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Journal of Hazardous Materials B98 (2003) 241–255

Journal of Hazardous Materials

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Oxidative degradation and detoxification of aqueous carbofuran by membrane anodic Fenton treatment

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Received 20 September 2002; received in revised form 12 December 2002; accepted 13 December 2002

Abstract

Anodic Fenton treatment (AFT), a new Fenton technology for the treatment of pesticide wastewater, has been reported previously. 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. The oxidative degradation by membrane AFT of carbofuran, a heavily used and toxic carbamate insecticide, was investigated in this study. The results show that the degradation kinetics of carbofuran with different initial concentrations obeys the AFT model, and the treatment efficiency increases with increasing initial concentration. Raising the treatment temperature can result in enhanced 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 show that AFT treatment can effectively remove COD and dramatically improve the biodegradability of carbofuran in solution. GC/MS analysis found four degradation products, revealing that the carbamate branch and 3-C in the furan ring are the first and second attack targets of hydroxyl radicals. As shown by the toxicity assay, the fatal toxicity of carbofuran to earthworms can be totally removed. The degradation of carbofuran by AFT is also a detoxification process.

Keywords: Carbofuran; Carbamate; Fenton treatment; Hydrogen peroxide; Detoxification; Degradation

1. Introduction

With improved environmental protection policies related to cleanup and disposal of the large-scale wastewater from pesticide industries, the handling and disposal of pesticide rinse

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doi:10.1016/S0304-3894(03)00007-4

water generated by individual farmers or commercial agrochemical applicators has become a significant waste management issue in the US [1]. Effective, inexpensive, and easily operated technologies are badly needed for treating this small-scale wastewater without the necessity of accumulation and transportation. Aqueous chlorine [2], ozonation [3], thiosulfate reduction [4–6], Fe(II) reduction [7], Fenton treatment [8–12], and titanium dioxide photocatalytic oxidation [13,14] have been reported as effective treatment strategies. Among them, Fenton treatment has received even more extensive attention because of its broad-spectrum of target compounds, high oxidation ability and reaction rate, and the simplicity of the treatment equipment [15–18]. During the Fenton treatment, ferrous ion reacts with hydrogen peroxide to generate the hydroxyl radical (Eq. (1)), a very strong oxidant to almost all organic contaminants:

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

Anodic Fenton treatment (AFT) was proposed by our laboratory as an improvement to the classic Fenton treatment (CFT) and the electrochemical Fenton treatment (EFT) [19]. The reaction treatment is separated into two half-cells. Ferrous ion is generated from iron in anodic half-cell by electrolysis, whereas water is reduced in the cathodic half-cell. Hydrogen peroxide is pumped into the anodic half-cell. The AFT has several significant advantages over CFT and EFT. First, the ferrous ion is delivered into the treatment system by electrolysis, overcoming the difficulty of handling hygroscopic ferrous salt. Secondly, the pH of the treatment effluent can be partially neutralized by combining effluents from the anodic and cathodic half-cells of the AFT. Thirdly, the Fenton reaction can occur in an optimal pH environment in the anodic half-cell, keeping the treatment efficiency high. To better understand the mechanism and to optimize the operating conditions of AFT, a kinetic model of AFT (with a saturated NaCl salt-bridge) was proposed. It fit the degradation kinetics of pure 2,4-D, diazinon, and formulated diazinon very well and demonstrated that the treatment efficiency is decreased with an increased delivery rate of Fenton reagent [20,21]. To make the AFT technology more convenient for practical application, an ion exchange membrane was substituted for the salt-bridge, an impractical approach for potential scale up since the salt-bridge requires frequent replacement of the saturated NaCl solution. The membrane AFT was tested on carbaryl, and the results showed that the treatment efficiency is higher than CFT and that the degradation of carbaryl could still be fitted by the AFT model. A strong functional stability of membrane was observed during 100 times of repeated use [22].

Carbofuran (2,3-dihydro-2,2-dimethylbenzofurarn-7-yl methylcarbamate) is a broad-spectrum, carbamate insecticide widely used to control certain soil-borne insects and nematodes [23]. As recently as 1995, more than 5 million pounds of carbofuran were applied in the US [24]. The use of carbofuran has received intensive concern [23,25–27] due not only to its heavy use, but also to its high oral toxicity. The oral LD_{50} of carbofuran for rats is 11 mg kg^{-1}. This toxicity is quite near to that of parathion, which is an extremely toxic organophosphorus pesticide with a LD_{50} of 8 mg kg^{-1} [28]. In the current study, carbofuran has been selected as a representative of carbamate insecticides. The purpose of this investigation is to test the effectiveness of the membrane AFT on the oxidative degradation, biodegradability increase, and detoxification of carbofuran. The degradation products were studied using GC/MS.

2. Materials and methods

2.1. Chemicals, test organisms and membrane

Carbofuran (99%) was purchased from Chem Services (West Chester, PA). Hydrogen peroxide (analytic grade), magnesium sulfate (analytic grade), potassium dichromate (analytic grade), potassium permanganate (analytic grade), acetonitrile (HPLC grade), and water (HPLC grade) were purchased from Mallinckrodt (Paris, KY). Sodium chloride (certified), phosphoric acid (analytic grade), potassium phosphate monobasic (certified), ferrous chloride (certified), sodium hydroxide (certified), starch soluble (certified), sodium thiosulfate (certified), potassium iodide (certified), sodium fluoride (certified) and methylene chloride (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ). Sulfuric acid (analytic grade) was purchased from EM Science (Gibbstown, NJ). Potassium phosphate dibasic (certified), ammonium sulfate (certified), calcium chloride (certified), calcium carbonate (certified), ferrous ammonium sulfate (certified), and silver sulfate (certified) were purchased from GFS Chemicals (Columbus, OH). Manganese sulfate (certified) was purchased from Sigma (St. Louis, MO). Mercury sulfate (certified), and 1,10-phenanthroline (99%) were purchased from Aldrich (Milwaukee, WI). Fine sand and sphagnum peat moss were purchased from K-mart (Ithaca, NY). Kaolinte clay was purchased from Lagula Clay Co. (City of Industry, CA).

The microorganisms used to seed the dilution water for BOD_5 determination were taken from the effluent of the domestic sewage treatment plant of Ithaca, NY. Earthworms *Eisenia foetida* were purchased from Carolina Biological Supply (Burlington, NC).

The anion exchange membrane (ESC-7001) with an electrical resistance of $8\,\Omega\,cm^{-2}$ in 1 M NaCl solution at 25 °C, was purchased from Electrosynthesis (Lancaster, NY).

2.2. Oxidation of carbofuran by AFT

A schematic of the membrane AFT apparatus is shown and specified in previous work [22]. Typically, 200 ml of 100 μM carbofuran with 0.02 M NaCl and the same volume of 0.08 M NaCl were respectively added into the anodic and cathodic half-cells. The ferrous ion was delivered into the anodic half-cell by electrolysis at 0.050 A. The hydrogen peroxide solution of 0.311 M was added into the anodic half-cell by a peristaltic pump at $0.50\,ml\,min^{-1}$. The delivery ratio of H_2O_2 to Fe^{2+} was kept at 10:1. The temperature was controlled at 25 ± 0.1 °C by a HAAKE K20 water circulator serving as a water bath. The electrolysis was started when the first drop of hydrogen peroxide was delivered into the anodic half-cell. At different treatment times, 1.00 ml of anodic solution was taken out and put into a 2-ml GC vial containing 0.10 ml of methanol (for quenching) and was analyzed for carbofuran using HPLC. Treatments were repeated for a total of three replicates.

In the experiments investigating the degradation of carbofuran with different initial concentrations, the initial concentration ranges were from 30 to 200 μM. In the temperature experiments, the treatment temperature was controlled at 10 ± 0.1, 18 ± 0.1, 25 ± 0.1, and 33 ± 0.1 °C.

2.3. Analysis of carbofuran and hydrogen peroxide concentration

The concentration of carbofuran was analyzed by a HP 1090 HPLC equipped with a diode array detector. The mobile phase was composed of acetonitrile and water (40:60, pH adjusted to 3 using phosphoric acid). A C-18 5 μm 250 mm × 4.6 mm (i.d.) PRISM RP column was used for separation. The detector wavelength was set at 220 ± 20 nm with 450 ± 80 nm as reference. Under these separation conditions, the retention time of carbofuran is 10.4 min. The concentration of hydrogen peroxide was determined by titration using standard potassium permanganate solution [29].

2.4. Determination of COD and BOD_5

The initial concentration of carbofuran in this section was 200 μM. At different treatment times, the AFT was stopped and samples were taken from the anodic half-cell for COD (chemical oxygen demand) and BOD_5 (biochemical oxygen demand) determination. Phosphate buffer (NaH_2PO_4 and Na_2HPO_4, each at 1.0 M) was added at a ratio of 1.0 ml per 50 ml sample to each sample to adjust pH. Daily fresh catalase solution (1.0 mg ml^{-1} in 0.5 M phosphate buffer solution) was then added at the same ratio as that of phosphate buffer to decompose the residual hydrogen peroxide.

COD was determined using the dichromate method. BOD_5 was determined using the iodometric method with azide modification [30]. To get rid of the interference from iron ion, sodium fluoride was used prior to the addition of sulfuric acid during the process of BOD_5 determination.

2.5. Degradation products identification by GC/MS

After 2 min treatment under typical operating conditions of AFT, 15 ml of anodic solution were withdrawn and immediately extracted with 3 ml of methylene chloride. After separation from the aqueous solution, the organic phase was dried with anhydrous sodium sulfate. The sample was then analyzed by an Agilent 6890N Network GC system equipped with an Agilent 5973 Network mass selective detector and Agilent 7683 series injector. The GC/MS conditions were as follows: a 30 m × 0.25 mm (i.d.) fused silica capillary column with 0.25 μm film thickness (HP 19091S-433) and a carrier gas of helium (10.50 psi) were used; initial temperature was 80 °C, increasing at 10 °C min^{-1} to 210 °C, at 30 °C min^{-1} from 210 to 305 °C, then kept at 305 °C for 5 min; injector port temperature was 220 °C; detector temperature was 250 °C.

2.6. Earthworm toxicity assay

Earthworms were exposed to the AFT treatment effluents of carbofuran in artificial soil, which was comprised of fine sand (69%, in dry weight), kaolinite clay (20%), sphagnum peat moss (10%), and calcium carbonate (1%) [31]. The AFT treatment effluents were prepared by treating 500 μM carbofuran solution and stopping at 0, 3, and 10 min under typical AFT conditions. One hundred milliliters of effluent was added to 300 g (dry weight) artificial soil and thoroughly mixed in plastic ziplock bag. With the addition of effluent, the

moisture content was adjusted to 40–45%. The spiked soil was then transferred to a 500-ml plastic jar. Ten earthworms with individual weights of 0.15–0.25 g were washed, dried on filter paper, weighed, and then placed on the surface of the soil. Earthworms that did not burrow into the soil after 5 min were replaced. All exposures were conducted at $20 \pm 1\,^{\circ}C$ with 8:16 h of light:dark cycle. Lost moisture was compensated for every day on a lost weight basis. Each blank and each effluent were tested in triplicates.

The soil was hand-sorted after 1, 3, 6 and 10 days to determine the mortality and the average body weight of earthworms. Earthworms that did not response to a mild mechanical touch were regarded as dead. After each assessment, soil and earthworms were put back in the original jars and the weight was recorded. This weight was used as the basis for the next day's moisture compensation.

2.7. The AFT kinetic model

A detailed derivation of the AFT kinetic model was published elsewhere [20]. The degradation kinetics of the target organic compound can be described by the following equation:

$$\ln \frac{[C]_t}{[C]_0} = -\frac{1}{2} K \lambda \pi \omega v_0^2 t^2 \tag{2}$$

where $K = kk_1$ ($\mu M^{-2}\,min^{-2}$), k ($\mu M^{-1}\,min^{-1}$) and k_1 ($\mu M^{-1}\,min^{-1}$) are the second-order rate constants of the Fenton reaction and the reaction between hydroxyl radical and target compound, respectively; $[C]_0$ (μM) and $[C]_t$ (μM) are the concentrations of the target compound at 0 and t min, respectively; λ (min) and π (min) are the average life of the hydroxyl radical and ferrous ion, respectively; ω is a constant related to the delivery ratio of hydrogen peroxide to ferrous ion and to the consumption ratio of hydrogen peroxide; v_0 ($\mu M\,min^{-1}$) is the delivery rate of ferrous ion by electrolysis; and t (min) is time.

Treatment efficiency is defined as the removal rate of the target compound per unit of Fenton reagent. Because the Fenton reaction and the hydroxyl radical reaction are fast reactions, the degradation rate parameter, $K\lambda\pi\omega$, can be used to signify treatment efficiency to compare treatments with the same delivery rate of the Fenton reagent.

3. Results and discussion

3.1. Degradation of carbofuran by AFT with different initial concentrations

Carbofuran is a relatively stable insecticide in aqueous solution. Its half-life ranges from 690 weeks at pH = 5 to 1 week at pH = 8 [32]. No significant degradation was found when the system was run with only electrolysis or iron or with only the addition of hydrogen peroxide under the same conditions as those in AFT (data not shown). As shown in Fig. 1, carbofuran with different initial concentrations can be rapidly degraded by AFT treatment, and higher concentrations take a longer time to degrade. The degradation kinetics can be fitted very well by the AFT model ($K\lambda\pi\omega$ data not shown). All regression coefficients are above 0.99.

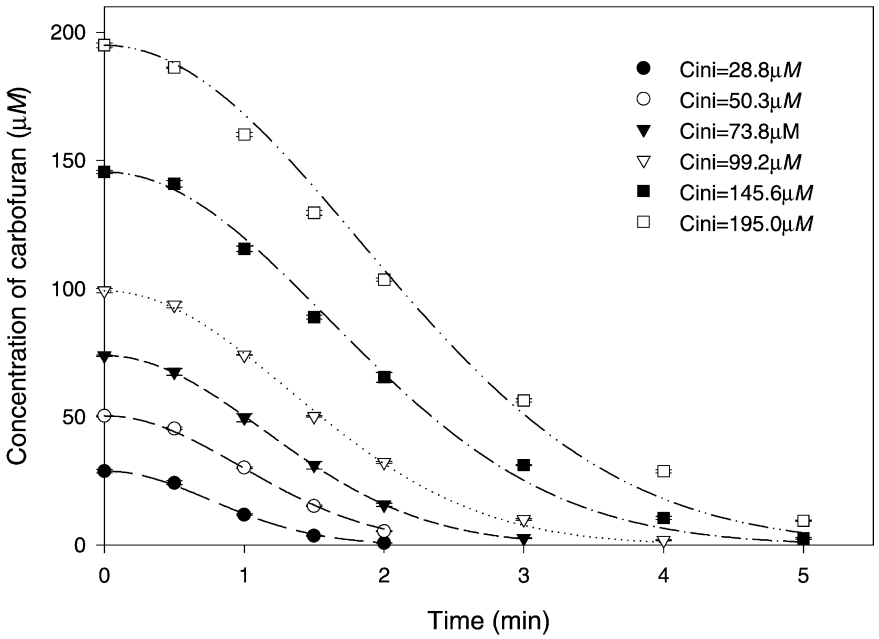

Fig. 1. Degradation of carbofuran by membrane AFT with different initial concentrations. Points are experimental data. Lines are fitting results using AFT kinetic model.

To better understand the effect of the initial concentration of carbofuran, the treatment efficiencies under these different initial concentrations were investigated. A relationship between the rate parameter ($K\lambda\pi\omega$) and the initial concentration (C_{initial}) was obtained:

$$\ln(K\lambda\pi\omega) = -4.478 - 1.062 \ln C_{\text{initial}}, \quad r = 0.99 \tag{3}$$

Since,

$$\ln \tfrac{1}{2} = -\tfrac{1}{2} K\lambda\pi\omega v_0^2 t_{1/2}^2 \tag{4}$$

$$v_0^2 = 6042\ (\mu\text{M}^2\ \text{min}^{-2}) \tag{5}$$

Then,

$$t_{1/2} = 1.422 C_{\text{initial}}^{0.53} \tag{6}$$

Eq. (6) illustrates that the increase of the half-life of carbofuran is significantly slower than the increase of carbofuran concentration, since the exponent of C_{initial} is only 0.53, far less than 1. This means that more carbofuran can be degraded within the same treatment time under the same delivery rate of Fenton reagent in concentrated solution than in dilute, and the increase of initial concentration of carbofuran is always beneficial to treatment efficiency. A similar phenomenon has been found in the decomposition of hydrogen peroxide in soil through a Fenton-like reaction [33]. The efficiency of $^{\bullet}$OH formation appeared to increase as the H_2O_2 concentration decreased.

The high reactivity and non-selectivity of hydroxyl radical may be the cause of these effects. When the concentration of the target compound increases, its availability to hydroxyl radical will also increase. This allows the target compound to compete for hydroxyl radicals with the Fenton reagent and other compounds in the system. On the other hand, when the initial concentration of the target compound is lower, a high delivery rate of Fenton reagents corresponds to higher concentrations of these reagents, increasing their ability to compete for hydroxyl radicals. Thus, Fenton treatment is especially suitable for concentrated wastewater.

3.2. Temperature dependency

All kinetics of carbofuran degradation at variable temperatures obey the AFT model very well (Fig. 2). The regression coefficients are above 0.99 (data not shown). The carbofuran half-life decreases with increasing temperature, implying that carbofuran can be more efficiently degraded by AFT at higher temperatures (Table 1). By assuming that $\lambda\pi\omega$ is a constant parameter with variable temperatures, $K\lambda\pi\omega$ can be used as a rate parameter to signify K at different temperatures. Total activation energy (E_a) for Fenton reaction and the reaction between hydroxyl radical and carbofuran can be obtained by applying the Arrhenius equation

$$\ln k' = \ln A + \frac{E_a}{RT} \tag{7}$$

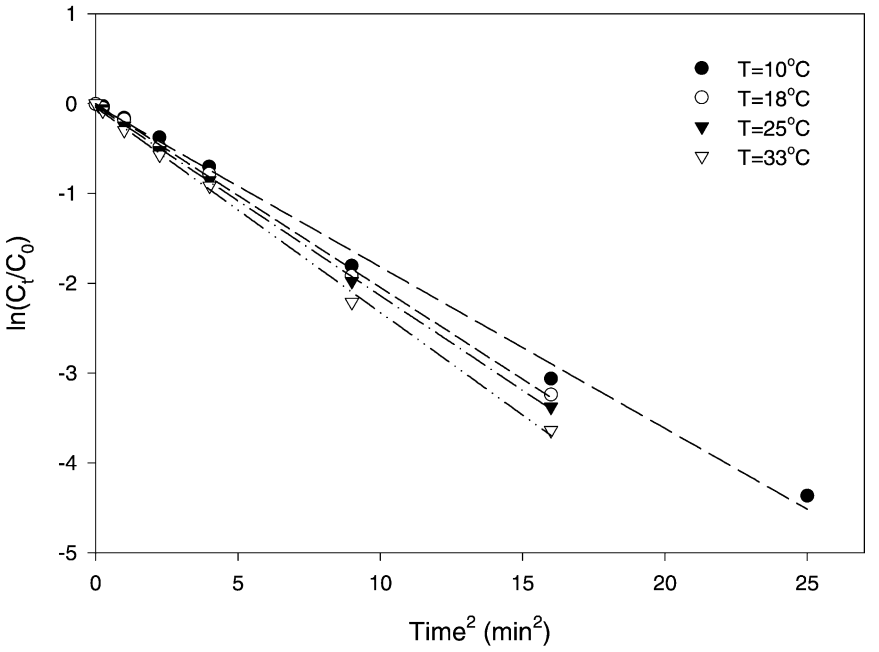

Fig. 2. Plot of $\ln(C_t/C_0)$ vs. t^2 at variable temperatures. Points are experimental data (mean value of triplicates). Lines are fitting results using the AFT kinetic model.

Table 1
Values of $K\lambda\pi\omega$ and half-life at different temperatures

T (K)	$K\lambda\pi\omega$ (μM^{-2})	Half-life, $t_{1/2}$ (min)[a]	Activation energy, E_a, from Arrhenius equation
283.2	$(5.995 \pm 0.116) \times 10^{-5}$	1.96	
291.2	$(6.773 \pm 0.073) \times 10^{-5}$	1.84	$\ln(K\lambda\pi\omega) = -6.458 \pm 921.8(1/T)$
298.2	$(7.074 \pm 0.060) \times 10^{-5}$	1.80	$r = 0.99$
306.2	$(7.686 \pm 0.119) \times 10^{-5}$	1.73	$E_a = 7.66$ (kJ mol^{-1})

Calculated activation energy of carbofuran degradation by membrane AFT.
[a] Calculated according to Eqs. (4) and (5).

where k' is the reaction rate constant, A is an empirical constant dependent on compound and non-thermal system conditions, R the universal gas constant (J K^{-1} mol^{-1}), and T is the temperature (K).

As listed in Table 1, the total pseudo-activation energy for the degradation of carbofuran by membrane AFT is estimated to be 7.66 kJ mol^{-1}, which is much lower than that for hydrolysis of carbamates, which range from 50 to 110 kJ mol^{-1} [34,35]. This result indicates that degradation of carbofuran is more favored thermodynamically in the AFT system than in merely alkaline or acidic aqueous solution.

3.3. Effect of AFT on the removal of COD and the improvement of biodegradability

COD is one of the frequently used synthetic parameters for wastewater containing organic pollutants. Generally, low COD represents low content of organic substances and less oxygen demand for complete oxidation in the environment. A good oxidative treatment method not only effectively decrease the concentration of target compound, but can also remove the COD of wastewater through the same process. The changes in COD during the degradation of carbofuran by membrane AFT have been investigated (shown in Fig. 3a). The concentration of carbofuran decreases promptly. Within 9 min treatment, 200 μM is totally removed. A pronounced decrease in COD was also found during this process. Only 30% COD still remained after 9 min treatment. The lower rate of COD elimination, compared with the dissipation of carbofuran, demonstrates the existence of some degradation products that have significant COD values. This time lag in COD removal has also been observed in the degradation of diazinon and its formulation by AFT [21].

BOD_5 is another important parameter for organic wastewater. As shown in Fig. 3b, the BOD_5 of 200 μM carbofuran without AFT treatment is only about 3 mg l^{-1}, implying that carbofuran is very hard for bacterium to utilize because of its toxicity or strong stability. BOD_5 gradually increases during the process, indicating that the degradation products of carbofuran become utilizable to the bacterium.

The value of BOD_5/COD is taken as a factor to assess the biodegradability of organics. A value higher than 0.3 signifies that the wastewater is biodegradable [36]. Those toxic and refractory organics which bacteria cannot utilize usually have very low values of BOD_5/COD. As shown by our results, carbofuran is such an organic compound, having an extremely low value of BOD_5/COD (0.04). However, with AFT treatment, the BOD_5/COD of carbofuran solution gradually increases. Three min of treatment takes the BOD_5/COD to a value of 0.3,

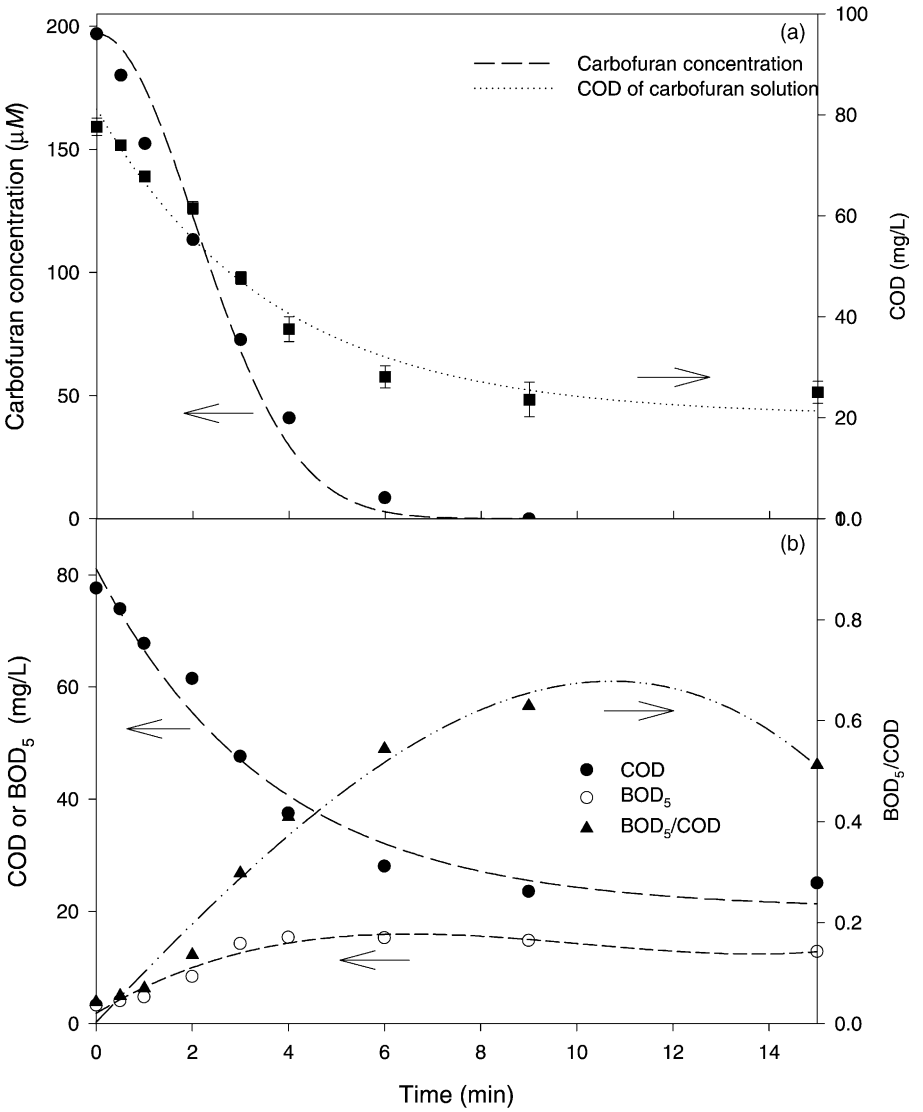

Fig. 3. Changes of carbofuran concentration, COD, and BOD_5 during the degradation of carbofuran by membrane AFT.

and the solution becomes biodegradable (Fig. 3b). Continuous AFT treatment can further increase the BOD_5/COD to 0.63 at 9 min. These results illustrate that the AFT can effectively improve the biodegradability of carbofuran. Those degradation products remaining in the treatment effluents of AFT are more easily utilized by bacteria and can thus be further decomposed in the environment. AFT appears to be a good preliminary treatment strategy for non-biodegradable organics.

3.4. Degradation products of carbofuran by AFT

GC/MS analysis of degradation products generated after 2 min of membrane AFT treatment shows five peaks in the TIC (total ion current) spectrum, corresponding to five compounds. By MS spectrum confirmation (Fig. 4f) and standard sample comparison, the peak with a retention time of 12.98 min is found to be carbofuran, the parent compound. The MS spectrum corresponding to the peak appearing at 7.62 min in the TIC spectrum is shown in Fig. 4b. By interpreting the MS spectrum, this peak is attributed to 2,3-dihydro-2,2-dimethylbenzofuran-7-ol, which is the product due to the cleavage of the carbamate group from the parent compound. This degradation product has also been detected in the hydrolysis [27], photolysis [28], and TiO_2 catalyzed photolysis [13] of carbofuran. The substance with the MS spectrum shown in Fig. 4c and retention time of 8.74 min in the TIC spectrum can be identified as 2,3-dihydro-2,2-dimethylbenzofuran-7-yl formate. It is an intermediate formed through partial cleavage of the carbamate branch. MS spectra corresponding to those peaks at 9.03 and 9.59 min in TIC are shown in Fig. 4d and e. They are attributed to 2,3-dihydro-3-oxo-2,2-dimethylbenzofuran-7-ol and 2,3-dihydro-3-hydroxyl-2,2-dimethylbenzofuran-7-ol, respectively. Both of them are formed by further oxidizing 2,3-dihydro-2,2-dimethylbenzofuran-7-ol on the furan ring. In addition to these four compounds, other degradation products still possibly exist in the oxidation system but are not detected because of their low concentration and extraction efficiency and limited sensitivity in GC/MS.

With these identified products, a suggested oxidation pathway of carbofuran by membrane AFT is shown in Fig. 5. The carbamate group appears to be the primary attack site by the hydroxyl radical and the first group removed during AFT treatment. After carbamate group removal, the hydroxyl radical continues attack by substituting a hydroxyl group for one of 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 (in Fig. 3), it can be anticipated that the furan ring and/or benzene ring is opened and further oxidative products are formed after 2 min of AFT treatment.

3.5. Reduction of toxicity of carbofuran by AFT treatment

The earthworm test is widely used in chemical acute toxicity assays [31,37–39]. It has also been accepted by the US EPA for short-term toxicity screening of hazardous waste sites [40]. In this study, the toxicity changes of carbofuran through AFT treatment have been evaluated using earthworm *Eisenia foetida*. As indicated by Fig. 6, there is no difference between carbofuran and the effluent with 3 min of AFT treatment after 1 day of incubation, but the mortalities for both of them are higher than that of the 10 min treatment effluent. With the extending of incubation time, the difference of mortalities between different effluents becomes more notable. After 6 days of exposure, the mortality for carbofuran is 16.7 ± 11.5, whereas those for 3 and 10 min treatment effluents are 6.7 ± 5.8 and 0, respectively. No significant difference in mortality between the 10 min treatment effluent and the blank was found, indicating that the fatal toxicity of 500 μM carbofuran has been removed with 10 min of AFT treatment. These results show that the AFT treatment is a detoxification process. The mortality rates between effluents of 10 min treatment with and without sample pretreatment (pH neutralization and residual hydrogen peroxide decomposition)

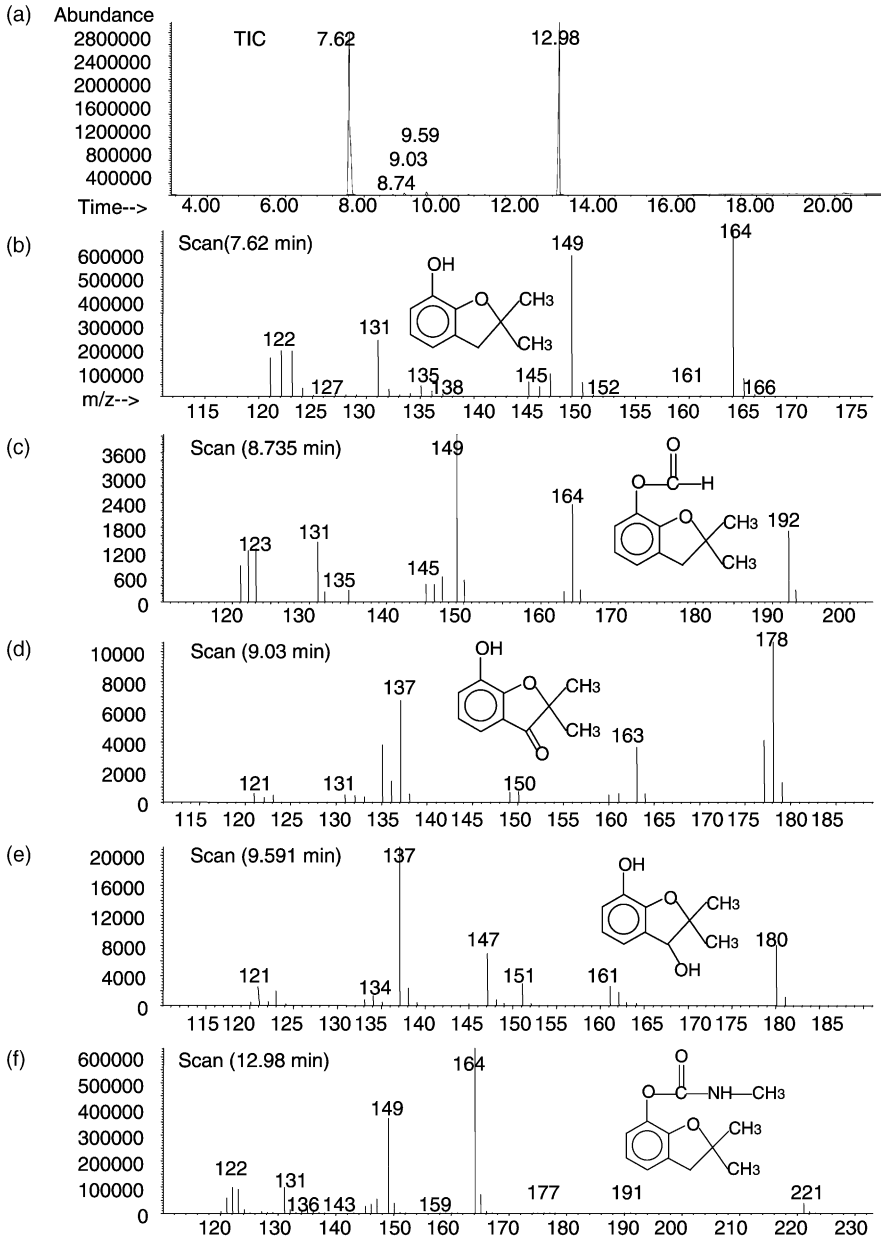

Fig. 4. TIC and MS spectra of carbofuran and its degradation products.

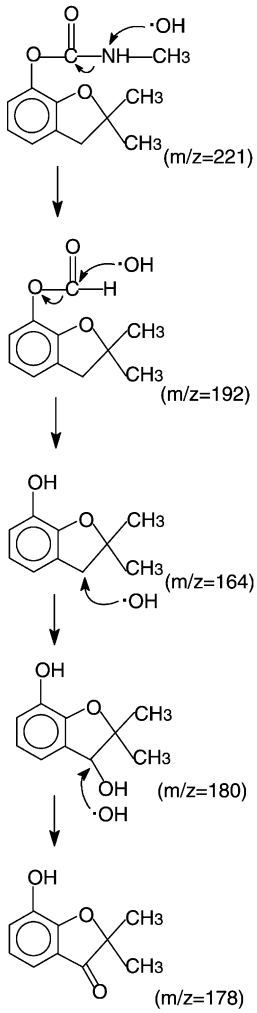

Fig. 5. Proposed oxidative degradation pathway of carbofuran by AFT.

displayed no pronounced differences either. This demonstrates that residual hydrogen peroxide and acid in the AFT effluent are not fatally toxic to earthworms in the soil. This result may due to the buffering capacity of soil and its ability to decompose hydrogen peroxide [33].

The average weight of living earthworms is a more sensitive indication parameter of toxicity than mortality [41]. As indicated by changes in average weight, the earthworms lost more weight after exposure to carbofuran than exposure to treatment effluents. The longer the treatment by AFT, the less weight the earthworms lost. No difference in weight loss was found between effluents with and without sample pretreatment. Unlike the mortality results, there appears to be a big difference in weight loss between 10-min treatment effluents and the

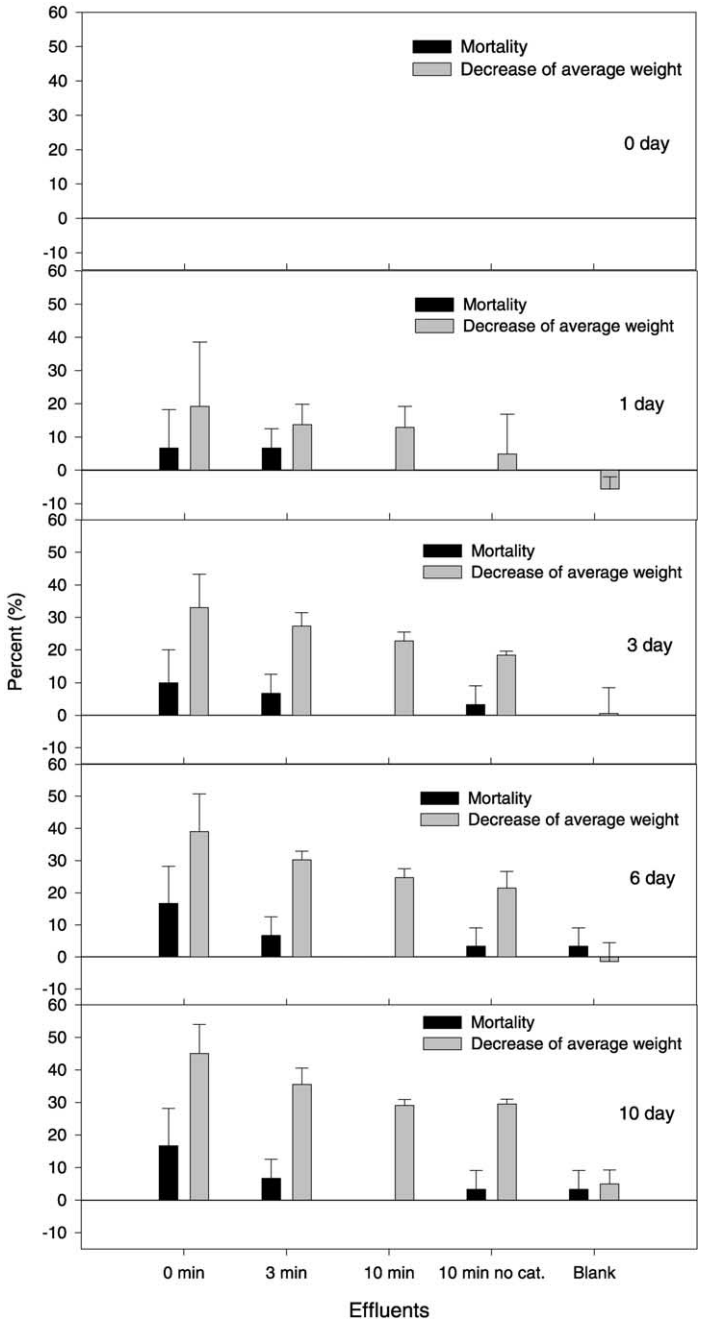

Fig. 6. Earthworm toxicity assay of carbofuran and its AFT treatment effluents. Sample "10 min no cat." is the effluent of 10 min treatment without pH neutralization and residual hydrogen peroxide decomposition. All other samples, including blank, have been neutralized and treated with catalase.

blank, suggesting that the AFT treatment largely removed the toxicity of carbofuran solution, but not totally. Some of the degradation products may still be slightly toxic to earthworms.

4. Conclusions

Carbofuran, a widely used and toxic carbamate insecticide, can be effectively degraded by membrane AFT. The degradation kinetics can obey the AFT model very well, as we previously proposed. The higher the carbofuran initial concentration, the higher the treatment efficiency will be. This can be attributed to the competition for hydroxyl radicals between carbofuran and the Fenton reagents. The degradation of carbofuran by AFT can be enhanced by increasing treatment temperature; the activation energy is estimated to be 7.66 kJ mol^{-1}, which is much lower than that of carbofuran hydrolysis in aqueous solution.

During the oxidative degradation of carbofuran by AFT, not only can carbofuran be removed effectively, but also the COD. Unlike COD, the BOD_5 increases gradually with the oxidation of carbofuran. As indicated by the BOD_5/COD during the treatment, which increased from 0.04 to 0.63 within 9 min, the AFT can dramatically improve the biodegradability of carbofuran wastewater. This suggests that the AFT is a good preliminary treatment strategy for toxic and refractive organics.

GC/MS identified four degradation products of carbofuran by AFT. They are 2,3-dihydro-2,2-dimethylbenzofuran-7-yl formate, 2,3-dihydro-2,2-dimethylbenzofuran-7-ol, 2,3-dihydro-3-hydroxyl-2,2-dimethylbenzofuran-7-ol and 2,3-dihydro-3-oxo-2,2-dimethylbenzofuran-7-ol. The carbamate branch and 3-C in the partially saturated furan ring are the first and second attack targets of hydroxyl radicals.

Earthworm toxicity tests confirm that the AFT treatment is a detoxification process for carbofuran since the fatal toxicity to earthworms can be removed. Degradation products may still have some negative effects on the growth of earthworms, but compared with the parent compound, the degradation products are much less toxic.

Acknowledgements

This work was supported in part by the NRI Competitive Grants Program/USDA Award 99-35102-8238 and in part by the Cornell University Agricultural Experiment Station federal formula funds, project 329423 (regional project W-045), received from CSREES, USDA. We sincerely appreciate the assistance of Emily Scherer for sample preparation methods for toxicity testing and Tatyana Dokuchayeva for operation of the GC/MS.

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