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Competitive Degradation and Detoxification of Carbamate Insecticides by Membrane Anodic Fenton Treatment

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The competitive degradation of six carbamate insecticides by membrane anodic Fenton treatment (AFT), a new Fenton treatment technology, was carried out in this study. The carbamates studied were dioxacarb, carbaryl, fenobucarb, promecarb, bendiocarb, and carbofuran. The results indicate that AFT can effectively degrade these insecticides in both single component and multicomponent systems. The carbamates compete for hydroxyl radicals, and their kinetics obey the previously developed AFT kinetic model quite well. Hydroxyl radical reaction rate constants were obtained, and they decrease in the following order: dioxacarb ≈ carbaryl > fenobucarb > promecarb > bendiocarb > carbofuran. The AFT is shown to have higher treatment efficiency at higher temperature. Degradation products of the carbamates were determined by gas chromatography/mass spectrometry, and it appears that degradation can be initiated by hydroxyl radical attack at different sites in the molecule, depending on the individual structure of the compound. Substituted phenols are the commonly seen degradation products. The AFT treatment can efficiently remove the chemical oxygen demand of the carbamate mixture, significantly increasing the biodegradability. Earthworm studies show that the AFT is also an effective detoxification process.

KEYWORDS: Carbamate; insecticide; degradation; detoxification; Fenton; wastewater treatment; earthworm; toxicity; anodic; dioxacarb; carbaryl; bendiocarb; fenobucarb; promecarb; carbofuran

INTRODUCTION

After the ban or restriction on various chlorinated hydrocarbon insecticides, such as 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)-ethane and lindane, carbamate insecticides gained prominence in many developed countries. They are now widely used in the U.S. and throughout the world (*1*). Contamination by carbamate insecticides has been extensively reported, however, and has become an environmental concern (*2*−*8*). There are also questions about the health effects of carbamates, making environmental cleanup and wastewater treatment a high priority (*9*−*11*).

Among the causes of pesticide pollution, the disposal of rinse water from pesticide containers and spray equipment and the disposal of unused, unwanted, or obsolete pesticide stocks has become a major problem and has received extensive attention nationally and internationally (*12*−*14*). Thus, efficient, low cost, fast, and easily operated technologies are badly needed for farmers or commercial applicators to treat these small-scale but high concentration pesticide wastewaters on site.

Fenton technologies seem more attractive than other advanced oxidation processes due to their effectiveness on a broad spectrum of compounds, strong oxidation activity, fast kinetics, and equipment simplicity (*14*−*19*). To overcome the disadvantages of classic Fenton treatment (*17*, *19*, *20*) and electrochemical Fenton treatment (*21*, *22*), AFT was developed as an alternative for treating small-scale pesticide wastewater on site (*23*, *24*). An ion exchange membrane was subsequently added to the AFT system in the degradation of carbaryl, making AFT technology more convenient and practical for potential scale-up. High treatment efficiency and strong functional stability of the membrane were observed (*25*). Timely and reliable waste treatment decreases potential pollution from the rinsing of pesticide containers and application equipment and from the disposal of unwanted pesticides. On the basis of the degradation of 2,4-D by AFT, a kinetic model (also known as the AFT model) was developed to better understand AFT reaction mechanisms and to optimize the operating conditions (*26*). This model was also found to be appropriate in fitting degradation kinetics of diazinon by AFT (*27*).

To understand the degradation kinetics of each component by AFT in a multiple component system, this study investigated the competitive degradation of six carbamate insecticides. The compounds included carbaryl (1-naphthyl methylcarbamate), carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), dioxacarb (2-(1,3-dioxolan-2-yl)phenyl methylcarbamate), bendiocarb (2,2-dimethyl-1,3-benzodixol-4-yl methylcarbamate), promecarb (3-isopropyl-5-methylphenyl methylcarbamate), and fenobucarb (2-(1-methylpropyl)phenyl methylcarbamate). Considerable work has been reported in the literature

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about the environmental behavior of carbaryl and carbofuran; however, papers about the other four carbamates are very limited. As shown by Mabury and Crosby (*28*), there is a relationship between pesticide reactivity toward hydroxyl radicals and environmental behavior. Information about these carbamates acquired from this study will supplement the knowledge about carbamates in the environment both directly and indirectly. The objectives of this study are (i) to exam the appropriateness of the AFT model for the degradation kinetics of different carbamate mixtures; (ii) to derive rate constants for reaction with hydroxyl radicals generated by AFT; (iii) to investigate the temperature dependency of degradation and calculate activation energies; (iv) to determine the effect of AFT on the biodegradability of these carbamates; (v) to identify degradation products by AFT and propose possible degradation pathways; and (vi) to estimate the detoxification of carbamate insecticides by AFT.

MATERIALS AND METHODS

Chemicals, Test Organisms, and Membrane. Carbaryl (99%), carbofuran (99%), dioxacarb (98%), bendiocarb (99%), fenobucarb (99%), and promecarb (98%) were 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, ammonium sulfate, calcium chloride, calcium carbonate, ferrous ammonium sulfate, and silver sulfate were all certified reagents and 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. Kaolinte clay was purchased from Lagula Clay Co. (City of Industry, CA).

The sludge inoculated for the BOD_5 determination (as defined by APHA) was taken from 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 ohm cm^{-2} in 1 M NaCl solution at 25 °C, was purchased from Electrosynthesis (Lancaster, NY).

Degradation of Carbamates by AFT. A schematic of the membrane AFT apparatus was shown and specified in our previous work (*25*). Under typical operating conditions, 200 mL of different concentrations of carbamate(s) with 0.02 M NaCl and 200 mL of 0.08 M NaCl were added to the anodic and cathodic half-cells, respectively. The ferrous ion was delivered to the anodic half-cell by electrolysis at 0.050 Amp. The hydrogen peroxide solution of 0.311 M was added to the anodic half-cell by a peristaltic pump at 0.50 mL/min. The delivery ratio of H_2O_2 to Fe^{2+} was 10:1. The temperature was controlled at 25 ± 0.1 °C by a HAAKE K20 water circulator serving as a water bath. The power supply was turned on to initiate electrolysis when the first drop of hydrogen peroxide was added to the anodic half-cell. At different treatment times, 1.0 mL of anodic solution was taken out and put into a 2 mL GC vial containing 0.10 mL of methanol (for quenching subsequently generated hydroxyl radicals) and was analyzed for carbamate concentration(s) using HPLC. Treatments were repeated for a total of three replicates.

The degradation kinetics of carbofuran were investigated using initial concentrations that ranged from 30 to 200 μM. When investigating competitive degradation between carbofuran and other carbamates, the concentration of each insecticide was 50 μM, and two or three compounds were added to the solution. Carbamates were studied individually in experiments where temperature was controlled at 10 ± 0.1, 18 ± 0.1, 25 ± 0.1, or 33 ± 0.1 °C.

Analysis of Carbamate and Hydrogen Peroxide Concentration. The concentration of carbamates was analyzed by a HP 1090 HPLC equipped with a diode array detector. For analysis of carbofuran, carbaryl, bendiocarb, dioxacarb, and the mixture containing carbofuran and one or two of these carbamates, the mobile phase was composed of acetonitrile and water (40:60, pH adjusted to 3 using phosphoric acid). For analysis of promecarb, fenobucarb, and the mixture of carbofuran with one of these carbamates, the mobile phase was composed of acetonitrile and water (70:30, pH 3). A C18 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 the reference. Under the first operating conditions, the retention times of carbofuran, carbaryl, bendiocarb, and dioxacarb were 10.36, 11.85, 9.12, and 4.87 min, respectively. Under the second operating conditions, the retention times of carbofuran, promecarb, and fenobucarb were 3.55, 5.26, and 5.00 min, respectively. The concentration of hydrogen peroxide was determined by titration using standard potassium permanganate solution (*29*).

Determination of COD and BOD_5. Under typical operating conditions, a mixture of six carbamates with individual concentrations of 50 μM was treated by membrane AFT. At different treatment times, the AFT was stopped and samples were taken from the anodic half-cell for COD and BOD_5 determination. To adjust pH, 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. Fresh catalase solution (1.0 mg/mL in 0.5 M phosphate buffer solution) was subsequently added at the same ratio as that of buffer to decompose the residual hydrogen peroxide.

COD was determined using the dichromate method, and BOD_5 was determined using the iodometric method with azide modification (*30*). To remove the interference from iron ion, sodium fluoride was used prior to the addition of sulfuric acid during the process of BOD_5 determination.

GC/MS Identification of Degradation Products. Each insecticide of the six carbamates was degraded individually by AFT under typical operating conditions. After a 2 min treatment, 15 mL of anodic solution was 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 helium carrier gas (10.50 psi) was used; initial temperature was 80 °C, increasing at 10 °C/min to 210 °C, at 30 °C/min from 210 to 305 °C, and then kept at 305 °C for 5 min; the injector port temperature was 220 °C; and the detector temperature was 250 °C. The structures of the degradation products were identified by interpreting the MS spectra obtained in this work and by checking with available standard spectra.

Earthworm Toxicity Assay. Earthworms were exposed to the AFT treatment effluents in artificial soil, which was comprised of fine sand (69%, dry weight), kaolinite clay (20%), sphagnum peat moss (10%), and calcium carbonate (1%) (*31*). To prepare effluents, a mixture of the six carbamate pesticides (80 μM each) was subjected to AFT under typical operating conditions. At 0, 3, and 10 min, the AFT was stopped and samples were taken from the anodic half-cell. One hundred milliliters of effluent was added to 300 g (dry weight) of artificial soil and thoroughly mixed in a plastic zip bag. With the addition of effluent, the moisture content of the soil 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 ± 1 °C with an 8:16 h light:dark cycle. Evaporated moisture was determined gravimetrically and replaced daily. All tests were conducted in triplicate.

The soil was hand-sorted after 1, 5, 7, and 10 days to determine the mortality and the decrease of average body weight of living earthworms. Earthworms that had no 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 as the basis for the next day's moisture compensation.

AFT Kinetic Model. The derivation of the AFT kinetic model was published in our previous paper (*25*). Assumptions for setting up the model include the following: (i) the concentration of ferrous ion, which is constantly generated by electrolysis and continuously consumed by reacting with hydrogen peroxide, is constant; (ii) hydrogen peroxide can be accumulated during the treatment; (iii) the Fenton reaction and the hydroxyl radical reaction with the target compound obey second-order kinetics; and (iv) the instantaneous concentration of hydroxyl radical is proportional to its generation rate. With these assumptions, the degradation kinetics of the target organic compound can be described by the following equation:

$$\ln\frac{[C]_t}{[C]_0} = -\frac{1}{2}K\lambda\pi\omega\nu_0^2 t^2 \quad (1)$$

where $K = kk'$ (μM^{-2} min^{-2}), k (μM^{-1} min^{-1}), and k' (μM^{-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; ν_0 (μM min^{-1}) is the delivery rate of ferrous ion by electrolysis; and t (min) is time. $K\lambda\pi\omega$, the degradation rate parameter, signifies the degradation rate when the delivery rate of ferrous ion is fixed.

RESULTS AND DISCUSSION

Competitive Degradation and Hydroxyl Reaction Rate Constants. In our previous studies, we showed that the AFT model could successfully fit the degradation kinetics of several target compounds in a single component system (*25*−*27*). The fit of the AFT model to the kinetics of coexisting compounds in a multitarget system has not yet been demonstrated. In this work, the competitive degradation between carbofuran and either one or two other carbamate(s) was carried out and fitted by the AFT model. Some of these results are shown in **Figure 1**. Both carbofuran and coexisting carbamate(s) can be efficiently degraded at different rates during the membrane AFT treatment. The degradation kinetics of each of the coexisting carbamates in either a two target or three target system are fitted very well by the AFT model. All values of rate parameters ($K\lambda\pi\omega$) and regression coefficients (r) of each coexisting carbamate in the competitive system investigated in this study are listed in **Table 1**.

Because λ, π, ω, and ν_0 should be the same for each of the coexisting targets in the same solution and k (the Fenton reaction rate constant) is a constant, the difference in degradation rate should be determined by k', the hydroxyl radical reaction rate constant for a given pesticide. Thus, the degradation rates of coexisting compounds in the same solution are proportional to their hydroxyl radical reaction rate constants. The following equation can describe the ratio of coexisting carbamates

$$\frac{k_1'}{k_2'} = \frac{(K\lambda\pi\omega)_1}{(K\lambda\pi\omega)_2} \quad (2)$$

where k_1' and k_2' are hydroxyl radical reaction rate constants for coexisting compounds **1** and **2**, respectively. According to Haag and Yao (*32*), the hydroxyl radical reaction rate constant for carbofuran (k') is 7×10^9 M^{-1} s^{-1}. The hydroxyl reaction rate constants of other carbamates can be calculated from eq 2 and are listed in **Table 2**. This method of deriving rate constants requires analysis of each pesticide to develop the degradation curve and is called the direct method. According to the data listed in **Table 2**, the reactivity of these carbamates toward hydroxyl radicals is in the following order: dioxacarb ≈ carbaryl > fenobucarb > promecarb > bendiocarb > carbofuran.

As described in our previous work (*26*), we can also calculate the hydroxyl radical reaction rate constant of the coexisting carbamates from the difference of carbofuran $K\lambda\pi\omega$ values between that obtained from a pure 50 μM carbofuran solution and that from 50 μM carbofuran coexisting with another 50 μM carbamate. This method is called the indirect method. This method does not require the concentration analysis of each carbamate during degradation to obtain its degradation rate

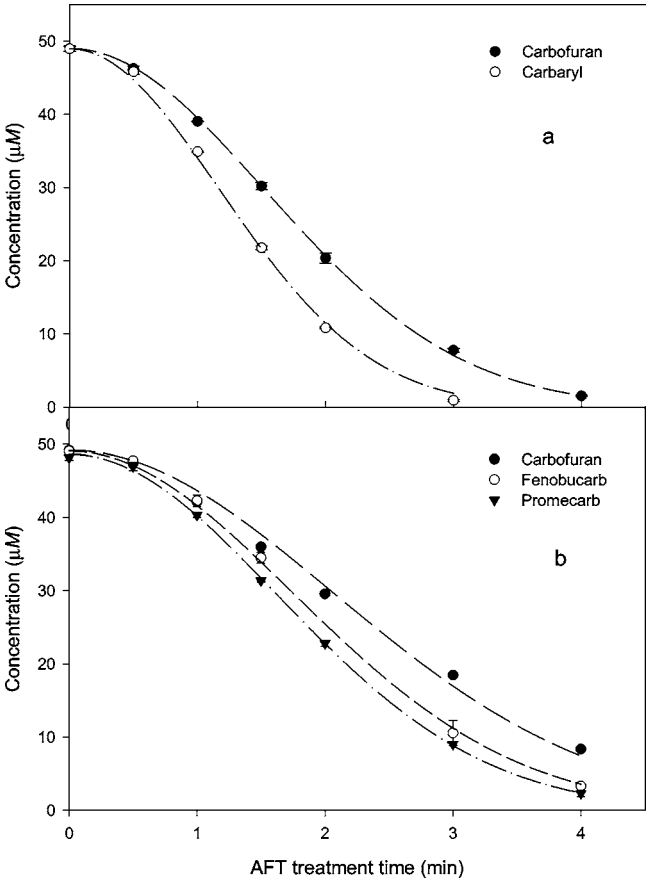

Figure 1. Competitive oxidation of carbamates by membrane AFT in two component (**a**) and three component (**b**) systems. Points are experimental data. Lines are fitting results using the AFT model.

Table 1. Rate Parameters ($K\lambda\pi\omega$) and Regression Coefficients (r) of Each Coexisting Carbamate

competitive system	$K\lambda\pi\omega$ (μM^{-2})	r
carbofuran (1) + carbaryl (2)	(1) $(6.875 \pm 0.086) \times 10^{-5}$	0.999
	(2) $(1.178 \pm 0.238) \times 10^{-4}$	0.999
carbofuran (1) + bendiocarb (2)	(1) $(7.769 \pm 0.089) \times 10^{-5}$	0.999
	(2) $(9.897 \pm 0.083) \times 10^{-5}$	0.999
carbofuran (1) + dioxacarb (2)	(1) $(6.375 \pm 0.109) \times 10^{-5}$	0.998
	(2) $(1.109 \pm 0.420) \times 10^{-4}$	0.993
carbofuran (1) + fenobucarb (2)	(1) $(6.802 \pm 0.076) \times 10^{-5}$	0.999
	(2) $(1.076 \pm 0.166) \times 10^{-4}$	0.998
carbofuran (1) + promecarb (2)	(1) $(6.965 \pm 0.096) \times 10^{-5}$	0.999
	(2) $(1.039 \pm 0.053) \times 10^{-4}$	0.999
carbofuran (1) + carbaryl (2) + dioxacarb (3)	(1) $(4.538 \pm 0.106) \times 10^{-5}$	0.997
	(2) $(8.179 \pm 0.036) \times 10^{-5}$	0.999
	(3) $(9.060 \pm 0.156) \times 10^{-5}$	0.998

Table 2. Hydroxyl Reaction Rate Constants (k') of Each Coexisting Carbamate Derived from Direct and Indirect Methods

carbamate	k' ($M^{-1}s^{-1}$) from direct method	k' ($M^{-1}s^{-1}$) from indirect method
dioxacarb	1.2×10^{10}	1.1×10^{10}
carbaryl	1.2×10^{10}	1.0×10^{10}
fenobucarb	1.1×10^{10}	1.0×10^{10}
promecarb	1.0×10^{10}	9.9×10^{9}
bendiocarb	8.9×10^{9}	8.3×10^{9}
carbofuran	7×10^{9}[a]	

[a] Data from Hagg and Yao (*36*).

parameter, but it does require an accurate correlation between the $K\lambda\pi\omega$ value and the initial concentration of carbofuran to estimate the equivalent carbofuran concentration of the coexisting target compound. This correlation was obtained in a previous study of carbofuran (*33*).

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

The calculated rate constant values of these coexisting carbamates using the indirect method are also listed in **Table 2**. The two calculation methods yielded consistently similar rate constants, confirming that the indirect method is reliable and acceptable. The application of the indirect method in obtaining hydroxyl radical reaction rate constants is quite convenient, especially when a large number of compounds is simultaneously studied. As compared with our data from this study and with data from Haag and Yao (*32*), Mabury and Crosby's data appear to be systematically lower (*28*). This difference might result from the fact that in their PNDA model they do not account for the consumption of hydroxyl radicals by species other than the probe parent compound and the PNDA. Our previous pesticide rate constants calculated with these same methods (*26*) compared well with literature values from Haag and Yao (*32*).

Effect of Temperature on Degradation. Degradation of the carbamates by membrane AFT at different temperatures obeys the AFT model very well (regression coefficients not shown). All $K\lambda\pi\omega$ values are listed in **Table 3**. The $K\lambda\pi\omega$ value increases with increasing temperature. Because the delivery rate of Fenton reagent was kept constant for all treatments and the hydroxyl radical reaction and Fenton reaction are fast reactions, the degradation rate parameter can also be used to signify the treatment efficiency. An increasing $K\lambda\pi\omega$ value with temperature indicates that a higher AFT treatment efficiency can be attained at a higher temperature.

On the basis of the changes of $K\lambda\pi\omega$ with the temperature, pseudo activation energies for the degradation of each carbamate by membrane AFT (a combination of the Fenton reaction and the hydroxyl radical reaction with the insecticide) were calculated using the Arrhenius equation (*25*). These activation energies are also listed in **Table 3**. As compared with those for hydrolysis of carbamates, ranging from 50 to 110 kJ/mol (*7*, *34*, *35*), these activation energies are much lower, indicating that carbamates are thermodynamically easier to degrade by AFT as compared to hydrolysis in an acidic/alkaline aqueous environment. Additionally, no correlation between the hydroxyl reaction rate constants and the activation energies of the carbamates by AFT was found. This implies that these carbamates may undergo different first steps in the degradation process. If they underwent the same initial degradation reaction, this result would indicate that the reactions between these carbamates and hydroxyl radicals are a kinetically controlled process.

Table 3. $K\lambda\pi\omega$ Values at Different Temperatures and Pseudo Activation Energies (E_a) of Carbamates by Membrane AFT

carbamate	temp (K)	$K\lambda\pi\omega$ (μM^{-2})	E_a (kJ/mol)
dioxacarb	283.2	$(1.128\pm0.031)\times10^{-4}$	26.4
	291.2	$(1.705\pm0.072)\times10^{-4}$	
	298.2	$(1.978\pm0.089)\times10^{-4}$	
	306.2	$(2.917\pm0.143)\times10^{-4}$	
carbaryl	283.2	$(7.028\pm0.036)\times10^{-5}$	13.3
	291.2	$(9.043\pm0.096)\times10^{-5}$	
	298.2	$(1.048\pm0.011)\times10^{-4}$	
	306.2	$(1.330\pm0.028)\times10^{-4}$	
fenobucarb	283.2	$(6.081\pm0.063)\times10^{-5}$	16.4
	291.2	$(7.534\pm0.066)\times10^{-5}$	
	298.2	$(8.722\pm0.056)\times10^{-5}$	
	306.2	$(1.020\pm0.013)\times10^{-4}$	
promecarb	283.2	$(6.130\pm0.112)\times10^{-5}$	14.9
	291.2	$(8.047\pm0.172)\times10^{-5}$	
	298.2	$(8.805\pm0.169)\times10^{-5}$	
	306.2	$(9.888\pm0.079)\times10^{-5}$	
bendiocarb	283.2	$(6.869\pm0.079)\times10^{-5}$	11.9
	291.2	$(8.030\pm0.066)\times10^{-5}$	
	298.2	$(9.123\pm0.122)\times10^{-5}$	
	306.2	$(9.911\pm0.116)\times10^{-5}$	
carbofuran	283.2	$(5.995\pm0.116)\times10^{-5}$	7.7
	291.2	$(6.773\pm0.073)\times10^{-5}$	
	298.2	$(7.074\pm0.060)\times10^{-5}$	
	306.2	$(7.686\pm0.119)\times10^{-5}$	

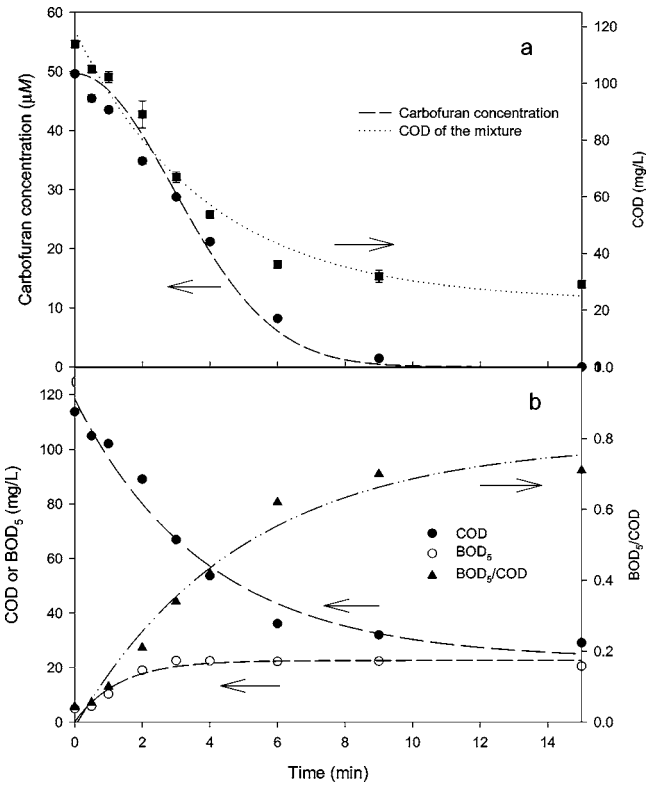

Figure 2. Changes of carbofuran concentration, COD, BOD_5, and BOD_5/COD during the degradation of the carbamate mixture by membrane AFT.

Improvement on Biodegradability. During AFT treatment of a mixture of the six carbamates (each concentration at 50 μM), both the carbofuran and the total COD can be effectively removed (**Figure 2a**). About 10 min of treatment can completely remove 50 μM carbofuran from the mixture. Because the degradation rate of carbofuran by AFT is the lowest among those of the six carbamates in the mixture, all other coexisting carbamates should have already been degraded within 10 min of treatment. The efficiency for total COD is slightly lower as

Table 4. Retention Times (t_r) and MS Spectra of the Degradation Products of Carbamates Determined by GC/MS

carbamate	degradation products	t_r (min)	MS spectrum, *m/z* (%)
dioxacarb	parent compound (**1a**)	14.08	223 ($M^{+\bullet}$, 0.1), 193 (0.1), 178 (1), 167 (8), 166 (76), 165 (58), 150 (2), 149 (23), 148 (4), 135 (5), 123 (6), 122 (55), 121 (100), 107 (16), 105 (8), 104 (13), 94 (14), 93 (8), 92 (6)
	2-(1,3-dioxolan-2-yl)phenol (**1b**)	9.17	167 (4), 166 ($M^{+\bullet}$,42), 165 (35), 150 (1), 149 (6), 135 (1), 123 (4), 122 (40), 121 (100), 108 (2), 107 (17), 105 (6), 104 (12), 95 (2), 94 (11), 93 (8), 92 (3)
	(2-hydroxylethyl)salicylate (**1c**)	10.58	182 ($M^{+\bullet}$,13), 165 (4), 164 (37), 138 (4), 122 (6), 121 (50), 120 (100), 94 (2), 93 (14), 92 (42), 86 (3), 84 (5)
	2-hydroxyl benzaldehyde (**1d**)	4.39	124 (1), 123 (8), 122 ($M^{+\bullet}$,100), 121 (93.3), 105 (1), 104 (13), 94 (6), 93 (20), 92 (3), 88 (2), 86 (11), 84 (17)
fenobucarb	parent compound (**2a**)	11.47	207 ($M^{+\bullet}$,0.5), 176 (0.3), 151 (3), 150 (29), 135 (2), 122 (9), 121 (100), 115 (2), 107 (8), 103 (7), 91 (12)
	2-(1-methylpropyl)phenyl formate (**2b**)	12.53	179 (M^{+1}, 2), 165 (3), 164 (26), 123 (2), 122 (21), 121 (100), 107 (7.2), 103 (14), 93 (4), 91 (14)
	2-(1-methylpropyl)phenol (**2c**)	7.21	151 (3), 150 ($M^{+\bullet}$,23), 135 (2), 133 (1), 122 (9), 121 (100), 119 (2), 115 (3), 107 (12), 103 (16), 91 (15)
	2-acetyl phenol (**2d**)	5.86	137 (4), 136 ($M^{+\bullet}$,48), 122 (8), 121 (100), 118 (1), 107 (1), 94 (3), 93 (21), 92 (3), 89 (2), 86 (5), 84 (7)
promecarb	parent compound (**3a**)	12.40	207 ($M^{+\bullet}$,2), 151 (8), 150 (73), 136 (10), 135 (100), 133 (3), 122 (4), 121 (5), 115 (5), 107 (6), 105 (6), 91 (16)
	3-isopropyl-5-methylphenyl formate (**3b**)	7.73	178 ($M^{+\bullet}$,0.1), 151 (3), 150 (38), 136 (10), 135 (100), 122 (4), 121 (6), 117 (6), 115 (9), 107 (11), 105 (6), 91 (21)
	3-(2-hydroxyl-isopropyl) 5-methylphenyl methylcarbamate (**3c**)	13.92	223 ($M^{+\bullet}$,1), 167 (6), 166 (47), 152 (11), 151 (100), 135 (7.3), 123 (5), 107 (9), 91 (8)
	3-acetyl-5-hydroxyl benzaldehyde (**3d**)	10.66	165 (9), 164 ($M^{+\bullet}$,82), 150 (12), 149 (100), 135 (23), 131 (5), 121 (26.5), 107 (21), 103 (25), 91 (36)
	3-isopropyl-5-hydroxyl benzaldehyde (**3e**)	10.23	165 (3), 164 ($M^{+\bullet}$,24), 150 (5), 136 (33), 135 (100), 121 (21), 117 (21), 117 (8), 115 (16), 107 (19), 105 (10), 91 (40)
	3-methyl-5-(2-hydroxy-2-propyl)phenol (**3f**)	9.77	167 (8), 166 ($M^{+\bullet}$,65), 152 (10), 151 (100), 148 (4), 135 (9), 123 (8), 121 (5), 119 (3), 109 (12), 108 (12), 107 (21), 91 (12)
bendiocarb	parent compound (**4a**)	12.16	224 (1), 223 ($M^{+\bullet}$,11), 167 (4), 166 (42), 152 (9), 151 (100), 149 (2), 126 (43), 123 (7)
	2,2-dimethyl-1,3-benzodixol-4-yl formate (**4b**)	7.58	195 (4), 194 ($M^{+\bullet}$,35), 179 (8), 166 (14), 152 (10), 151 (100), 127 (5), 126 (70), 125 (6), 123 (7)
	2,2-dimethyl-1,3-benzodixol-4-ol (**4c**)	7.21	167 (6), 166 ($M^{+\bullet}$,62), 152 (9), 151 (9100), 149 (1), 128 (1), 127 (6), 126 (87), 125 (6), 123 (9)
carbofuran	parent compound (**5a**)	12.98	222 (0.8), 221 ($M^{+\bullet}$,6), 206 (0.1), 191 (0.1), 177 (0.3), 166 (1), 165 (11), 164 (100), 150 (6), 149 (57), 147 (8), 131 (16), 123 (14), 122 (16)
	2,3-dihydro-2,2-dimethylbenzofuran-7-yl formate (**5b**)	8.74	193 (7), 192 ($M^{+\bullet}$,43), 164 (58), 149 (100), 145 (10), 135 (7), 131 (36), 123 (32), 122 (30)
	2,3-dihydro-2,2-dimethylbenzofuran-7-ol (**5c**)	7.63	166 (1), 165 (11), 164 ($M^{+\bullet}$,100), 150 (8), 149 (85), 147 (14), 146 (6), 145 (8), 136 (3), 135 (6), 132 (4), 131 (34), 123 (27), 122 (28), 121 (24)
	2-hydro-3-hydroxyl-2,2-dimethylbenzofuran-7-ol (**5d**)	9.59	181 (5), 180 ($M^{+\bullet}$,38), 163 (2), 162 (8), 161 (12), 151 (14), 147 (33), 138 (11), 137 (100), 134 (6), 123 (9), 121 (11)

Table 4. (Continued)

carbamate	degradation products	t_r (min)	MS spectrum, *m*/*z* (%)
carbofuran	2-hydro-3-oxo-2,2-dimethylbenzofuran-7-ol (**5e**)	9.02	179 (12), 178 ($M^{+\bullet}$,100), 177 (39), 164 (5), 163 (34), 161 (5), 160 (4), 150 (6), 149 (6), 137 (63), 136 (13), 135 (36), 122 (3), 121 (6)
carbaryl	parent compound (**6a**)	12.31	201 ($M^{+\bullet}$,3), 146 (1), 145 (11), 144 (100), 128 (1), 127 (3), 126 (1), 117 (3), 116 (28), 115 (56), 114 (3), 113 (2), 89 (7), 88 (2), 87 (2)
	1-naphthol (**6b**)	9.00	146 ($M^{+\bullet}$,1), 145 (11), 144 (100), 126 (1), 117 (4), 116 (41), 115 (89), 114 (4), 113 (3), 100 (1), 98 (1), 90 (2), 89 (10), 88 (3), 87 (3), 86 (2), 85 (1)
	1,4-naphtho-quinone (**6c**)	8.10	160 ($M^{+\bullet}$,10), 159 (11), 158 (100), 131 (9), 130 (39), 104 (59), 103 (9), 102 (53)
	(phthalic acid-O-)yl *N*-methylcarbamate (**6d**)	12.60	223 ($M^{+\bullet}$,5), 205 (4), 150 (10), 149 (100), 105 (4), 104 (5), 97 (4), 85 (3), 83 (3)

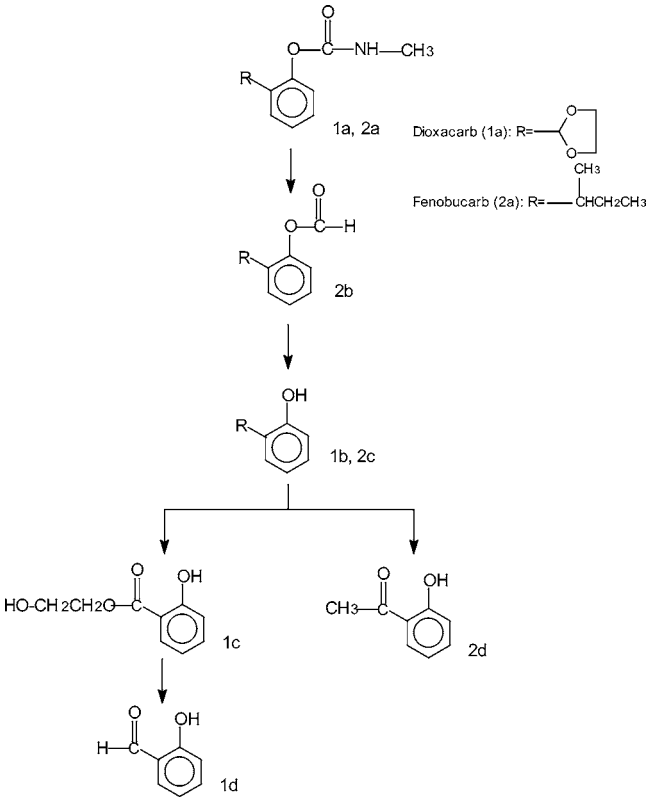

Figure 3. Degradation pathways of dioxacarb and fenobucarb by membrane AFT.

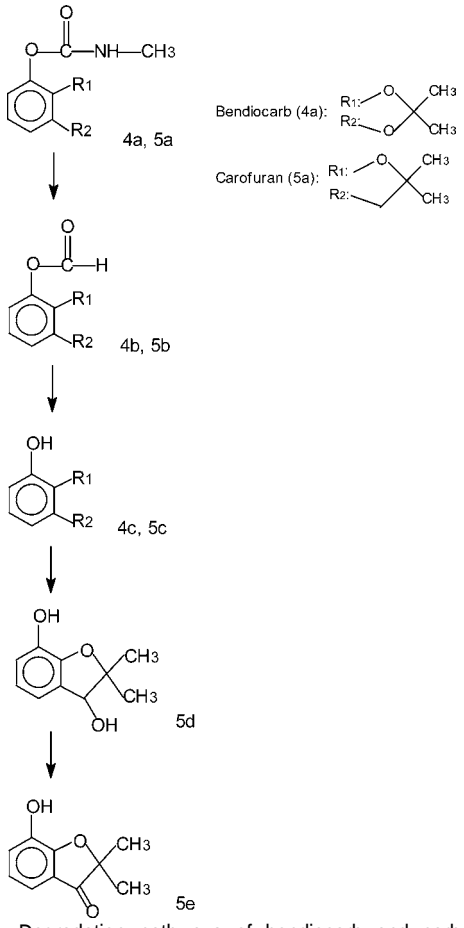

Figure 4. Degradation pathways of bendiocarb and carbofuran by membrane AFT.

compared with the removal efficiency of parent compounds. After 10 min of treatment, 27% COD still remains, indicating the existence of a significant amount of degradation products with substantial COD values.

After AFT treatment, the BOD_5 value of the carbamate mixture gradually increased from 4.9 at 0 min to 22.5 mg/L at 3 min and was maintained at this level for 15 min (**Figure 2b**). The increased BOD_5 demonstrated that the mixture became more utilizable for bacteria through the AFT treatment. BOD_5/COD is usually used as a parameter to assess the biodegradability of certain organics in water, and compounds with a ratio greater than 0.3 are regarded as biodegradable (*36*). The value of BOD_5/COD for the carbamate mixture prior to AFT treatment was only 0.04, illustrating that the carbamates are biorefractory or toxic. As shown in **Figure 2b**, BOD_5/COD can be dramatically increased by AFT treatment. After a 3 min treatment, the BOD_5/COD reached 0.34, indicating that the waste was more likely to be biodegradable. A 15 min treatment raised the BOD_5/COD ratio of the carbamate mixture solution to 0.71. Thus, AFT is a very effective preliminary treatment method for refractory or toxic organics. The effluents from the AFT can be combined with common sewage for further treatment.

Degradation Pathways of Carbamates by AFT. Degradation products of carbamates identified by GC/MS analysis and their MS spectra are listed in **Table 4**. Because of the sensitivity limit of the MS detector, low concentration, and the difficulty of volatilization in the GC inlet port, some degradation compounds may not have been detected. On the basis of the

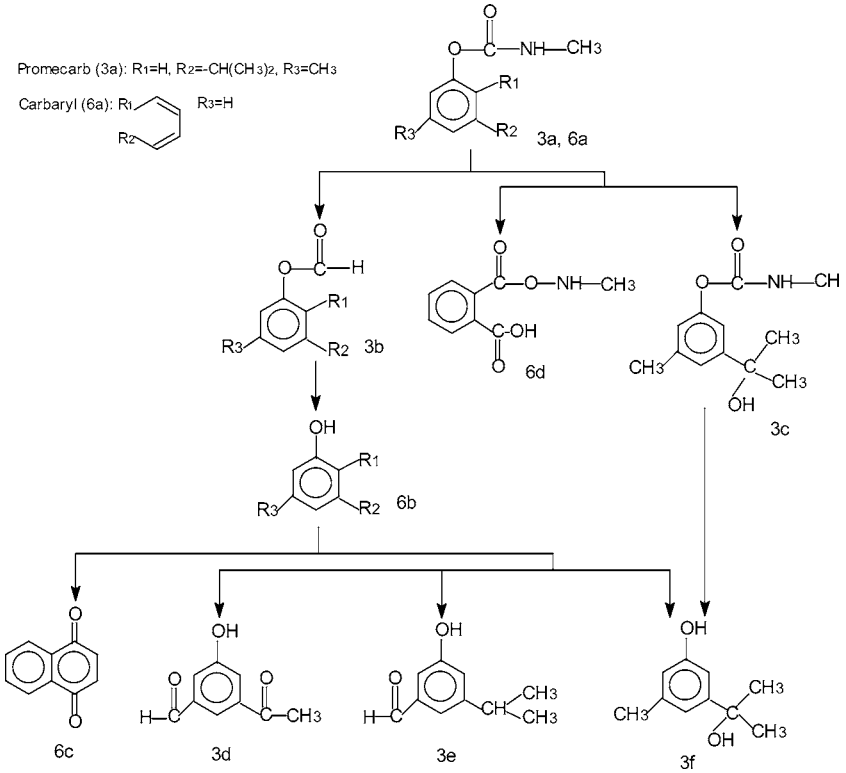

Figure 5. Degradation pathways of promecarb and carbaryl by membrane AFT.

identified degradation products, degradation pathways of these carbamates by membrane AFT are proposed. **Figure 3** shows the degradation pathway of dioxacarb (**1a**) and fenobucarb (**2a**). The carbamate branch seems to be the first target attacked by hydroxyl radicals. The cleavage of the carbamate branch results in a substituted phenol (**1b** and **2c**). Subsequently, hydroxyl radicals begin to attack remaining ring substituents. For dioxacarb, the dioxolane ring opens and salicylate (**1c**) is formed. Further attack can remove the hydroxyethyl branch to form 2-hydroxy benzaldehyde (**1d**). For fenobucarb, hydroxyl attack removes the ethyl and forms a carbonyl in its place, generating 2-acetyl phenol (**2d**).

Bendiocarb (**4a**) and carbofuran (**5a**) have very similar structures. The only difference is that bendiocarb has a 1,3-dioxol-ring, while carbofuran has a furan ring. Their degradation pathways are also similar (**Figure 4**). As described above, attack of the carbamate branch by hydroxyl radicals is the first step. The carbamate can be deaminated, generating formates (**4b** and **5b**). Continuous attack removes the formate group, giving rise to the substituted phenol (**4c** and **5c**), which has been found after photodegradation of bendiocarb (*37*) and carbofuran (*38*). Moreover, carbofuran can further react with hydroxyl radicals at the 3-C of the furan ring substituting the hydroxy group for the H atom (**5d**) and forming carbonyl (**5e**) by subsequent hydroxyl radical attacks.

The degradation products of promecarb and carbaryl suggest that the carbamate branch need not always be the first target attacked by hydroxyl radicals (**Figure 5**). The hydroxyl radical can react with and remove the carbamate branch of carbamate insecticides, leading to substituted phenols (**6b** and **3d**−**f**). Concurrently, hydroxyl radicals can also initially attack the alkyl group. For carbaryl, hydroxyl radicals can open one aromatic ring of naphthalene to generate product **6d** (*27*). For promecarb, hydroxyl radicals can attack the isopropyl group by substituting a hydroxy group for the H atom to form product **3c**.

From the overall degradation pathways of these six carbamates by membrane AFT, it appears that the carbamate branch is the common initial target of hydroxyl radicals. The degradation products resulting from this attack, substituted phenols, are the commonly seen degradation products for each of them. Some of these phenols can also be found in photolysis (*37*−*39*) and hydrolysis (*40*, *41*) of carbamates. For promecarb and carbaryl, hydroxyl radicals can also initiate attack at the alkyl site. Thus, the degradation of carbamates by the AFT can be initiated by hydroxyl radical attack at different sites on carbamate molecules. This is consistent with the result obtained in the temperature experiments, confirming that these carbamates undergo different first steps in the degradation process.

Reduction of Toxicity. Earthworms are important contributors to soil fertility and therefore need protection from agrochemicals and industrial compounds. Hence, the earthworm toxicity test is widely used to predict the potential impact of pesticides on earthworm populations in agricultural land and to model the potential hazard of industrial chemicals to the terrestrial ecosystem (*42*). It has been reported that carbamates are very toxic to earthworms and can kill them rapidly (*43*). A more recent study found that carbaryl strongly inhibits earthworm acetylcholinesterase and may also competitively inhibit biotransformations relying on cytochrome P-450 (*44*).

The toxicity changes of carbamate mixtures treated by AFT were examined using earthworm *E. foetida* in this study. Earthworms suffered no mortality when exposed to a combined carbamate concentration of 48 μmol in 300 g of soil (0.16 μmol/g) for 10 days. Because of the limited solubility of some of the carbamates, the concentrations could not be increased sufficiently to observe acutely toxic levels. However, changes in average earthworm weight, a sensitive parameter of sublethal toxicity (*31*), showed that AFT treatment reduced the overall toxicity of the carbamate mixture (**Figure 6**). Almost no significant difference in average weight loss was found between earthworms exposed to a 10 min treatment effluent and the blank control. In summary, the untreated carbamate mixture was more toxic to earthworms than treatment effluents, and longer AFT treatment times decreased toxicity.

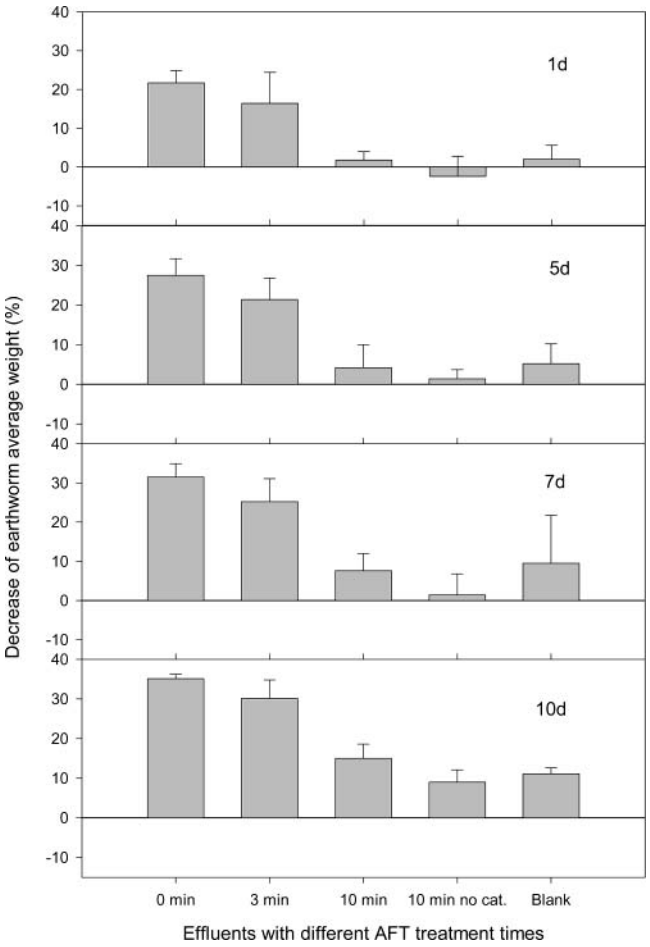

Figure 6. Earthworm toxicity of carbamate mixture with different AFT treatment times at different incubation days.

To investigate the effect of residual hydrogen peroxide and acidity after AFT, an aliquot of the 10 min effluent without phosphate buffer and catalase treatment was directly spiked into the soil. Acidity and residual hydrogen peroxide had no effect on earthworms in soil (shown as 10 min no cat. in Figure 6). The lack of adverse effects probably resulted from decomposition of residual hydrogen peroxide and neutralization of the acidic pH by the buffering capacity of the soil.

Conclusion. Membrane AFT treatment effectively degraded six carbamate insecticides in both single and multicomponent systems. Different carbamates can compete with each other for hydroxyl radicals, but the degradation of each was still well-predicted by the AFT kinetic model. Degradation can be initiated by hydroxyl radical attack at different sites on the carbamate molecules. AFT not only efficiently removes COD of the carbamate mixture solution but also greatly increases biodegradability. Earthworm toxicity tests demonstrate that AFT is also a detoxification process. The AFT treatment of carbamate insecticides has great potential for reducing the risk of contaminated wastewater.

ABBREVIATIONS USED

AFT, anodic Fenton treatment; HPLC, high-performance liquid chromatography; COD, chemical oxygen demand; BOD_5, 5 day biochemical oxygen demand; GC/MS, gas chromatography/mass spectrum.

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LITERATURE CITED

(1) Davies, J. E.; Lee, J. A. Changing profiles in human health effects of pesticides. In *Pesticide Science and Biotechnology*; Greenhalgh, R., Roberts, T. R., Eds.; Blackwell Scientific: Oxford, England, 1987; pp 533−538.

(2) Iwakuma, T.; Shiraishi, H.; Nohara, S.; Takamura, K. Runoff properties and change in concentrations of agricultural pesticides in river system during a rice cultivation period. *Chemosphere* **1993**, *27* (4), 677−691.

(3) Kawata, K.; Yasuhara, A. Annual concentration variations in the atmosphere, and estimated inhalation intake of fenitrothion and fenobucarb. *Chemosphere* **1992**, *25* (6), 821−825.

(4) Kumari, B.; Madan, V. K.; Kumar, R.; Kathpal, T. S. Monitoring of seasonal vegetables for pesticide residues. *Environ. Monit. Assess.* **2002**, *74*, 263−270.

(5) Holman, R. E.; Leidy, R. B.; Walker, A. E. Evaluation of selected pesticides in North Carolina surface water supplies: Intake study. *J. Am. Water Resour. Assoc.* **2000**, *36* (1), 75−85.

(6) Johnson, W. G.; Lavy, T. L. Persistence of carbofuran and molinate in flooded rice culture. *J. Environ. Qual.* **1995**, *24*, 487−493.

(7) Lemley, A. T.; Zhong, W. Z. Kinetics of aqueous base and acid-hydrolysis of aldicarb, aldicarb sulfoxide and aldicarb sulfone. *J. Environ. Sci. Health.* **1983**, *B18* (2), 189−206.

(8) Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999−2000: a national reconnaissance. *Environ. Sci. Technol.* **2002**, *36*, 1202−1211.

(9) Elespuru, R.; Lijinsky, W.; Stelow, J. K. Nitrosocarbaryl as a potent mutagen of environmental significance. *Nature* **1974**, *247*, 386−387.

(10) Zahm, S. H.; Weisenburger, D. D.; Babbit, P. A.; Saal, R. C.; Cantor, K. P.; Blair, A. A case control study of non-Hodgkin's lymphoma and agricultural factors in Eastern Nebraska. *Am. J. Epidemiol.* **1988**, *128*, 901.

(11) Zheng, T.; Zahm, S. H.; Cantor, K. P.; Weisenburger, D. D.; Zhang, Y.; Blair, A. Agricultural exposure to carbamate pesticides and risk of non-Hodgkin's Lymphoma. *JOEM* **2001**, *43* (7), 641−649.

(12) Felsot, A. S. Options for cleanup and disposal of pesticide wastes generated on a small-scale. *J. Environ. Sci. Health* **1996**, *B31* (3), 365−381.

(13) Chiron, S.; Fernandez-Alba, A. R.; Rodriguez, A. Pesticide chemical oxidation processes: an analytical approach. *Trends Anal. Chem.* **1997**, *16* (9), 518−527.

(14) Huston, P. L.; Pignatello, J. J. Degradation of selected pesticide active ingredients and commercial formulations in water by the photoassisted Fenton reaction. *Water Res.* **1999**, *33* (5), 1238−1246.

(15) Chiron, S.; Fernandez-Alba, A.; Rodriguez, A.; Garcia-Calvo, E. Pesticide chemical oxidation: state-of-the-art. *Water Res.* **2000**, *34* (2), 366−377.

(16) Carey, J. H. An introduction to advanced oxidation processes (AOP) for destruction of organics in wastewater. *Water Pollut. Res. J. Can.* **1992**, *27* (1), 1−21.

(17) Arnold, S. M.; Hickey, W. J.; Harris, R. F. Degradation of atrazine by Fenton's reagent: condition optimization and product quantification. *Environ. Sci. Technol.* **1995**, *29*, 2083−2089.

(18) Oturan, M. A. An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2,4-D. *J. Appl. Electrochem.* **2000**, *30*, 475−482.

(19) Tang, W. Z.; Huang, C. P. The effect of chlorine position of chlorinated phenols on their dechlorination kinetics by Fenton's reagent. *Waste Manage.* **1995**, *15* (8), 615−622.
(20) Sedlak, D. L.; Andren, A. W. Oxidation of chlorobenzene with Fenton reagent. *Environ. Sci. Technol.* **1991**, *25*, 777−782.
(21) Pratap, K.; Lemley, A. T. Electrochemical peroxide treatment of aqueous herbicide solutions. *J. Agric. Food Chem.* **1994**, *42*, 209−215.
(22) Pratap, K.; Lemley, A. T. Fenton electrochemical treatment of aqueous atrazine and metolachlor. *J. Agric. Food Chem.* **1998**, *46*, 3285−3291.
(23) Saltmiras, D. A.; Lemley, A. T. Degradation of Ethylene thiourea (ETU) with three Fenton treatment process. *J. Agric. Food Chem.* **2000**, *48*, 6149−6157.
(24) Saltmiras, D. A.; Lemley, A. T. Anodic Fenton treatment of Treflan MTF (r). *J. Environ. Sci. Health* **2001**, *A36* (3), 261−274.
(25) Wang, Q.; Lemley, A. T. Oxidation of carbaryl in aqueous solution by membrane anodic Fenton treatment. *J. Agric. Food Chem.* **2002**, *50*, 2331−2337.
(26) Wang, Q.; Lemley, A. T. Kinetic model and optimization of 2,4-D degradation by anodic Fenton treatment. *Environ. Sci. Technol.* **2001**, *35*, 4509−4514.
(27) Wang, Q.; Lemley, A. T. Oxidation of diazinon by anodic Fenton treatment. *Water Res.* **2002**, *36* (13), 3237−3244.
(28) Mabury, S. A.; Crosby, D. G. Pesticide reactivity toward hydroxyl and its relationship to field persistence. *J. Agric. Food Chem.* **1996**, *44*, 1920−1924.
(29) Huckaba, C. E.; Keyes, F. G. J. The accuracy of estimation of hydrogen peroxide by potassium permanganate titration. *Am. Chem. Soc.* **1948**, *70*, 1640−1644.
(30) Taras, M. J., Greenberg, A. E., Hoak, R. D., Rand, M. C., Eds. *Standard Methods for the Examination of Water and Wastewater*, 13th ed.; American Public Health Association: Washington DC, 1971; pp 474−481, 489−499.
(31) Mostert, M. A.; Schoeman, A. S.; Merwe, M. V. D. The toxicity of five insecticides to earthworms of the *Pheretima* group, using an artificial soil test. *Pest Manage. Sci.* **2000**, *56*, 1093−1097.
(32) Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol.* **1992**, *26*, 1005−1013.
(33) Wang, Q.; Lemley, A. T.; Scherer, E. Oxidative degradation and detoxification of aqueous carbofuran by membrane anodic Fenton treatment. *J. Hazard. Mater.* **2002**, *B98*, 241−255.
(34) Wei, J.; Furrer, G.; Schulin, R. Kinetics of carbosulfan degradation in the aqueous phase in the presence of a cosolvent. *J. Environ. Qual.* **2000**, *29*, 1481−1487.
(35) Mabey, W.; Mill, T. Critical review of hydrolysis of organic compounds in water under environmental conditions. *J. Phys. Chem. Ref. Data* **1978**, *7* (2), 383−415.
(36) Zhu, W.; Yang, Z.; Wang, L. Application of ferrous hydrogen peroxide for treatment of DSD-acid manufacturing process wastewater. *Water Res.* **2001**, *35* (8), 2087−2091.
(37) Climent, M. J.; Miranda, M. A. Gas chromatographic-mass spectrometric study of photodegradation of carbamate pesticides. *J. Chromatogr.* **1996**, *A738*, 225−231.
(38) Bachman, J.; Patterson, H. H. Photodecomposition of the carbamate pesticide carbofuran: Kinetics and the influence of dissolved organic matter. *Environ. Sci. Technol.* **1999**, *33*, 874−881.
(39) Pramauro, E.; Prevot, A. B.; Vincenti, M.; Brizzolest, G. Photocatalytic degradation of carbaryl in aqueous solutions containing TiO_2 suspensions. *Environ. Sci. Technol.* **1997**, *31*, 3126−3131.
(40) Wei, J.; Furrer, G.; Kaufman, S.; Schulin, R. Influence of clay minerals on the hydrolysis of carbamate pesticides. *Environ. Sci. Technol.* **2001**, *35*, 2226−2232.
(41) Rajagopal, B. S.; Panda, S.; Sethunathan, N. Bull. Accelerated degradation of carbaryl and carbofuran in a flooded soil pretreated with hydrolysis products, 1-naphthol and carbofuran phenol. *Environ. Contam. Toxicol.* **1986**, *36*, 827−832.
(42) Van Gestel, C. A. M. Validation of earthworm toxicity tests by comparison with field studies: a review of benomyl, carbendazim, carbofuran, and carbaryl. *Ecotoxicol. Environ. Saf.* **1992**, *23*, 221−236.
(43) Edwards, C. A.; Thompson, A. R. Pesticides and the soil fauna. *Residue Rev.* **1973**, *45*, 25−32.
(44) Ribera, D.; Narbonne, J. F.; Arnaud, C.; Saint-Denis, M. Biochemical responses of the earthworm *Eisenia fetida andrei* exposed to contaminated artificial soil, effects of carbaryl. *Soil Biol. Biochem.* **2001**, *33*, 1123−1130.

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