	4.1	6.3	6.0	58	5
5	10	100	0	6.5	4.3	100	34
6	5	200	0	6.7	4.5	100	33
7	5	0	9.7	6.8	6.7	0	1
8	5	100	0.1	6.7	4.5	99	33
9	8.54	170.72	0	6.9	3.9	100	43
10	5	100	0.1	6.7	4.4	99	34
11	1.46	29.28	7.4	6.7	6.3	24	6

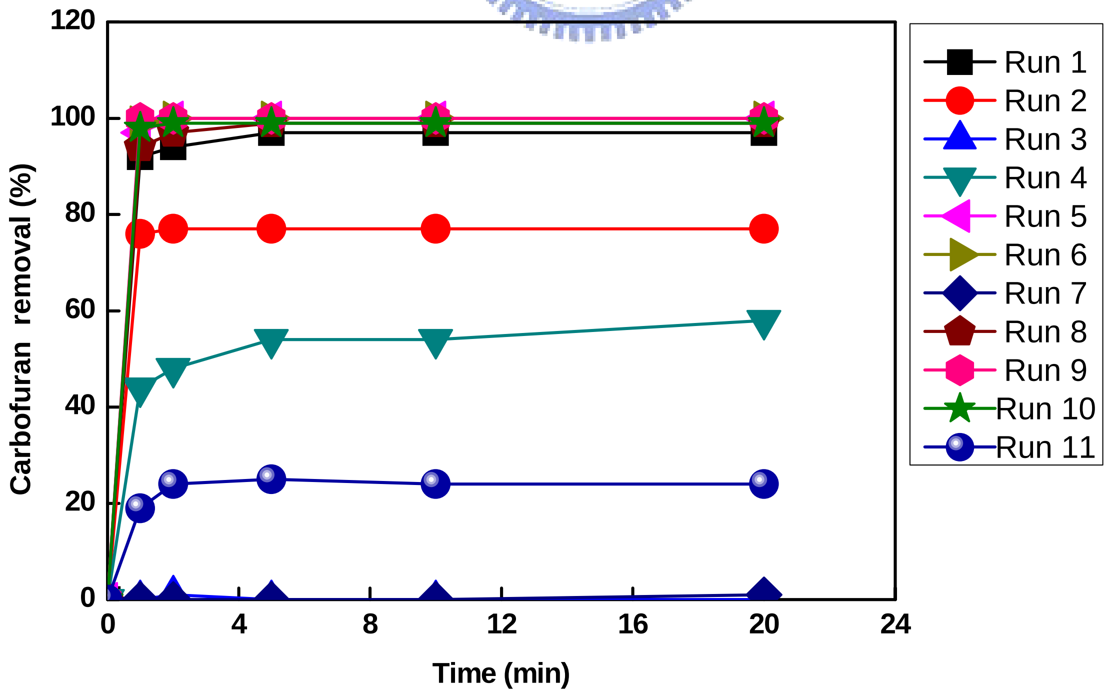

Figure 4-9 Carbofuran removal in CCD-2

4.2.1 Profiles of pH, ORP and H_2O_2 in CCD-2

The variations of pH, ORP and H_2O_2 in CCD-2 are shown as Figures 4-10, 4-11 and 4-12. The initial pH of all eleven experiments was kept at 3, and during the Fenton process, insignificant variations in pH were observed in the experiments (Figure 4-10). ORP profiles observed in CCD-2 were similar as that of CCD-1. ORP of the systems were increased after the additions of Fe^{2+} and H_2O_2 solutions. However, a decrease in ORP was noticed during the progress of Fenton experiments. For Run 1 the ORP was 423 mv at the beginning and increased to 478 mv after the addition of Fe^{2+} and H_2O_2 solutions. After 20 minutes of reaction the ORP value decreased to 473 mv (Figure 4-11). The ORP value was influenced by the H_2O_2 concentration in solution. These results were similar to the one obtained in CCD-1.

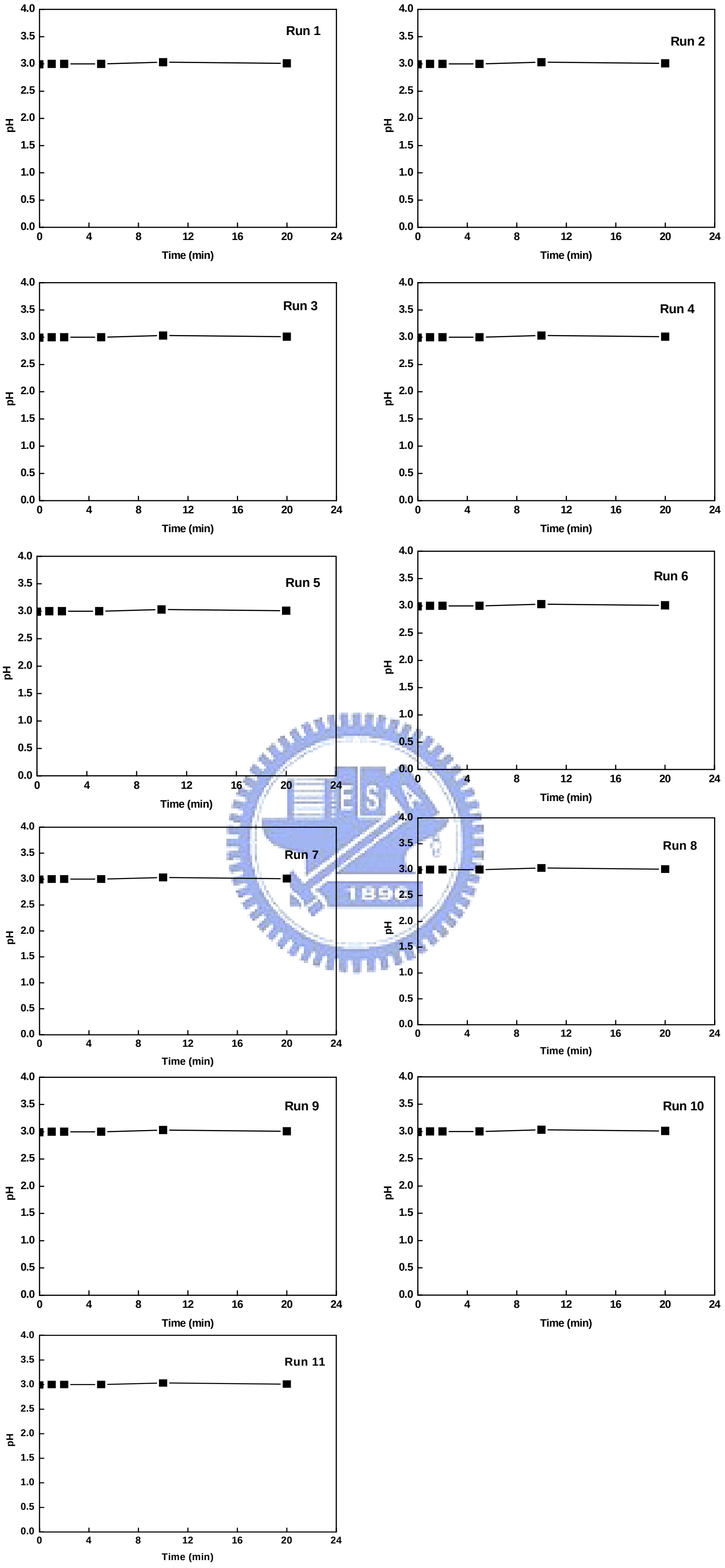

Figure 4-10 The variations of pH in CCD-2

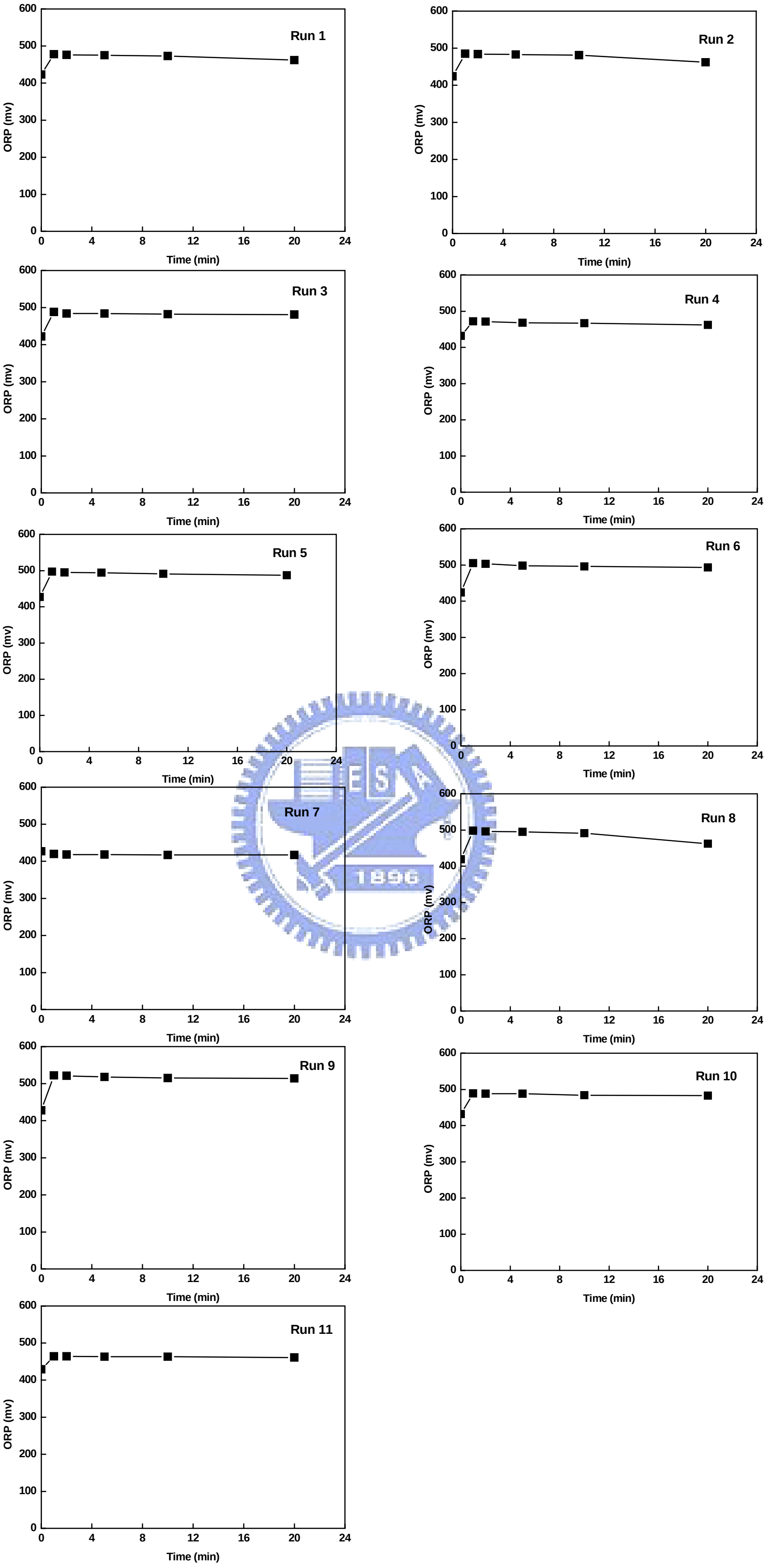

Figure 4-11 The variations of ORP in CCD-2

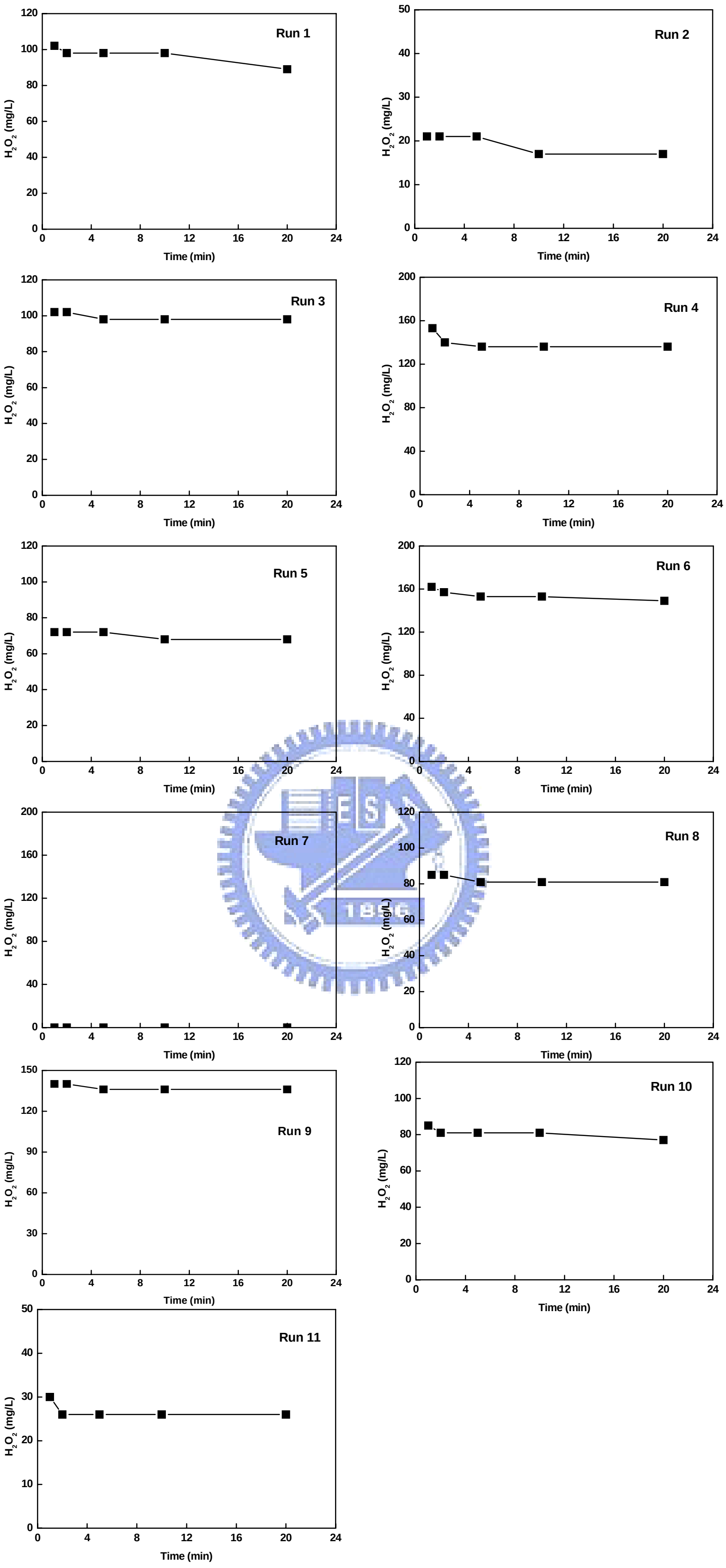

Figure 4-12 The variations of H_2O_2 concentration in CCD-2

Using Minitab®14.1, the response surface (Figure 4-13) and contour plot (Figure 4-14) were made from the data of Table 4-3. The figures are similar to the results in CCD-1. The increase in the additions of Fe^{2+} and H_2O_2 increased the carbofuran removal percentage due to the production of large amount of OH radicals. Figure 4-13 shows the effect of H_2O_2 concentration on the carbofuran removal percentage. Higher H_2O_2 concentrations resulted in higher carbofuran removal. The effects of Fe^{2+} concentration and carbofuran degradation in the Fenton process is also depicted in Figure 4-13. These results are in agreement with the observations of previous researchers, where an increase in Fe^{2+} results in increased degradation of carbofuran (Bautista *et al.*, 2007; Catalkaya and Kargi, 2007; Oliveria *et al.*, 2006).

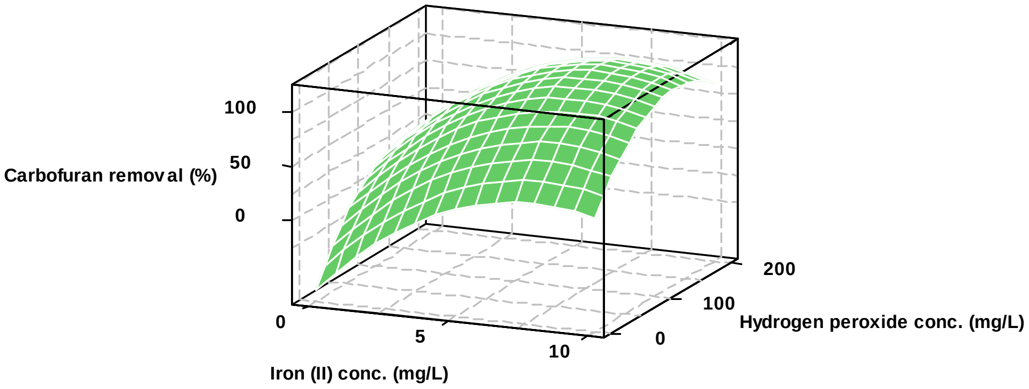

Figure 4-13 Response surface of carbofuran removal in CCD-2

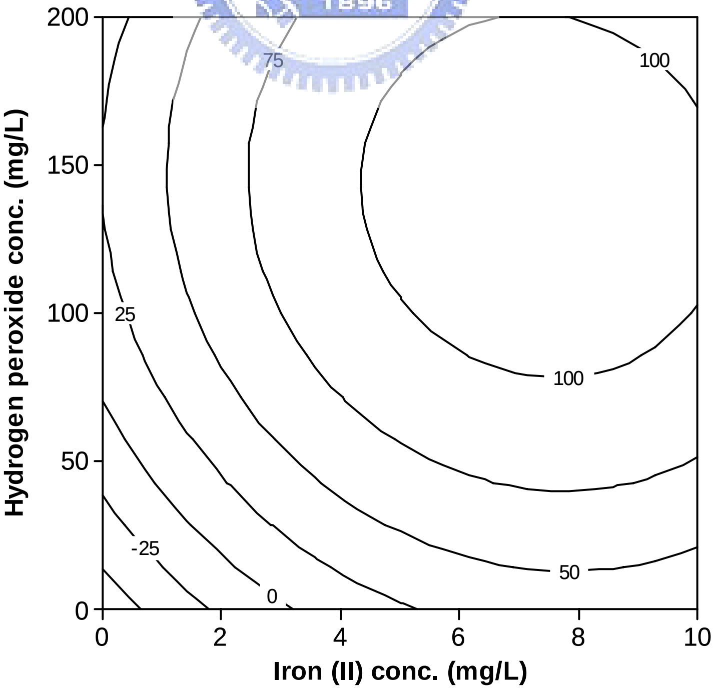

Figure 4-14 Contour plot of carbofuran removal in CCD-2

4.2.2 Modeling the optimal conditions for Fenton process

The analysis of variance (ANOVA), as calculated by Minitab®14.1, for the carbofuran removal is shown in Table 4-4. The P-values obtained from ANOVA in Table 4-4 are smaller than 0.05, which indicate that the result of the carbofuran removal can be fitted well by a second-order equation. The second-order model for the CCD-2 is given in Eq. 4-3, and the correlation R^2 and adjusted R^2 values (ignoring the insignificant terms) of Eq. 4-3 are shown in Table 4-4. Both the R^2 and adjusted R^2 values are greater than 80% (90.7% and 81.4%, respectively), which indicate that the second-order model fits well with the experimental data. The P-value less than 0.05 for any factor in analysis of variance (ANOVA) indicate a significant effect of the corresponding variable on the response.

The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function (Y) and the independent variables (X) are as follows:

$$Y = -66 + 25.81X_1 + 1.22X_2 - 1.63X_1^2 - 0.004X_2^2 + 0.01X_1X_2 \quad \text{......}(4\text{-}3)$$

Where, Y is the carbofuran removal rate (%), and X_1 and X_2 are the Fe^{2+} (mg/L) and H_2O_2 concentrations (mg/L), respectively.

Table 4-4 Analysis of variance for carbofuran removal in CCD-2

Central Composite Design-2

Central Composite Design

Factors: 2 Blocks: none Center points: 3

Runs: 11 Alpha: 1.414

Response Surface Regression

The analysis was done using coded units.

Estimated regression coefficients for carbofuran removal

Term	Coefficient	Standard deviation	T	P
Constant	-65.8297	27.3246	-2.409	0.061
Fe^{2+}	25.8119	7.2313	3.569	0.016
H_2O_2	1.2240	0.3617	3.384	0.02
$Fe^{2+} * Fe^{2+}$	-1.6361	0.6025	-2.716	0.042
$H_2O_2 * H_2O_2$	-0.0041	0.0015	-2.716	0.042
$Fe^{2+} * H_2O_2$	0.0110	0.0358	-0.307	0.771

S = 9.347 R-square = 90.7% R-square (adj) =81.4%

Analysis of variance for carbofuran removal

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	15593	15593	3118.66	9.73	0.013
Linear	2	11906	5363	2681.77	8.36	0.025
Square	2	3656.8	3656	1828.4	5.70	0.051
Interaction	1	30.2	30.25	30.25	0.09	0.771
Residual Error	5	1603.4	1603.42	320.68		
Lack-of-Fit	3	1600.8	1600.75	533.58	400.19	0.002
Pure Error	2	2.7	2.67	1.33		
Total	10	17196				

Calculated by Minitab®14.1

Minitab®14.1 also calculated a residual versus fitted value plot to test the accuracy of the model shown in Eq. 4-3. The residual versus fitted value plot for carbofuran removal rate is shown in Figure 4-15. No abnormal construction such as a funnel or bell shape is seen in Figure 4-15, which signifies that the model given in Eq. 4-3 is correct and the hypotheses are valid.

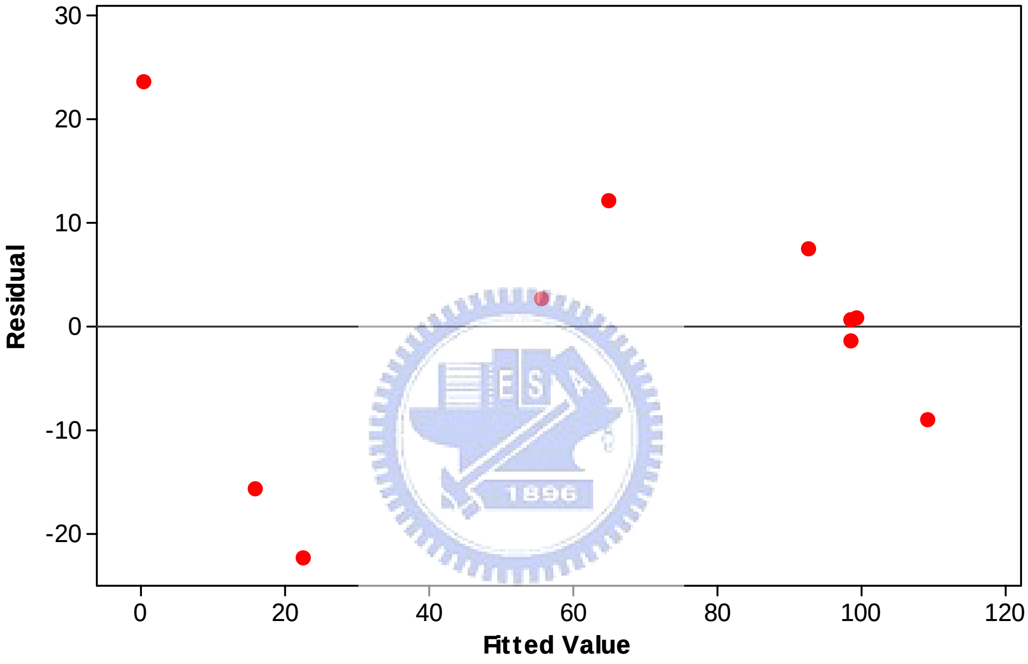

Figure 4-15 Residual versus fitted value plot for carbofuran removal in CCD-2

A normal probability plot was made to test the normality of the error distribution (Figure 4-16). The linear profile shown in Figure 4-16 indicates that the experimental data fit in good proportion with the normal distribution. This shows that the error distribution is normal.

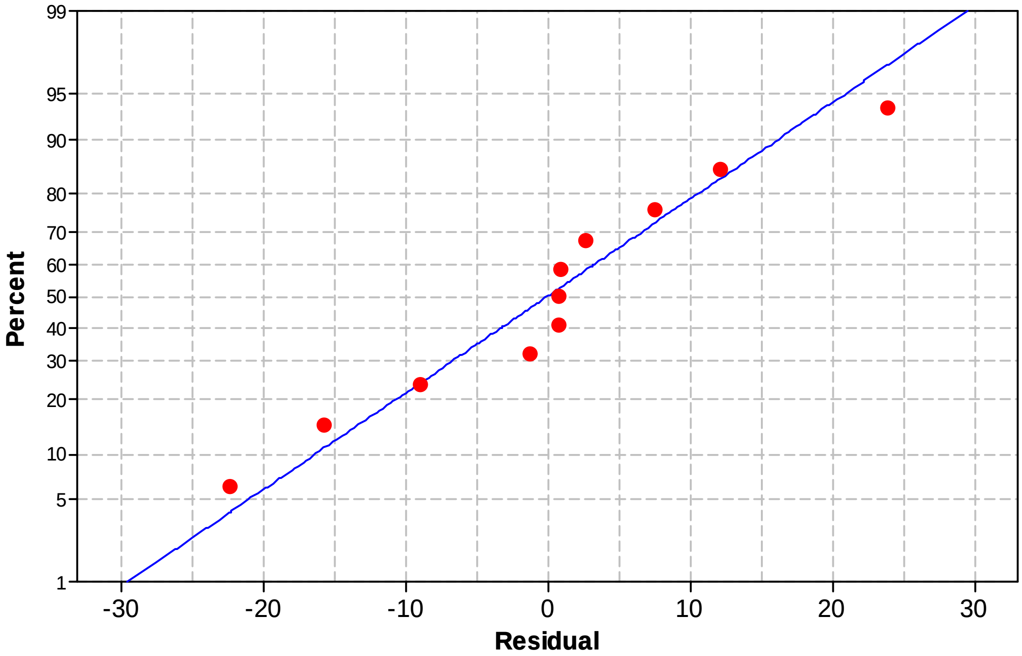

Figure 4-16 Normal probability plot of residuals for carbofuran removal in CCD-2

4.2.3 Determination of optimal conditions

The optimal conditions for maximum carbofuran removal was observed from Figure 4-14, which corresponds to Fe^{2+} concentration of 7 to 8 mg/L and H_2O_2 concentration of 120 mg/L to 150 mg/L. Similarly, Eq. 4-3 can be used to find the optimal point corresponds to the highest carbofuran removal in Figure 4-14.

From Eq. 4-3, $b = \begin{bmatrix} 25.81 \\ 1.22 \end{bmatrix}$, and $B = \begin{bmatrix} -1.64 & -0.005 \\ -0.005 & -0.004 \end{bmatrix}$

Substituting the values of b and B^{-1} into Eq. 4-2 yields,

$$X_S = -\frac{1}{2} B^{-1} b = \frac{1}{2} \begin{bmatrix} 25.81 \\ 1.22 \end{bmatrix} \begin{bmatrix} 0.61 & -0.77 \\ -0.77 & 251 \end{bmatrix} = \begin{bmatrix} 7.4 \\ 143 \end{bmatrix}$$

The result shows the optimal Fe^{2+} and H_2O_2 concentrations, respectively i.e. $X_1 = 7.4$

mg/L and X_2 = 143 mg/L.

4.3 Determination of carbofuran degradation pathway

The intermediate compounds formed in the Fenton degradation of carbofuran in the aqueous solution after 20 min were analyzed by GC-MS. Four products were identified by the molecular ion and mass fragment ions, and were compared with NIST library data. Table 4-5 summarizes the molecular weights of these products. From mass spectrum, the product retention time of 12.88 min was found to be carbofuran, the parent compound. By interpreting the mass spectrum, the product with a retention time of 7.44 min was identified as 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol, which is the product due to the cleavage of the carbamates group from carbofuran. This product was also detected in the hydrolysis (Wei *et al.*, 2001), photolysis (Bachman and Patterson, 1999), TiO_2 photocatalysis (Kuo and Lin, 2000) and AFT (Wang *et al.*, 2003) of carbofuran. The product with a retention time of 13.80 min was identified as 7-hydroxy-2,2-dimethyl-benzofuran-3-one. This was formed by further oxidizing 2,2-dimethyl-2,3-dihydro-benzofuran-7-ol on the furan ring. Wang *et al.* (2003) also reported these products as intermediates of carbofuran under AFT. The product retention time of 3.6 min was attributed to the 1,4-Benzenedicarboxaldehyde anion, which was formed by opening the furan ring and demethylation from 7-hydroxy-2,2-dimethyl-benzofuran-3-one. Further degradation products formed if any are not detected in the present study, which can be attributed to their low concentration, low extraction efficiency and/or limited sensitivity of the GC-MS. The intermediate products of carbofuran identified in the present study are listed in Table 4-5 and the possible carbofuran degradation pathway is proposed in Figure 4-17.

Table 4-5 Intermediate products of carbofuran identified by GC-MS

Product name	Molecular Weight	Formula	Retention time (min)
1,4-benzenedicarboxaldehyde anion	134	$C_8H_6O_2$	3.60
7-benzofuranol, 2,3-dihydro-2,2-dimethyl	164	$C_{10}H_{12}O_3$	7.44
Carbofuran	221	$C_{12}H_{15}NO_3$	12.88
7-hydroxy-2,2-dimethyl-benzofuran-3-one	178	$C_{10}H_{10}O_3$	13.80

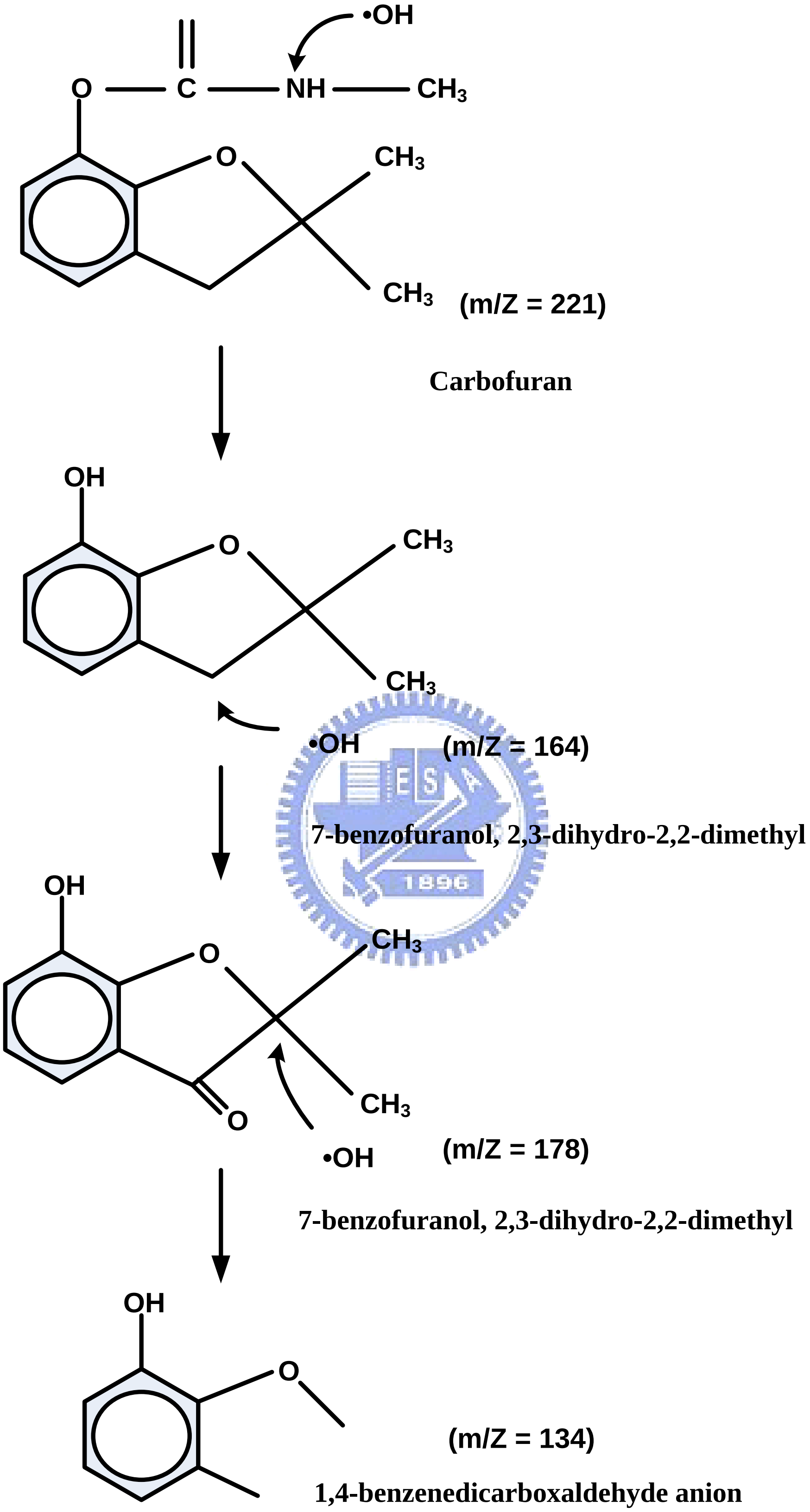

Figure 4-17 Carbofuran degradation pathway in the Fenton process

Chapter 5

Summary and conclusions

Based on the extensive experimental investigations, the following conclusions can be drawn.

1. Oxidation with Fenton's reagent has proven to be an efficient and fast process for degrading carbofuran in contaminated water. Significant percentages of carbofuran removal were achieved in just 20 min of reaction time.
2. Carbofuran degradation was strongly affected by the initial concentrations of H_2O_2 and Fe^{2+}. The central composite design and response surface methodology indicate that the optimal Fe^{2+} and H_2O_2 concentrations are 9.5 and 217 mg/L, respectively for an initial carbofuran concentration of 50 mg/L at pH 3. Similarly, the optimal Fe^{2+} and H_2O_2 concentrations are 7.4 and 143 mg/L, respectively for an initial carbofuran concentration of 10 mg/L at pH 3.
3. The initial concentration of carbofuran was an important parameter affecting the efficiency of pesticide removal by the Fenton process. Increase in initial carbofuran concentration decreased the overall carbofuran removal percentage. Complete degradation of 10 mg/L of carbofuran was achieved after 20 min of reaction under the optimum conditions of Fenton process.
4. Carbofuran was degraded into 7-benzofuranol, 2,3-dihydro-2,2-dimethyl, 7-hydroxy-2,2-dimethyl-benzofuran-3-one and 1,4-benzenedicarboxaldehyde anion. The other degradation intermediates of carbofuran formed in the system if any are not identified. Hence, the further study on the identification of complete carbofuran mineralization pathway may be an interesting future research goal.

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