



Degradation of carbofuran in aqueous solution by ultrasound and Fenton processes: Effect of system parameters and kinetic study

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ABSTRACT

To establish an efficient oxidation process for carbofuran degradation, the effects of some operating parameters such as dosages of H_2O_2 , Fe^{2+} and initial carbofuran concentrations were observed during carbofuran degradation by the ultrasound process, Fenton process and a combined ultrasound/Fenton process. The degradation kinetics of carbofuran was also examined based on the experimental data. The results show that more than 99% of the carbofuran was degraded by the ultrasound/Fenton process within short reaction time periods. Increased dosages of H_2O_2 and Fe^{2+} enhanced the degradation of carbofuran in the ultrasound and Fenton oxidation processes, but initial carbofuran concentrations decreased carbofuran degradation in both the Fenton and ultrasound/Fenton processes. The degradation kinetics of carbofuran by the three oxidation processes was found to be in accordance with first-order reaction kinetics. The results provide fundamental information about the treatment of carbofuran wastewater and/or other pesticides by the ultrasound/Fenton oxidation process.

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1. Introduction

Advanced oxidation processes (AOPs) are generally used to degrade hazardous and non-biodegradable organic materials and convert them into carbon dioxide by producing $\bullet OH$ radicals during the oxidation process [1,2]. Several kinds of AOPs (e.g. ultrasound [1,3,4], Fenton [5–9], ozone [10,11] and ultraviolet light [12,13]) have been effectively used in the treatment of wastewater containing pesticide, phenols, chlorophenols and azo dyes.

Carbofuran (2,3-dihydro-2,2-dimethylbenzofurarn-7-yl methylcarbamate, $C_{12}H_{15}NO_3$) is a well-known methylcarbamate pesticide used to inhibit insect activity in soybeans, rice, sugar cane, tobacco, maize, potatoes and vegetables. The use of carbofuran has aroused considerable concern not only due to its heavy rate of use (10.5% of the total pesticides in Taiwan, 2003–2007) but also due to its high oral toxicity [14]. Several biological and chemical treatment methods have been investigated to reduce the amount of carbofuran present in wastewater [9,12–19]. Chaudhry and Ali [15] isolated 15 bacteria from soil samples and used them as a biological method of degrading carbofuran. All isolates were gram negative and were oxidase- and catalase-positive rods, occurring singly or as short chains. The results indicated that the carbofuran is the bacteria's sole source of nitrogen or carbon, and that they hydrolyze the carbofuran to carbofuran phenol. In addition, some of the bacteria

were observed to degrade the carbofuran rapidly, up to 40% being lost as $^{14}CO_2$ in a 1 h reaction. These results suggested that the isolates degrade carbofuran by utilizing an oxidative pathway. Bano and Musarrat [18] isolated NJ-101, initially identifying it as *Pseudomonas* sp. occurring in agricultural soil. The isolates exhibited efficient degradation of carbofuran at a constant rate of 0.035 day^{-1} in accordance with first-order rate kinetics. Their ability to perform several biological activities in tandem suggested that isolate NJ-101 was unique. However, isolation and cultivation of the bacterial well needed a long time. The chemical processes are considered in the degradation of carbofuran.

Other researchers [16] used a chemical UV/TiO₂ process to treat wastewater containing 222 mg/L carbofuran at pH 2.8. Their results indicated that 90% of the carbofuran was oxidized within a 6 h reaction time, but complete mineralization of the carbofuran to carbon dioxide by UV/TiO₂ process took 15 h. Hua and Thompson [17] investigated the treatment efficiency of 30 mg/L carbofuran degradation by an ultrasonic process at an ultrasound energy output of 1800 W. These results indicated that 90% of the carbofuran was oxidized within a 30–60 min reaction period, and that increased ultrasonic energy output and decreased initial carbofuran concentration enhanced carbofuran degradation.

In another study, a combined O₃/UV process was also used to treat wastewater containing 100 mg/L carbofuran at pH 2; in this case, 90% of the carbofuran was oxidized within 50 min [12]. That study also investigated the effect of a range of other treatment methods, including photo-Fenton, O₃/UV, UV/H₂O₂ and Fenton processes. They found that the photo-Fenton method produced sig-

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nificantly higher treatment efficiency than the other processes. It is evident from these results that a combination of several chemical processes is effective in enhancing the degradation of organic pollutants. Ma et al. [9] used the Fenton process to degrade carbofuran in aqueous systems; they found that more than 90% of the carbofuran was removed within 5 min by the Fenton reaction at 5 mg/L of Fe^{2+} and 100 mg/L of H_2O_2 , and that increasing the Fe^{2+} and/or H_2O_2 concentrations beyond 5 mg/L and 100 mg/L respectively removed all the carbofuran.

The objectives of the present study were to investigate the degradation of carbofuran by the ultrasound, Fenton and a combined ultrasound/Fenton processes under different reaction conditions; carbofuran degradation rate constants were also investigated using the first-order kinetic model.

2. Materials and methods

2.1. Materials

The chemical reagents used in this study were carbofuran ($\text{C}_{12}\text{H}_{15}\text{NO}_3$, purity > 98%), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, purity > 99.5%), and an aqueous solution of hydrogen peroxide (H_2O_2 , 30% (w/w) in water). During the analytical processes, titanium sulfate solution ($\text{Ti}(\text{SO}_4)_2$), hydrogenophthalate potassium ($\text{C}_8\text{H}_5\text{KO}_4$) (KHP) and dichloromethane (CH_2Cl_2) were used in determining H_2O_2 concentration, total organic carbon (TOC) concentration and carbofuran concentration. These chemicals were the purest grade commercially available and were used without further purification.

2.2. Experimental apparatus

A schematic drawing of the reactor is shown in Fig. 1. A 0–750 W sonicator (Microson VCX 750, USA) equipped with a sealed converter (Model CV 33, 63.5 mm in diameter and 183 mm in length) and titanium probe tip (Part. no. 630-0210, 25 mm in diameter and 122 mm in length) operated at 20 kHz was used in this study. The amplitude in the ultrasound and ultrasound/Fenton tests was adjusted at 40% (300 W power output) without pulse length setup. Reactions were performed in a cylindrical reactor (1 L working volume) with a cooling jacket and a circulating temperature controller to maintain the reaction temperature at 25 °C during the ultrasound, Fenton and ultrasound/Fenton tests. A magnetic mixer

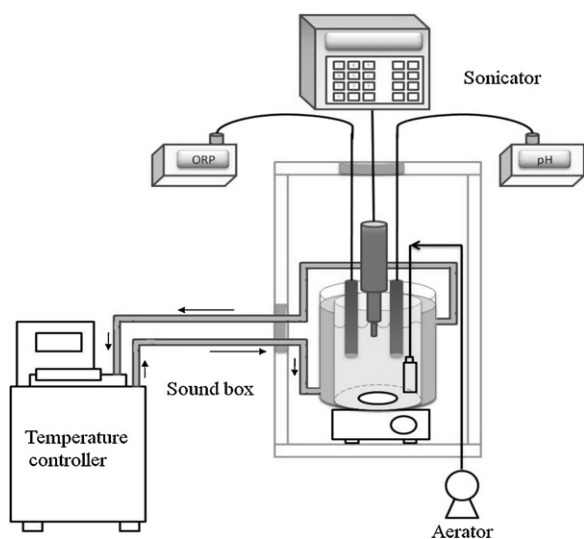


Fig. 1. Schematic diagram of the experimental apparatus designed for carbofuran decomposition.

Table 1

Design of reaction parameters in the decomposition of carbofuran by the ultrasound, Fenton and ultrasound/Fenton processes.

Process	Parameters	Range
Ultrasound	Concentration of carbofuran (mg/L)	20
	pH value	3
	H_2O_2 addition (mg/L)	0–500
Fenton	Concentration of carbofuran (mg/L)	10–200
	pH value	3
	H_2O_2 addition (mg/L)	100
	Fe^{2+} addition (mg/L)	1
Ultrasound/Fenton	Concentration of carbofuran (mg/L)	50–200
	pH value	3
	H_2O_2 addition (mg/L)	100
	Fe^{2+} addition (mg/L)	1–20

controlled the mixing speed of the solution at 100 rpm. Aeration inside the reactor was maintained at 0.2 L of air/min. Sensors for oxidation–reduction potential (ORP) and pH (Suntex PC-3200, Taiwan) were placed in the solution; the ORP and pH profiles were monitored online. Prior to commencing the experiment, the ORP sensor was rechecked using a standard solution of 220 mV.

2.3. Experimental conditions and procedure

The value of the initial pH in all experiments was 3 attained by adding 1 N H_2SO_4 as required. During the reactions, the pH values varied freely without any hand correction. In the ultrasound process, the effect on carbofuran degradation of H_2O_2 dosage ranging from 0 mg/L to 500 mg/L was observed. In the Fenton process, the dosage of H_2O_2 was 100 mg/L and the dosage of Fe^{2+} was 1 mg/L. The effect of initial carbofuran concentration (10–200 mg/L) on carbofuran degradation by the Fenton process was studied.

The values of experimental variables such as H_2O_2 , ferrous iron and carbofuran concentrations were designed based on the other studies [13,14,16–18] and our preliminary study [9]. In the ultrasound/Fenton process, the dosage of H_2O_2 was 100 mg/L. The effects of initial carbofuran concentration (50–200 mg/L) and Fe^{2+} dosages (1–20 mg/L) were studied. The reaction parameters for the ultrasound, Fenton and ultrasound/Fenton processes are shown in Table 1.

2.4. Sample analysis

Concentrations of carbofuran were analyzed by gas chromatography equipped with a mass spectrometry (GC–MS–QP2010, Shimadzu, Japan) using a DB-5MS column (length 30 m, thickness 0.25 μm , diameter 0.25 mm) in the GC oven. Before analysis, 5 mL water samples were collected at set time intervals and 1 mL of dichloromethane was added and mixed with the water sample for 30 min at a mixing speed of 150 rpm following the steps described

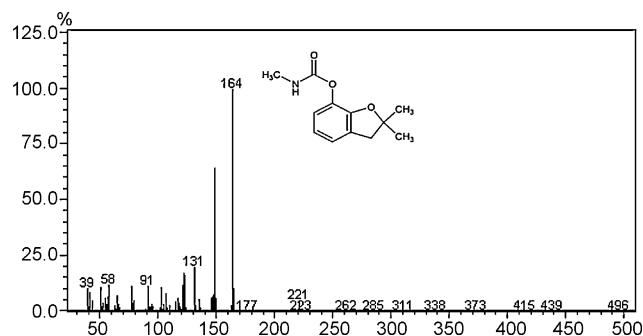


Fig. 2. Mass spectrum of carbofuran determination in GC–MS analysis.

Table 2
Results of carbofuran degradation, TOC removal and first-order kinetic constants in the degradation of carbofuran by an ultrasonic process with different H₂O₂ dosages.

Methods	Factors H ₂ O ₂ dosage (mg/L)	Carbofuran degradation (%)	TOC removal (%)	First-order reaction kinetics	
				$K (\times 10^{-3} \text{ min}^{-1})$	R^2
Ultrasound	0	22	3	2.4	0.814
	10	34	6	2.7	0.810
	50	36	10	3.0	0.899
	100	39	14	3.9	0.986
	200	44	20	4.6	0.972
	300	14	5	1.0	0.909
	400	12	5	0.9	0.868
	500	12	4	0.8	0.805

in Wang and Lemley [14]. The GC oven temperature ranged from 80 °C (holding time 2 min) to 210 °C (holding time 3 min) at a ramp of 10 °C/min and from 210 °C to 305 °C at a ramp of 30 °C/min. The injector and detector temperatures were maintained at 220 °C and 250 °C respectively. High purity (99.99%) helium was used as a carrier gas (1.5 mL/min) and the sample was analyzed in splitless mode. Mass spectra were obtained by electron-impact (EI) at 70 eV using the full-scan mode.

Prior to sample analysis, a calibration curve was plotted with known concentrations of carbofuran (between 1 mg/L and 30 mg/L) and an area response with an R^2 of 0.995. Fig. 2 shows the mass spectrum of carbofuran determination in GC–MS analysis. Based on the appearance of mass spectrum including peak 131, 164 and 221 and comparison with the mass spectra library in GC–MS, it can be identified as the carbofuran where the similarity was greater than 99%. The hydrogen peroxide concentration was measured by the spectrophotometric determination using a 412 nm wavelength spectrophotometer (UV-2102, Unico TM, USA) and potassium titanium oxalate.

Mineralization of an organic compound is generally defined as its being readily oxidized to carbon dioxide; hence, in the present study, carbofuran mineralization was effected by removing all of the organic carbon. TOC concentrations were measured with the oxalate wet oxidation method using a TOC analyzer (TOC-500, Shimadzu, Japan) for which hydrogenophthalate potassium was adopted as the reference standard. Method detection limits (MDLs) and recovery of carbofuran, H₂O₂ and TOC concentrations are: carbofuran 0.08 mg/L, H₂O₂ 0.11 mg/L and TOC 0.04 mg/L at 97.9 ± 2.8%, 94.9 ± 5.9% and 97.0 ± 3.6% recoveries respectively.

3. Results and discussion

3.1. Treatment of carbofuran by the ultrasound process

The ultrasound process was first used in waste treatment and medical research in 1927 and has been applied to wastewater treatment since 1956. Two reaction mechanisms have been proven to be effective in destroying the molecular structure of refractory organic matters: direct pyrolysis inside the cavitation bubbles produced by the passage of ultrasound waves through water; and indirect oxidation by hydroxyl ($\cdot\text{OH}$) radical attack taking place in the ultrasonic process. In the present study, the ultrasonic process was used to treat the 20 mg/L carbofuran wastewater with different H₂O₂ concentrations at pH 3 for a reaction period of 120 min, where the sampling time intervals were 10 min, 20 min, 30 min, 60 min, 90 min and 120 min.

Several authors have used different treatment methods to degrade carbofuran, all of them finding that the degradation of carbofuran followed a first-order kinetics process [12,13,18]. Accordingly, first-order kinetics was used in the present study to determine the rate constant (K) of carbofuran degradation. The results of carbofuran degradation, TOC removal and rate constants in Table 2 show that degradation of the carbofuran increased from 22% to 44% with increasing H₂O₂ dosages of 0–200 mg/L within 120 min. Dosages greater than 300 mg/L led to a decrease in carbofuran degradation to around 12–14%. Sun et al. [20] investigated the effect of H₂O₂ dosage on the degradation of AB1 dyes by the ultrasound/Fenton process and found that the reaction was significantly influenced by H₂O₂ dosage: the decoloration efficiency

Table 3
Results of carbofuran degradation, TOC removal and first-order kinetic constants in the degradation of carbofuran by the Fenton process for different carbofuran concentrations.

Methods	Factors	Carbofuran degradation (%)	TOC removal (%)	First-order reaction kinetics		
				$K (\times 10^{-3} \text{ min}^{-1})$	R^2	
Fenton ^a	Carbofuran concentration (mg/L)	10	81	10	25.7	0.987
		20	42	8	16.3	0.991
		50	40	7	12.5	0.954
		100	39	6	11.9	0.912
		200	15	6	4.9	0.984
		Ultrasound/Fenton	Fe ²⁺ dosage (mg/L)	1 ^b	52	8
5	100			12	– ^c	–
10	100			40	–	–
20	100			46	–	–
Carbofuran concentration (mg/L)	50 ^d			100	14	102.7
	100		63	10	41.3	0.922
	200		38	9	37.1	0.866

^a Dosages of Fe²⁺ and H₂O₂ were 1 mg/L and 100 mg/L, respectively.

^b Initial carbofuran concentration and dosage of H₂O₂ were 20 mg/L and 200 mg/L, respectively.

^c The concentration of carbofuran was lower than MDL in the first collected sample (reaction time 1 min).

^d Dosages of Fe²⁺ and H₂O₂ were 10 mg/L and 100 mg/L, respectively.

increased from 67% to 92.39% as a consequence of increasing H_2O_2 dosage from 0.5 mM to 8.0 mM after 10 min. Further increase of the H_2O_2 dosage from 8.0 mM to 32.0 mM, however, slowed the degradation rate of AB1. This might be due to the increase in $\cdot\text{OH}$ radical formation when H_2O_2 is first added, but at higher H_2O_2 concentrations $\cdot\text{OH}$ might be consumed by various mechanisms, including the scavenging effects of H_2O_2 and the recombination of $\cdot\text{OH}$ radicals [21]. This might explain the results of the present study, in which it was observed that continued increase of H_2O_2 dosage led to a decrease in the carbofuran degradation. Comparable results for TOC removal and the first-order rate constants are shown in Table 2: TOC removal gradually increased from 3% to 20% within 30 min and the first-order rate constant increased from $2.4 \times 10^{-3} \text{ min}^{-1}$ to $4.6 \times 10^{-3} \text{ min}^{-1}$ with H_2O_2 dosages from 0 mg/L to 200 mg/L, after which H_2O_2 dosages greater than 200 mg/L resulted in a decline in both TOC removal and first-order rate constant.

3.2. Treatment of carbofuran by the Fenton process

Ma et al. [9] applied the Fenton process to the degradation of carbofuran in an aqueous system. Batch experiments at pH 3 were designed using the central composite approach for the two independent variables Fe^{2+} and H_2O_2 . Experimental results indicated that more than 90% of the carbofuran was removed from an initial carbofuran concentration of 10 mg/L within 5 min using 5 mg/L of Fe^{2+} and 100 mg/L of H_2O_2 . Increases in Fe^{2+} and/or H_2O_2 dosages beyond 5 mg/L and 100 mg/L, respectively, produced 100% carbofuran removal.

In the present study, the Fenton process was carried out using Fe^{2+} and H_2O_2 concentrations of 1 mg/L and 100 mg/L, respectively, added to initial carbofuran concentrations around 10 mg/L to 200 mg/L and a reaction time of 30 min where the sampling time intervals are 1 min, 2 min, 5 min, 10 min, 20 min and 30 min. The resulting carbofuran degradation, TOC removal and first-order rate constants are given in Table 3. It was observed that the carbofuran degradation decreased from 81% to 15% when the initial carbofuran concentration increased from 10 mg/L to 200 mg/L. In addition, 59% of the carbofuran was degraded within 1 min when the initial carbofuran concentration was 10 mg/L (data not shown). This indicates that adding the Fenton reagents Fe^{2+} and H_2O_2 produces $\cdot\text{OH}$ radicals in aqueous solution, leading to rapid degradation of carbofuran. When the initial carbofuran concentration was increased to 200 mg/L, however, further addition of Fenton reagents was insufficient to effectively degrade the carbofuran; the degradation of carbofuran was seen to decrease to 15% (Table 3).

Mineralization of carbofuran by the Fenton process at different initial carbofuran concentrations is also shown in Table 3, where the TOC removal fell slightly from 10% to 6% as the initial carbofuran concentration increased from 10 mg/L to 200 mg/L, indicating that the traditional Fenton process can effectively degrade and transfer the carbofuran to other products or intermediates but is ineffective in mineralizing the carbofuran to carbon dioxide. Several authors [6,8,22,23] have reported similar results.

Comparing the carbofuran degradation rate constants (Table 3), the rate constant decreased from $25.7 \times 10^{-3} \text{ min}^{-1}$ (carbofuran 10 mg/L) to $4.9 \times 10^{-3} \text{ min}^{-1}$ (carbofuran 200 mg/L); that is, lower initial carbofuran concentration yields greater carbofuran degradation.

3.3. Treatment of carbofuran by the ultrasound/Fenton process

From the above, it is clear that carbofuran mineralization is insignificant over short reaction periods for aqueous systems when either the ultrasound process, or the Fenton process. Therefore, in the present study we have examined the effect of combining the ultrasound and Fenton processes (termed the ultrasound/Fenton

process) for the degradation of carbofuran. In addition, the effect of Fe^{2+} dosage and initial carbofuran concentration on the degradation and mineralization of carbofuran have been investigated.

Fig. 3 shows the results for carbofuran degradation, removal of TOC and consumption of H_2O_2 in the degradation of carbofuran by the combined ultrasound/Fenton process. In this case, the initial carbofuran concentration and the dosages of H_2O_2 were 20 mg/L and 200 mg/L and the dosages of Fe^{2+} were 1 mg/L, 5 mg/L, 10 mg/L and 20 mg/L. In Fig. 3(a), the carbofuran degradation reached 52% within 30 min at the Fe^{2+} dosage of 1 mg/L. It is also seen in Fig. 3(a)

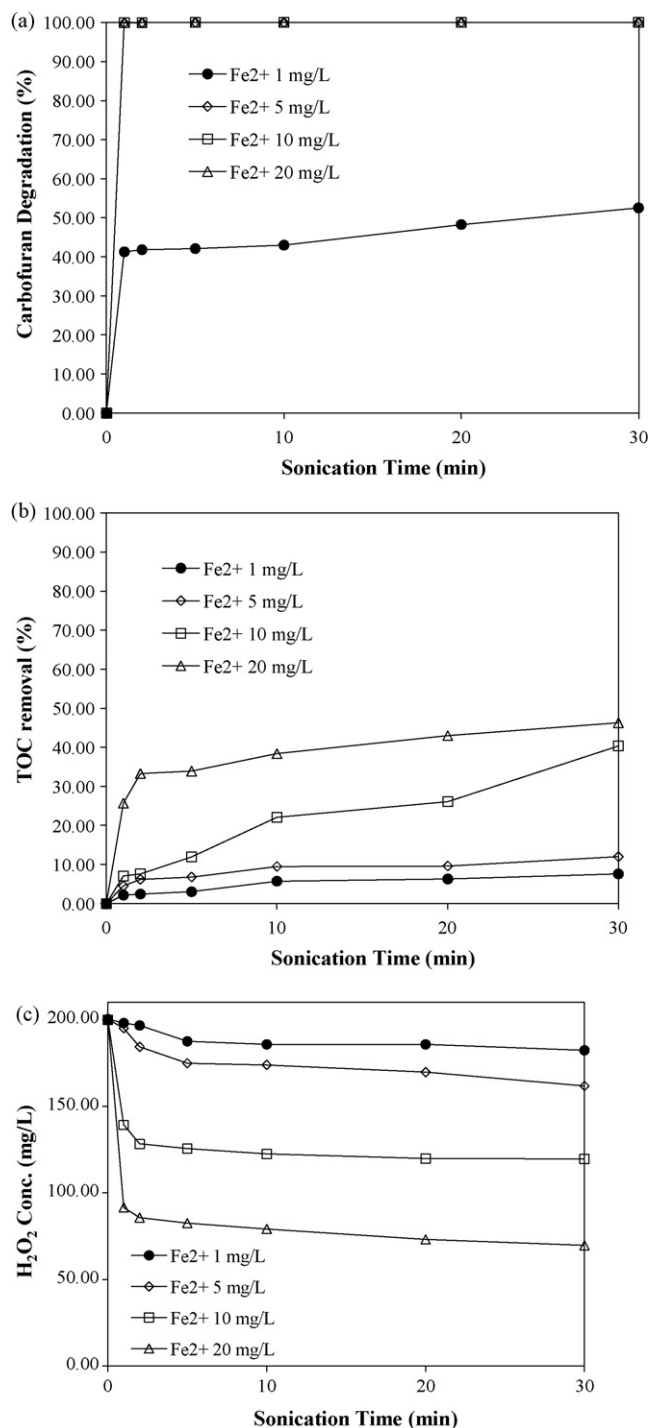


Fig. 3. Effect of different Fe^{2+} dosages on carbofuran degradation in the ultrasound/Fenton process (a) degradation of carbofuran, (b) removal of TOC, and (c) residual of H_2O_2 .

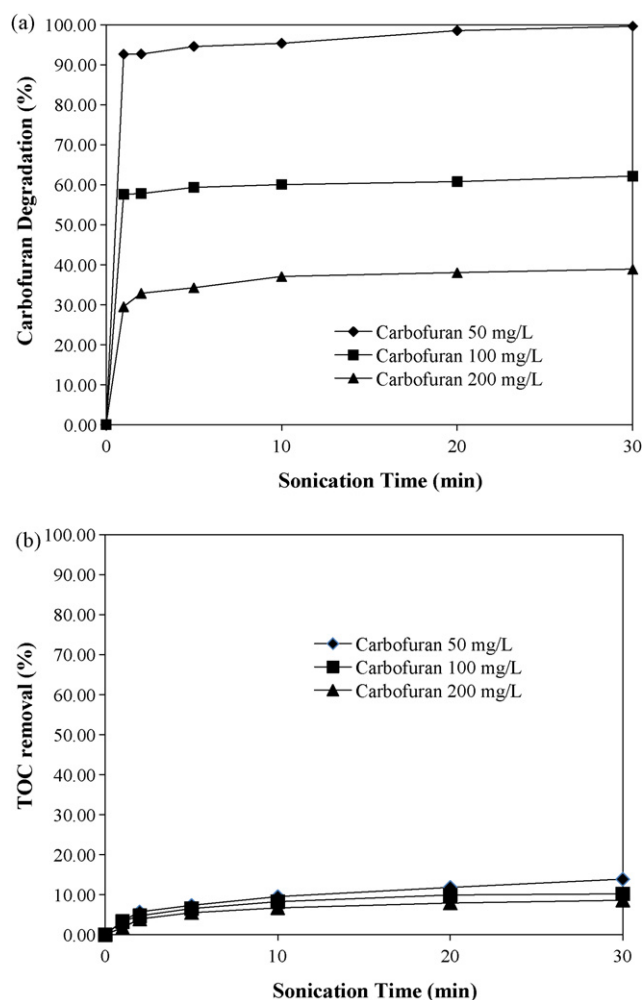


Fig. 4. Effect of initial carbofuran concentrations on the decomposition of carbofuran in the ultrasound/Fenton process (a) degradation of carbofuran and (b) removal of TOC ($\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 10/100$ mg/L).

that the residual carbofuran concentrations since the first sampling time were all lower than the MDL of carbofuran for the Fe^{2+} dosages of 5 mg/L, 10 mg/L and 20 mg/L. Therefore, these three experimental lines were overlapped. Calculation of the rate constants was not necessary because no carbofuran was present in the aqueous solution after the ultrasound/Fenton process had been carried out for 1 min (Table 3).

Other researchers have reported comparable results: Liang et al. [2] found that the ultrasound/Fenton process decomposed more than 99% of 4-chlorophenol within a reaction time of 2 min; Sun et al. [20] combined the ultrasound and Fenton processes to treat azo dye acid black 1 wastewater, achieving 99% removal efficiency in a very short time at the ultrasound frequency of 40 kHz and adding 0.025 mM Fe^{2+} and 8.0 mM H_2O_2 .

In the present study, Fig. 3(b) shows the results of TOC removal at different Fe^{2+} dosages using the ultrasound/Fenton process. Removal of TOC was 8% for Fe^{2+} dosage of 1 mg/L, increasing to 46% at 20 mg/L Fe^{2+} within 30 min. Fig. 3(c) shows residual H_2O_2 for an initial H_2O_2 dosage of 200 mg/L. Consumption of H_2O_2 increased from 9% to 65% when the Fe^{2+} dosage was increased from 1 mg/L to 20 mg/L. Higher consumption of H_2O_2 led to higher production of $\cdot\text{OH}$ radicals and oxidation potential in the ultrasound/Fenton process, enhancing degradation and mineralization of carbofuran.

Fig. 4 shows the results of carbofuran degradation and TOC removal by the ultrasound/Fenton process for different initial car-

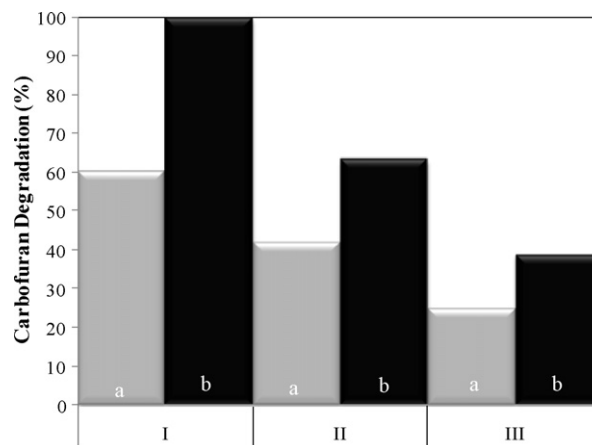


Fig. 5. Effect of initial carbofuran concentration on the degradation of carbofuran by the ultrasound/Fenton process. (Fe^{2+} : 10 mg/L, H_2O_2 : 100 mg/L; (a) Fenton process; (b) ultrasound/Fenton process; carbofuran concentration I: 20 mg/L, II: 100 mg/L, III: 200 mg/L.)

bofuran concentrations. Dosages of Fe^{2+} and H_2O_2 were 10 mg/L and 100 mg/L and the initial carbofuran concentrations ranged from 50 mg/L to 200 mg/L. It is evident from Fig. 4(a) that approximately 90% of the carbofuran was immediately degraded when the initial carbofuran concentration was 50 mg/L; degradation gradually increased to almost 100% after 30 min. When the initial carbofuran concentration was increased to 100 mg/L or more, however, degradation after 30 min significantly decreased to 60% (carbofuran 100 mg/L) and 35% (carbofuran 200 mg/L). Fig. 4(b) shows that 14% of TOC was removed after 30 min, by which time the 50 mg/L carbofuran solution was oxidized. As the carbofuran concentration was increased to 100 mg/L and 200 mg/L, TOC removal fell further to 10%.

Fig. 5 compares the effect of initial carbofuran concentrations on the degradation of carbofuran by both the ultrasound/Fenton process and the Fenton process with the Fe^{2+} and H_2O_2 dosages of 10 mg/L and 100 mg/L, respectively. Phases I–III represent the initial carbofuran concentrations of 20, 100 mg/L and 200 mg/L, respectively. Degradation efficiencies were 60%, 42% and 25% for the Fenton process alone after the reaction time of 30 min. When the ultrasound and Fenton process were combined, carbofuran degradation efficiencies rose to 99%, 63% and 39% for initial carbofuran concentrations of 20 mg/L, 100 mg/L and 200 mg/L, respectively. Table 3 shows that more than 99% of the carbofuran was degraded by the combined ultrasound/Fenton process for the initial carbofuran concentration of 50 mg/L; the rate constant was $102.7 \times 10^{-3} \text{ min}^{-1}$, much higher than for the other reaction conditions. As the initial carbofuran concentrations increased to 100 mg/L and 200 mg/L, the rate constants dropped to $41.3 \times 10^{-3} \text{ min}^{-1}$ and $37.1 \times 10^{-3} \text{ min}^{-1}$.

4. Conclusion

The degradation of carbofuran in aqueous solution was investigated by ultrasonic, Fenton and ultrasound/Fenton processes under different experimental conditions, including different dosages of H_2O_2 and Fe^{2+} and a range of initial carbofuran concentrations. More than 99% carbofuran degradation efficiency combined with 46% mineralization was achieved after 30 min reaction time for the initial carbofuran concentration of 20 mg/L and H_2O_2 and Fe^{2+} dosages of 100 mg/L and 20 mg/L, respectively, all at pH 3.

Degradation efficiency was enhanced by an increase in the Fenton reagents H_2O_2 and Fe^{2+} , but an increase in initial carbofuran concentration had a negative impact on degradation. The kinetics

study indicated that the degradation kinetics of carbofuran closely followed the first-order kinetics model, with the effects of the experimental parameters on the degradation of carbofuran resulting in comparable reaction rate constants.

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