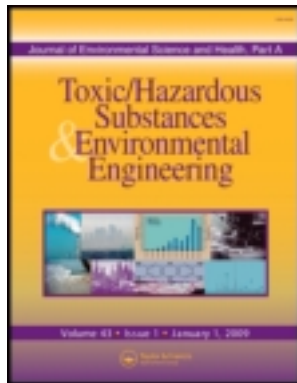


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Degradation of carbofuran-contaminated water by the Fenton process

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In this study, the Fenton process was applied for the degradation of carbofuran from aqueous system. Batch experiments were conducted at two different carbofuran concentrations i.e., 10 and 50 mg/L, and at pH 3. Batch experiments at each carbofuran concentration were designed by central composite design (CCD) with two independent variables i.e. Fe²⁺ and H₂O₂. Experimental results indicate that more than 90% of carbofuran removal was observed within 5 mins of Fenton reaction at 5 mg/L of Fe²⁺ concentration and 100 mg/L of H₂O₂ concentration. Increases in Fe²⁺ and/or H₂O₂ concentrations beyond 5 and 100 mg/L, respectively produced 100% carbofuran removal. Based on the experimental observations, the optimal Fe²⁺ and H₂O₂ dosages required for 10 mg/L of aqueous carbofuran removal were estimated as 7.4 and 143 mg/L, respectively. During this study, three carbofuran intermediates such as 7-benzofuranol,2,3,-dihydro-2,2-dimethyl, 7-hydroxy-2,2-dimethyl-benzofuran-3-one and 1,4-Benzene-di-carboxaldehyde were identified using GC/MS analyses.

Keywords: Carbofuran, Fenton process, central composite design (CCD), intermediates, degradation pathway.

Introduction

Carbofuran (2,3-dihydro-2,2-dimethylbenzofurarn-7-yl methylcarbamate, i.e. C₁₂H₁₅NO₃) is one of the most toxic carbamates pesticides used for the control of insects found in a wide variety of field crops including potato, corn and soybean. In Taiwan, carbofuran accounts about 7% of the 15,478 tons of insecticides produced per year to control the insects of rice, sugarcane, tobacco, maize, potatoes, soybeans and vegetables.^[1] Carbofuran is highly soluble in water (700 mg/L at 25°C)^[2] as well as in other solvents like acetone (150 g/kg) and acetonitrile (140 g/kg). The persistence of carbofuran in water is directly related to the pH. It is stable in acidic water and subject to increasing chemical hydrolysis at alkaline pH. 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. The use of carbofuran has received intensive concern not only due to its heavy use but also due to its high oral toxicity. Residues of carbofuran, even in small quantities can accumulate in the surrounding soil and groundwater, which can create potential toxicity

to human health. The lethal dose for 50% of target species on long term exposure (LD₅₀) of carbofuran is 11 mg/kg.^[3]

Since, the biological treatment methods require long residence times and the thermal treatment can produce secondary pollutants, oxidative reactions are preferred for the effective destruction of pollutants at a faster rate.^[4] Therefore, a variety of effective treatment techniques such as ultrasonic process,^[5] UV + Fe(III),^[6] UV/TiO₂,^[7] and UV/O₃^[8] have been applied for carbofuran removal from aqueous samples. Katsumata et al.^[6] reported that an initial carbofuran concentration of 10 mg/L was completely degraded within 50 min at pH 2.8 with a Fe³⁺ concentration of 8 × 10⁻⁴ mol/L. This reaction was found to follow the first-order kinetics with a rate constant of 1.60 × 10⁻³ per second. The variation of carbofuran removal efficiency was in good proportion with the initial Fe³⁺ concentration at different pH values investigated.^[6]

The Fenton process is very effective in the removal of many hazardous organic pollutants from water and wastewater. During Fenton process, no energy input is necessary to activate hydrogen peroxide (H₂O₂) and therefore, it offers a cost-effective source of OH radicals. Furthermore, it commonly requires a relatively short reaction time compared with other advanced oxidation processes (AOPs). Therefore, Fenton

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process is used for the transformation of various environmentally-important organic compounds, including 2,4-dichlorophenol,^[8] aniline,^[9] herbicide tebuthiuron,^[10] atrazine,^[11] and 4-chlorophenoxyacetic acid.^[12] 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. Results indicate that the removal of diuron 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 of reaction. However, only 58% of diuron was mineralized after 240 min of reaction under the optimal operating conditions indicating the formation of intermediate products. The optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ /diuron concentration for the maximum diuron removal (98.5%) was estimated as 302/38/20 mg/L.^[13] Therefore, the objective of this study is to determine the optimal Fe^{2+} and H_2O_2 dosages for the maximum carbofuran removal in Fenton process at two different initial carbofuran concentrations. In addition, carbofuran degradation pathway in the Fenton process is investigated at the optimal conditions.

Materials and methods

Materials

Carbofuran (purity > 98%) was purchased from Shida Chemical Industries, Taoyuan, Taiwan. All other chemicals and solvents used in this study were of the purest grade commercially available and used without further purification.

Experimental design

A reactor with 1 L working volume as shown in Figure 1 was used for conducting Fenton experiments. All the experiments were carried out at room temperature controlled using a water bath. Carbofuran solutions (10 and 50 mg/L) were prepared synthetically and reacted with H_2O_2 and Fe^{2+} at pH 3. During the reaction, profiles of pH and ORP were monitored using pH and ORP meters (Suntex pc-3200, Taiwan), respectively.

In order to maintain the credibility of experiments and to decrease the total number of experiments, a central composite design (CCD) was applied with two main factors i.e., Fe^{2+} and H_2O_2 concentrations. Subsequently, the optimal operating conditions were obtained by the response surface method (RSM). The levels of Fe^{2+} and H_2O_2 concentrations selected for the CCD were 0–10 mg/L and 0–200 mg/L, respectively. The CCD matrixes generated for random experimental designs are listed in Tables 1 and 2.

Analytical methods

Carbofuran concentration in the sample was analyzed by a HPLC (Hitachi L-2130, Japan) equipped with a UV-

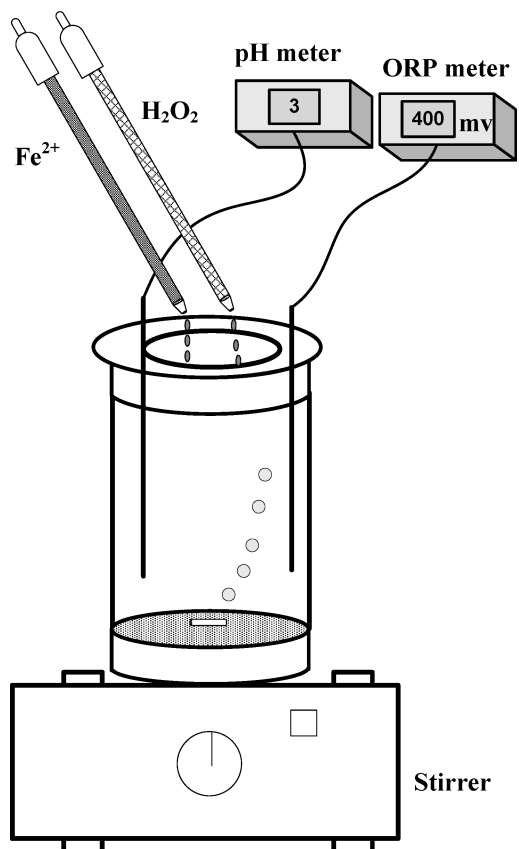


Fig. 1. Schematic diagram of carbofuran degradation by the Fenton process.

detector and a C_{18} column (4.6 mm \times 150 mm). The mobile phase of HPLC was composed of methanol and water with a volume ratio of 0/100 to 50/50. The wavelength of UV detector was set at 280 nm and methanol was pumped at a flow rate of 1.0 mL/min. At these conditions, carbofuran was identified after a retention time (Rt) of 12.3 min. Prior to sample analysis, a calibration curve was plotted with known concentration of carbofuran (between 20 and 160 mg/L) and area response with an R^2 of 0.99.

The hydrogen peroxide concentration was determined using a KI titration method.^[14] The concentration of total organic carbon (TOC) measured by a TOC analyzer (OI Analytic Model 1010) was used to represent the carbofuran mineralization. The standard methods NIEA W418, 51C and NIEA W419, 51A with a spectrophotometer (UV-VIS Detector L-2420) were followed for the determination of nitrite and nitrate concentrations, respectively.

To extract the intermediates, 5 mL of sample was mixed with 1 mL of dichloromethane and 1 mL of ethyl acetate and shaken rigorously for 30 min (Wang and LemLey, 2003). The extracted sample was injected into a HP6890 GC coupled with a HP5973 mass selective detector (GC/MS) for the determination of carbofuran intermediates. The

Table 1. Reaction conditions of Fe^{2+} and H_2O_2 concentrations conducted in the degradation of 50 mg/L carbofuran by Fenton process.

Run no.	Fe^{2+} (mg/L)	H_2O_2 (mg/L)	Carbofuran removal (%)	TOC removal (%)
1	5	100	28	6
2	8.54	29.28	13	3
3	0	100	0	0
4	1.46	170.72	13	3
5	10	100	39	13
6	5	200	57	10
7	5	0	0	0
8	5	100	28	3
9	8.54	170.72	37	0
10	5	100	25	3
11	1.46	29.28	2	3

Note: Standard deviations (SD) of carbofuran and TOC removals were $27 \pm 1.7\%$ and $4 \pm 1.7\%$, respectively, at the center point, i.e. Runs 1, 8 and 10.

GC was equipped with a HP-5 capillary column (30 m \times 0.25 mm i.d., thickness of 0.25 μm). 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 and from 210 to 305°C at a rate of 30°C/min and finally held at 305°C for 5 min. The injector and detector temperatures were maintained at 220 and 250°C, respectively.^[3] Helium was used as a carried gas (1.5 mL/min) and the sample was analyzed in splitless mode. The mass spectra were obtained by the electron-impact (EI) mode at 70 eV using the full-scan mode.

Table 2. Reaction conditions of Fe^{2+} and H_2O_2 concentrations conducted in the degradation of 10 mg/L carbofuran by Fenton process.

Run no.	Fe^{2+} (mg/L)	H_2O_2 (mg/L)	Carbofuran removal (%)	TOC removal (%)
1	5	100	97	22
2	8.54	29.28	77	10
3	0	100	0	0
4	1.46	170.72	58	5
5	10	100	100	34
6	5	200	100	33
7	5	0	0	1
8	5	100	99	33
9	8.54	170.72	100	43
10	5	100	99	34
11	1.46	29.28	24	6

Note: Standard deviations (SD) of carbofuran and TOC removals were $98.3 \pm 1.2\%$ and $29.7 \pm 6.7\%$, respectively, at the center point, i.e. Runs 1, 8 and 10.

Results and discussion

Effect of Fe^{2+} and H_2O_2 concentrations

It is recognized that the increase in the concentrations of Fe^{2+} and H_2O_2 can increase the degradation of organic compounds by amplifying the oxidant level in the reaction system. This finding is in agreement with the results found in other studies.^[8,13] However, the presence of too much H_2O_2 in the solution can reduce the degradation efficiency.^[8] The reaction conditions of Fe^{2+} and H_2O_2 concentrations, carbofuran removal and TOC reduction corresponding to the Fenton experiments conducted at 50 mg/L carbofuran are listed in Table 1. The carbofuran removal profiles at different reaction conditions are shown in Figure 2. The mineralization of carbofuran is in the range of 0 to 13% (reduction of TOC as shown in Table 1). The highest carbofuran removal of 57% was observed in Run 6 conducted at an initial Fe^{2+} and H_2O_2 concentrations of 5 and 200 mg/L, respectively.

Comparing the Runs 1, 6 and 7 (Fe^{2+} of 5 mg/L and H_2O_2 of 100, 200 and 0 mg/L), it can be noticed that removals of carbofuran are 28%, 57% and 0% in Runs 1, 6 and 7, respectively (Table 1). This indicates that the increase in H_2O_2 concentration can proportionately increase the removal of carbofuran (H_2O_2 is 0 mg/L in Run 7). Similarly, comparing the Runs 1, 3 and 5 (H_2O_2 of 100 mg/L and Fe^{2+} of 5, 0 and 10 mg/L) indicate that the increase in Fe^{2+} concentration can increase the removal of carbofuran (carbofuran removals in Runs 1, 3 and 5 were 28%, 0% and 39%, respectively).

Using the experimental findings, the response surface and contour plot were prepared using Minitab[®] 14.1, and the results are shown in Figures 3 and 4, respectively. It can be seen from Figures 3 and 4 that the removal of carbofuran is increasing with increases in Fe^{2+} and H_2O_2 concentrations. These results are in agreement with Oliveria et al.^[8]

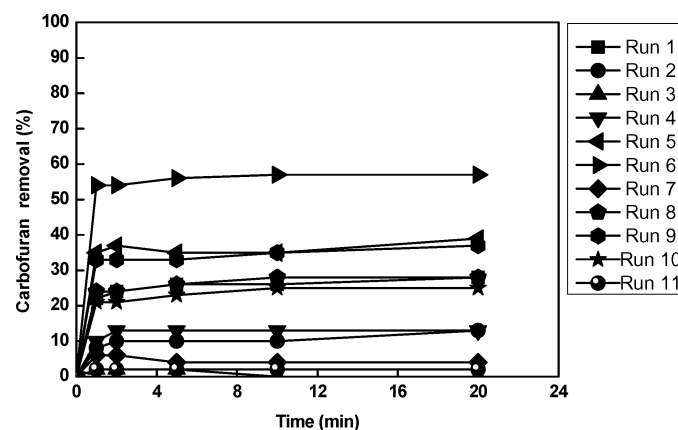


Fig. 2. Profiles of carbofuran removal by the Fenton process under different reaction conditions. (Initial carbofuran of 50 mg/L and pH 3).

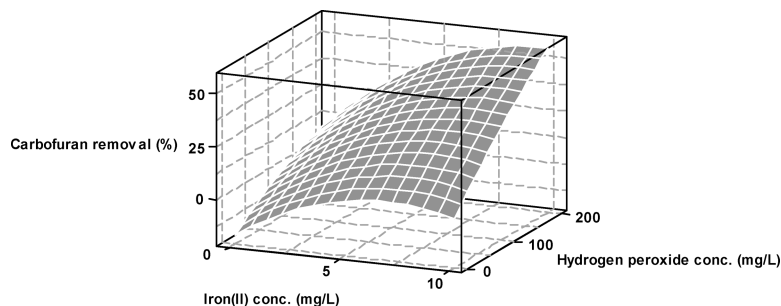


Fig. 3. Response surface depicts the carbofuran degradation with initial carbofuran of 50 mg/L and pH 3.

Effect of carbofuran concentrations

To understand the effect of lower initial carbofuran concentration in Fenton process, the experiments were repeated at an initial carbofuran concentration of 10 mg/L. Table 2 shows the reaction condition of Fe^{2+} and H_2O_2 concentration for 11 runs, and the Runs 1, 8 and 10 indicate the triplicate reactions. The experimental outcomes of the investigation are shown in Figures 5 to 7. Almost 100% carbofuran removals were observed in Run 1 (Fe^{2+} of 5 mg/L, H_2O_2 of 100 mg/L), Run 5 (Fe^{2+} of 10 mg/L, H_2O_2 of 100 mg/L), Run 6 (Fe^{2+} of 5 mg/L, H_2O_2 of 200 mg/L) and Run 9 (Fe^{2+} of 8.54 mg/L, H_2O_2 of 170.72 mg/L) within 5 min of reaction (Fig. 6). This indicates that the Fenton process is useful in decomposing the carbofuran at low concentration i.e., 10 mg/L. A TOC reduction of 43% in Run 9 indicates the potential of carbofuran mineralization by the Fenton process.

Applying the experimental data in Minitab[®] 14.1, the response surface and contour plot were prepared as shown in Figures 6 and 7, respectively. An increasing trend in carbofuran removal was observed with the increases in Fe^{2+} and H_2O_2 concentrations (Figs. 6 and 7). However, a de-

creasing trend in the carbofuran removal is observed when the Fe^{2+} and H_2O_2 concentrations are higher than 7.4 and 143 mg/L, respectively. As a whole, it can be concluded that the addition of 7.4 mg/L of Fe^{2+} and 143 mg/L of H_2O_2 could produce better reaction conditions for the degradation of 10 mg/L of carbofuran in Fenton process.

Based on the above description, the result of carbofuran removals were summarized and a relationship between the carbofuran removal and the mole concentrations of Fe^{2+} multiplied by H_2O_2 was developed as shown in Figure 8 (initial carbofuran 50 mg/L) and Figure 9 (carbofuran 10 mg/L). Figure 8 indicates the possibility of increasing the carbofuran removal with the increased addition of Fenton reagents. In addition, the molar concentrations of Fe^{2+} multiplied by H_2O_2 is greater than 0.5 mM \times mM, a stable carbofuran removal profile was observed. A comparable result is shown in Figure 9. The removal of carbofuran reaches almost 100% at 10 mg/L of initial carbofuran condition, when the molar concentrations of Fe^{2+} multiplied by H_2O_2 is greater than 0.25 mM \times mM. This shows that 0.25 mM \times mM of Fenton reagent is profitable for the complete degradation of 10 mg/L or lower initial carbofuran concentration.

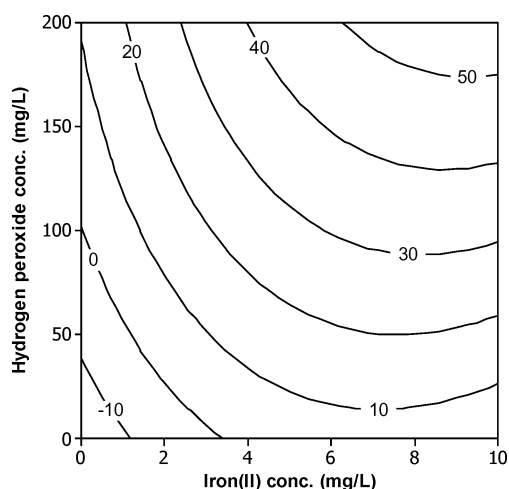


Fig. 4. Contour plot of carbofuran degradation with the concentration of Fe^{2+} and H_2O_2 at initial carbofuran of 50 mg/L and pH 3.

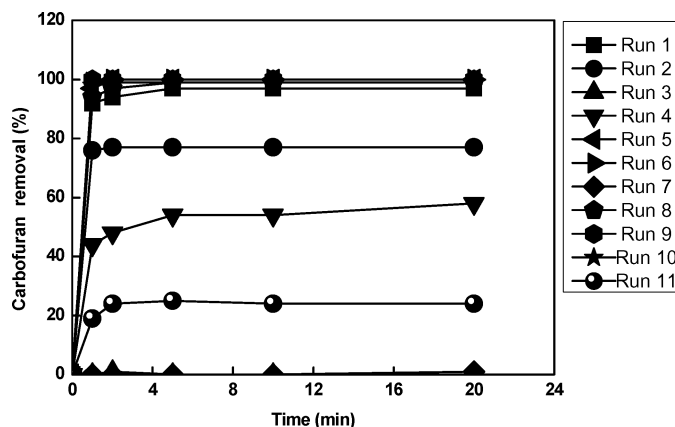


Fig. 5. Profiles of carbofuran removal by the Fenton process under different reaction conditions. (Initial carbofuran of 10 mg/L and pH 3).

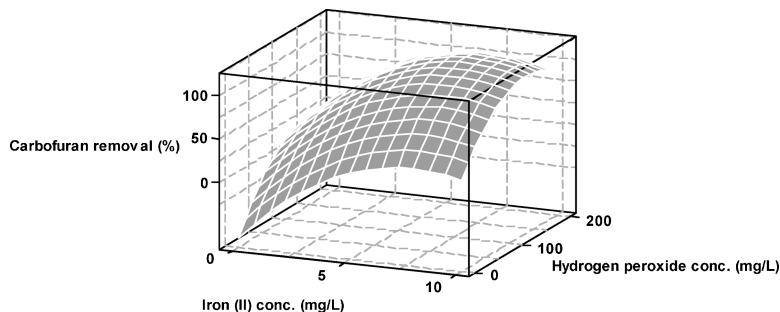


Fig. 6. Response surface depicts the carbofuran degradation with initial carbofuran of 10 mg/L and pH 3.

Carbofuran removal in the present study is compared with other studies in Table 3. Bano and Musarrat^[15] indicated that 40 days are necessary for the complete degradation of 100 mg/L carbofuran by *Pseudomonas sp.* at 30°C. Katsumata et al.^[6] and Tennakone et al.^[7] applied photolytic method for the degradation of carbofuran at pH 2.8. Results indicate that more than 90% of 10 mg/L initial carbofuran could be degraded by photolytic method with a reaction time of 50 min.^[6] The reaction time was prolonged to 6 hours for 90% of degradation at an initial carbofuran concentration of 222 mg/L.^[7] Wang and LemLey^[3] investigated the removal of carbofuran (22 mg/L) by anodic Fenton process at 25°C and found that complete degradation was observed within 5 min of reaction. In the present study, a complete degradation of 10 mg/L of carbofuran was observed within 2 min of Fenton process at pH 3, which agrees the result shown by Wang and LemLey.^[3]

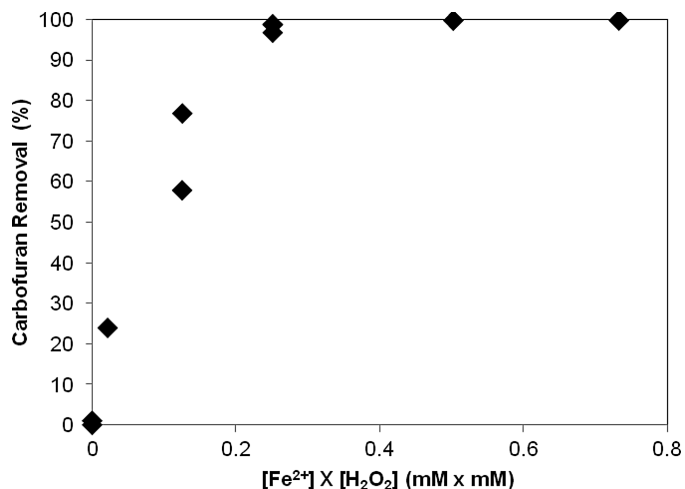


Fig. 8. Relationship between the removal of carbofuran and the mole concentration of Fe^{2+} multiplied by H_2O_2 . (initial carbofuran concentration: 50 mg/L).

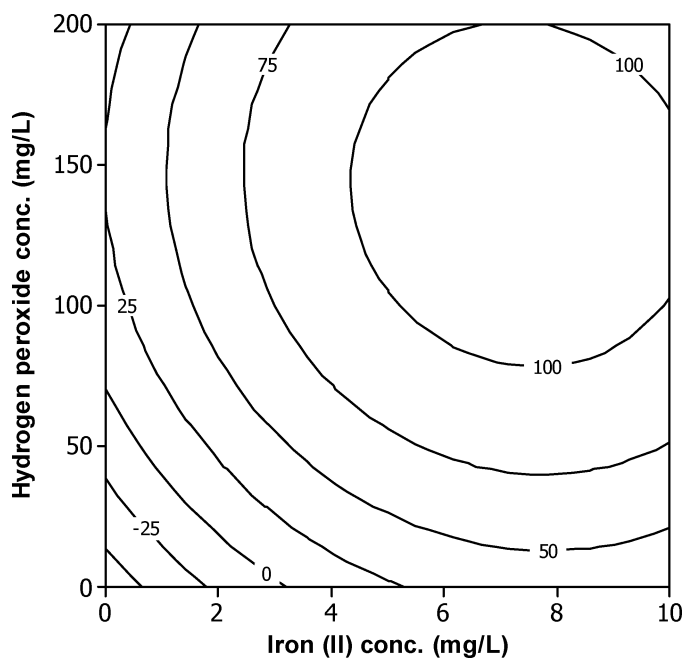


Fig. 7. Contour plot of carbofuran degradation with the concentration of Fe^{2+} and H_2O_2 at initial carbofuran of 10 mg/L and pH 3.

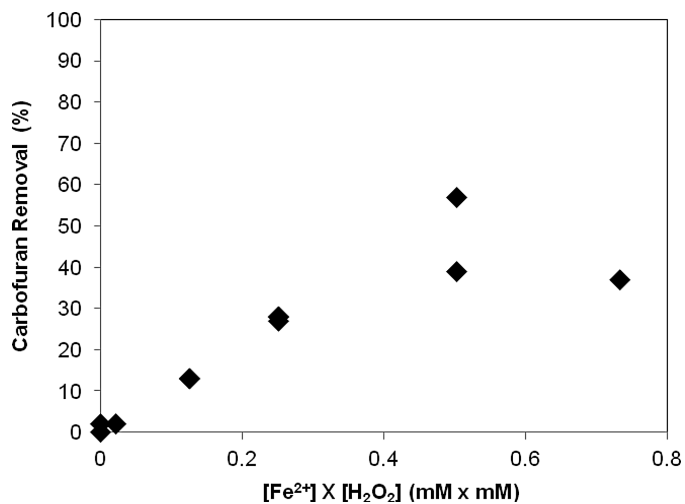


Fig. 9. Relationship between the removal of carbofuran and the mole concentration of Fe^{2+} multiplied by H_2O_2 . (initial carbofuran concentration: 10 mg/L).

Table 3. Summarization of carbofuran removal by different methods cited in references and this study.

Study	Carbofuran (mg/L)	Methods	Reaction time	Removal ratio
Tennakone et al. ^[7]	222	TiO ₂ + UV at 26°C pH 2.8, 400 W	6 h	90%
Hua and Thompson ^[5]	30	Ultrasonic 1800 W 20 kHz, Ar : O ₂ (4:1)	30–60 mins	>90%
Wang and LemLey ^[3]	22	Anodic Fenton at 25°C	5 mins	100%
Bano and Musarrat ^[15]	100	Pseudomonas sp. at 30°C	40 d	100%
Katsumata et al. ^[6]	10	UV + Fe(III) at pH 2.8	50 mins	>90%
This study	10 – 50	Fenton process at pH 3	20–30 mins	100%

Reaction mechanisms

Bachman and Patterson^[16] identified the photoproducts of carbofuran i.e., 2,3-dihydro-2,2-dimethyl-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. Wang and LemLey^[3] analyzed

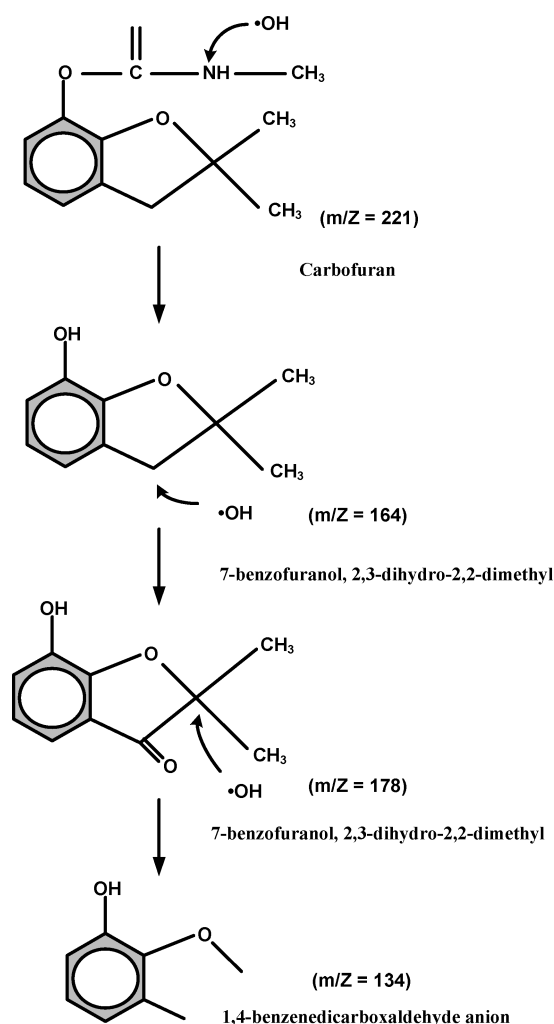


Fig. 10. Possible carbofuran degradation pathway by the Fenton process.

the degradation products generated after 2 min of membrane anodic Fenton treatment in GC/MS. It is found that 2,3-dihydro-2,2-dimethylbenzofuran-7-yl was produced first and further oxidized to 2,3-dihydro-2,2-dimethyl-benzofuran-7-ol, 2,3-dihydro-3-oxo-2,2-dimethylbenzofuran-7-ol and 2,3-dihydro-3-hydroxyl-2,2-dimethylbenzofuran-7-ol. In this study, three intermediates including 1,4-benzenedicarboxaldehyde anion, 7-benzofuranol, 2,3-dihydro-2,2-dimethyl (or named as 2,3-dihydro-2,2-dimethyl-benzofuran-7-ol) and 7-hydroxy-2,2-dimethyl-benzofuran-3-one were identified using GC/MS at retention times of 3.6 min, 7.44 min and 13.8 min, respectively. Based on the intermediates identified, the possible carbofuran degradation pathway is proposed in Figure 10.

Conclusion

Carbofuran degradation was strongly affected by the initial concentrations of H₂O₂ and Fe²⁺. The central composite design and response surface methodology indicate that the optimal Fe²⁺ and H₂O₂ concentrations are 9.5 and 217 mg/L, respectively, for an initial carbofuran concentration of 50 mg/L at pH 3. Similarly, the optimal Fe²⁺ and H₂O₂ concentrations are 7.4 and 143 mg/L, respectively for an initial carbofuran concentration of 10 mg/L at pH 3. A decrease in overall carbofuran removal was observed with an increase in initial carbofuran concentration.

Complete degradation of 10 mg/L of carbofuran was achieved within 20 min of Fenton reaction at the optimum conditions. 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 experimental findings indicate that the Fenton process has proven to be an efficient method for the degradation of carbofuran-contaminated water. However, the application of Fenton process for the degradation of real-time carbofuran-contaminated wastewater i.e., agricultural runoff can provide more useful information for the design of the Fenton process and for the treatment of pesticide contaminated wastewater.

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