Oxidation of Carbaryl in Aqueous Solution by Membrane Anodic Fenton Treatment

QIQUAN WANG AND ANN T. LEMLEY*

Graduate Field of Environmental Toxicology, TXA, MVR Hall, Cornell University,
Ithaca, New York 14853-4401

Carbaryl, a commonly used insecticide, was used in this study as a probe to investigate a new Fenton treatment technology, ion exchange membrane anodic Fenton treatment (membrane AFT). It was found that the degradation kinetics of carbaryl by membrane AFT obeys a previously published AFT model quite well. The NaCl (electrolyte) concentration in two half-cells was optimized for two kinds of membrane. Effects of the H_2O_2/Fe^{2+} ratio and the Fenton reagent delivery rate were also investigated. The treatment efficiency for anion membrane AFT is higher than for salt-bridge AFT under the same operating conditions. Decreasing the delivery rate of Fenton reagents and increasing the treatment temperature also increase the treatment efficiency. The activation energy for carbaryl degradation by anion membrane AFT was estimated to be 14.7 kJ·mol^{-1}. 1-Naphthol, 1,4-naphthoquinone, and (phthalic acid-*O*-)yl *N*-methylcarbamate were detected by GC-MS as the degradation products of carbaryl by Fenton treatment. No decrease in carbaryl degradation rate was found during repeated use (100 times) of the anion exchange membrane. High and stable treatment efficiency can be achieved using an anion exchange membrane rather than a salt-bridge in the AFT system. Because of its effectiveness and convenience, the use of an ion exchange membrane as a substitute for the salt-bridge used in the previous AFT system has brought the AFT technology a major step closer to practical application.

KEYWORDS: Carbaryl; Fenton treatment; anodic; ion exchange membrane; hydrogen peroxide; oxidation; waste water; pesticide

INTRODUCTION

Water contamination by pesticides is an undesirable effect of chemical use in production agriculture. This is a serious problem and one that compounds itself because some pesticides and their degradation products bioaccumulate and persist in the environment (*1*) and may even be toxic and carcinogenic (*2*). The handling of waste water, disposing and recycling of containers, and remediation of contaminated soils have become very important issues in U.S. pesticide waste management (*3*). Effective, low-cost, and easily operated technologies are greatly needed for treating small-scale waste generated by individual farmers or commercial agricultural applicators.

As one of the advanced oxidation technologies, Fenton treatment has recently received extensive attention (*4−9*). The hydroxyl radical (•OH) generated from the Fenton reaction (eq 1) is found to be a strong oxidant to many toxic or non-

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$
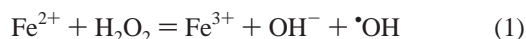
biodegradable organics in waste water. However, the direct use of the Fenton reaction in treatment creates two difficulties. One

is the low pH of the effluent, requiring neutralization prior to drainage. The optimal pH for the Fenton reaction is around 3 (*6, 10*). The use of iron(III) chelates in place of Fe^{2+} to overcome acidic reaction conditions has been explored, but the treatment rate is much lower (*11*). The other difficulty is the handling of ferrous salts and accurately delivering the ferrous solution into the reaction system, because ferrous salt is hygroscopic and aqueous ferrous ion is readily oxidized.

To overcome these difficulties, anodic Fenton treatment (AFT) was proposed as an improvement to classic Fenton treatment (CFT) (*12*). The treatment system is separated into two half-cells, which are connected via a salt-bridge. The ferrous ion is delivered into the anodic half-cell by electrolysis from an iron anode (eq 2). Hydrogen peroxide is constantly added to

$$\text{anode:} \qquad Fe \rightarrow Fe^{2+} + 2e \qquad (2)$$

$$\text{cathode:} \qquad 2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad (3)$$
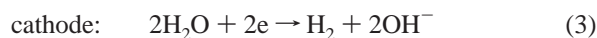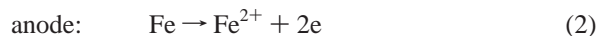
the anodic half-cell by a pump. In the cathodic half-cell, water is reduced on a graphite cathode (eq 3). The most significant advantages of AFT over other Fenton treatment technologies are that the Fenton reaction occurs in self-developed optimal acidic conditions (pH ∼3) and that the pH of the treatment

2332 *J. Agric. Food Chem.*, Vol. 50, No. 8, 2002

Wang and Lemley

effluent can be partially neutralized from 3 to 5 by combining the solutions from the two half-cells. Also, handling large amounts of ferrous salt in practical applications is no longer needed.

Degradation of 2,4-D by AFT has been investigated and published elsewhere (*13*). A kinetic model was established to describe the concentration changes of the target organic during AFT treatment and to optimize the operating conditions. However, there are still practical inconveniences when using AFT due to the use of the NaCl saturated salt-bridge. The saturated NaCl solution inside the salt-bridge can leak from the glass frits and be easily diluted by the treatment solution. It always needs to be replaced after each treatment to maintain treatment efficiency. To make this technology more practical, our goal was to substitute an ion exchange membrane for the salt-bridge and test its effectiveness.

Carbaryl (1-naphthyl *N*-methylcarbamate), a carbamate insecticide with a wide range of activity and a relatively low degree of animal toxicity, was one of the most commonly used insecticides. According to U.S. EPA estimates, nonagricultural usage alone of carbaryl in 1995−1996 reached 1−3 million pounds per year (*14*). Carbaryl has been found to react with nitrite under certain conditions to give rise to *N*-nitrosocarbaryl, which can be considered to be one of the strongest genetically active agents, a potent mutagen, and a carcinogen (*15*−*17*).

Carbaryl was chosen as the target compound in this study to investigate the AFT system with an ion exchange membrane. The objectives of this work were (i) to optimize the NaCl (electrolyte) concentration in two half-cells with either a cation or anion exchange membrane based on an optimized degradation rate, (ii) to investigate the effect of H_2O_2/Fe^{2+} ratio and treatment temperature on the degradation rate, (iii) to study the effect of Fenton reagent delivery rate on treatment rate, (iv) to probe the influence of repeated use of the membrane on treatments, and (v) to identify the degradation products of carbaryl upon AFT.

MATERIALS AND METHODS

Chemicals. Carbaryl (99%) was purchased from Chem Services (West Chester, PA). Hydrogen peroxide (analytical grade), acetonitrile (HPLC grade), and water (HPLC grade) were purchased from Mallinckrodt (Paris, KY). Sodium chloride (certified), hydrated ferrous sulfate (certified), phosphoric acid (analytical grade), and hexanes (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ).

Membranes. Cation exchange membrane (ESC-7000) and anion exchange membrane (ESC-7001) were purchased from Electrosynthesis (Lancaster, NY). The electrical resistances in 1 M NaCl solution at 25 °C are 6 and 8 ohm·cm^{-2}, respectively, for the cation and anion membranes.

Degradation of Carbaryl by Membrane AFT. Degradation experiments were carried out in two 300-mL glass half-cells that served as anodic and cathodic half-cells. These two half-cells were separated by an ion exchange membrane. The experimental apparatus is shown in **Figure 1**. Typically 200 mL of 100 μM carbaryl solution with 0.02 M NaCl was added into the anodic half-cell, and the same volume of 0.08 M NaCl aqueous solution was added into the cathodic half-cell. Each of the two half-cells was stirred using a magnetic stirring bar. A 2 cm × 10 cm × 0.2 cm iron plate and a 1 cm (i.d.) × 10 cm (l) graphite rod were used as anode and cathode, respectively. The electrolysis current was supplied by a BK Precision DC power supply 1610 and was controlled at 0.050 A. Hydrogen peroxide solution of 0.311 M (prepared by dilution from a solution of known concentration) was delivered into the anodic half-cell using a Fisher Scientific peristaltic pump at a rate of 0.50 mL·min^{-1}. The delivery rate of ferrous ion was calculated from the electrolysis current that can be adjusted through the power supply. The ratio of H_2O_2/Fe^{2+} was 10:1. The temperature was kept at 24.7 ± 0.5 °C. The electrolysis was started by turning on
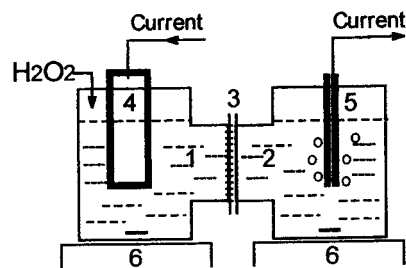
Figure 1. Apparatus of membrane anodic Fenton treatment: (1) anodic half-cell; (2) cathodic half-cell; (3) ion exchange membrane; (4) iron plate; (5) graphite stick; (6) magnetic stirring plate.

the power supply when the first drop of hydrogen peroxide entered the anodic half-cell. At different time intervals 1.00 mL of anodic solution was removed from the anodic half-cell and added into a 2-mL GC vial containing 0.10 mL of methanol (to quench the subsequently generated hydroxyl radical) for HPLC analysis. Treatments were repeated two times for a total of three replications.

To optimize NaCl concentration in the two half-cells, cation and anion exchange membranes were tested separately. Three anodic NaCl concentrations, 0.02, 0.04, and 0.08 M, were chosen. The NaCl concentration ratios of cathode/anode ranged from 0.125:1 to 5:1. To investigate the effect of the H_2O_2/Fe^{2+} ratio on the carbaryl degradation rate, H_2O_2 solutions of different concentrations were used in different treatments while the electrolysis current was kept at 0.050 A. The H_2O_2/Fe^{2+} ratio ranged from 1:1 to 50:1. The anion exchange membrane was used in these experiments.

To investigate the effect of different delivery rates of Fenton reagents, the H_2O_2/Fe^{2+} ratio was kept at 10:1. The electrolysis current was varied from 0.01 to 0.100 A. To find out the effect of temperature on the treatment, water baths of different temperatures (12.3 ± 1.0, 19.3 ± 0.3, 24.7 ± 0.5, and 29.7 ± 0.2 °C) were used. The anion exchange membrane was also used in these two studies.

Degradation of Carbaryl by Salt-Bridge AFT. Treatments were carried out in two 250-mL beakers connected by a salt-bridge filled with NaCl saturated solution. The operating conditions were the same as those of the typical membrane AFT.

Degradation of Carbaryl by CFT. Treatments were performed in a 250-mL beaker. Two hundred milliliters of 100 μM carbaryl solution (with and without 0.02 M NaCl) was added to the beaker. One milliliter of 0.0311 M FeSO$_4$ solution and 1.00 mL of 0.311 M of H_2O_2 solution, corresponding to concentrations of a 5-min AFT treatment at 0.020 A, were added to the reaction system. The other operating conditions were the same as those of a typical membrane AFT.

Analysis of Carbaryl and Hydrogen Peroxide Concentration. The concentration of carbaryl was determined by an HP 1090 HPLC equipped with a diode array detector. The mobile phase of HPLC was composed of acetonitrile and water (50:50, pH was adjusted to 3 by adding phosphoric acid). A C18 5 μm, 250 mm × 4.6 mm (i.d.) PRISM RP column was used for analysis. The chosen wavelength for quantification was 280 ± 20 nm. Under these conditions, carbaryl retention time is 6.90 min. The concentration of hydrogen peroxide was analyzed by titration in acidic solution using potassium permanganate standard solution (*18*).

Degradation Product Identification by GC-MS. After 3 min of treatment by membrane AFT under typical operating conditions, 15 mL of anodic solution was taken out and immediately extracted using 3 mL of hexane. The sample was 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 100 °C, increasing at 25.8 °C/min to 305 °C and kept at this temperature for 14 min; injector port temperature was 220 °C; detector temperature was 250 °C.

Degradation Kinetic Model and Definition of Treatment Efficiency. A detailed derivation of a universal kinetic model for the

Oxidation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 8, 2002 **2333**
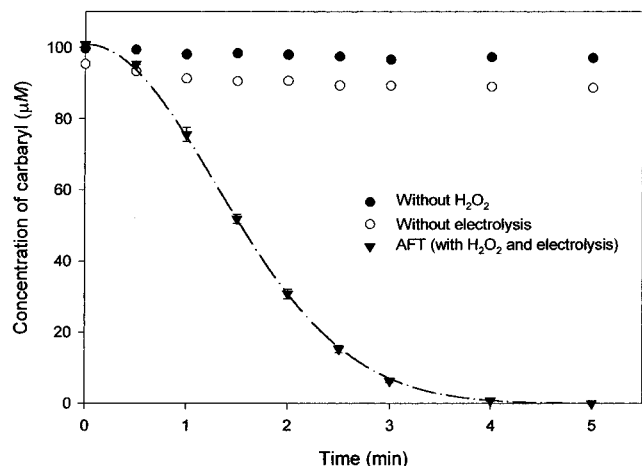
Figure 2. Concentration changes of carbaryl by electrolysis without H_2O_2, H_2O_2 without electrolysis, and anion membrane AFT. Experimental data points are fitted by the AFT kinetic model.

degradation of different organics by AFT has been published elsewhere (*13*). Here we briefly summarize this established model. During AFT treatment, ferrous ion is constantly delivered into an anodic half-cell by electrolysis at a fixed rate. It is also continuously consumed by reacting with hydrogen peroxide, which is delivered simultaneously into the reaction system. We assume (i) the concentration of ferrous iron in the reaction system is constant, (ii) hydrogen peroxide can be accumulated in the reaction system when the ratio of hydrogen peroxide to ferrous ion is >1, (iii) the Fenton reaction obeys second-order kinetics, (iv) the instantaneous concentration of hydroxyl radical is proportional to its generation rate, and (v) the kinetics of the hydroxyl radical reaction with organics are second order. On the basis of these assumptions, the following equation can be established to describe the changes of carbaryl concentration during AFT:

$$\ln \frac{[C]_t}{[C]_0} = -\frac{1}{2} K\lambda\pi\omega\nu_0^2 t^2 \qquad (4)$$

In eq 4, $K = kk_1$ ($\mu M^{-2} \cdot min^{-2}$), k ($\mu M^{-1} \cdot min^{-1}$), and k_1 ($\mu M^{-1} \cdot min^{-1}$) 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 lifetimes 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 ($\mu M \cdot min^{-1}$) is the delivery rate of ferrous ion by electrolysis; and t (min) is time. We call this kinetic model the AFT model.

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 can be used as a parameter of treatment efficiency to compare treatments with the same delivery rate of the Fenton reagents.

RESULTS AND DISCUSSION

Degradation of Carbaryl and Model Fitting. Carbaryl can be rapidly degraded by anion membrane AFT (**Figure 2**). Five minutes of treatment (0.050-A electrolysis and 10:1 ratio of H_2O_2/Fe^{2+}) can totally degrade 100 μM carbaryl in a 200-mL solution. As shown by the agreement between the data points and the model regression line in **Figure 2**, the degradation kinetics of carbaryl can be fitted by the AFT model very well. A high regression coefficient (*r*), 0.99, was obtained. If only electrolysis or hydrogen peroxide is applied to the same solution, no significant degradation of carbaryl is found. This implies that the dissipation of carbaryl in anion membrane AFT

treatment is due to hydroxyl radical oxidation, rather than electrolysis or hydrogen peroxide oxidation.

Optimization of NaCl Concentration in Two Half-Cells. NaCl was used in the treatment system as an electrolyte. It can affect not only the electrolysis voltage between the two electrodes but also the treatment efficiency (*19*). Degradation of carbaryl by AFT with cation and anion exchange membranes under different concentrations of NaCl was studied. All degradation kinetics of carbaryl obeyed the AFT model quite well (data not shown), with regression coefficients (*r*) >0.99. $K\lambda\pi\omega$ can be used as a rate parameter to estimate the effect on the treatment efficiency of NaCl concentration in the two half-cells because the electrolysis current and the delivery rate of hydrogen peroxide are fixed. The changes in $K\lambda\pi\omega$ and electrolysis voltage with NaCl concentration ratio (cathode /anode) at three anodic NaCl concentrations are shown in **Figure 3**. For the cation membrane AFT system, the treatment efficiency with 0.04 M anodic NaCl is higher than it is with the other two anodic NaCl concentrations, 0.02 and 0.08 M (**Figure 3a**). However, for anion membrane AFT, the highest treatment efficiency is reached by using 0.02 M anodic NaCl concentration (**Figure 3b**).

With an increase in the NaCl concentration ratio (cathode/ anode), the electrolysis voltage decreases for both membrane types and all anodic NaCl concentration levels (**Figure 3a′,b′**). For each anodic NaCl concentration, it appears that the lower the voltage, the higher the treatment efficiency. For a given anodic NaCl concentration, there will be a lower total electrolyte concentration at a lower NaCl concentration ratio. This can result in a higher electrolysis voltage and the oxidation of other substances at the anode, therefore causing a low electrolysis current efficiency resulting in low treatment efficiency. Apparently, the electrolysis voltage is not the only factor that affects the treatment efficiency. Because the hydroxyl radical can react with the chloride ion (eq 5) (*20*), higher anodic NaCl concentra-
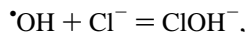
$$^\bullet OH + Cl^- = ClOH^-,$$
$$k = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (pH } \sim 2) \quad (5)$$

tion could also decrease treatment efficiency. This may be the reason the treatment efficiency corresponding to the 0.08 M anodic NaCl concentration in the cation membrane AFT system is lower than that of the other two concentrations.

The ion exchange membrane property may be the third factor affecting the treatment efficiency. In the cation membrane AFT system, the membrane allows only anodic Na^+ and H^+ to pass through to the cathodic half-cell. With an increase of cathodic NaCl concentration, the movement of Na^+ from anode to cathode may become more difficult because of the concentration gradient between the two half-cells. More H^+ than Na^+ may move into the cathodic half-cell. To regenerate H^+ and keep the optimal pH for the Fenton reaction, some of the Fenton reagent may be consumed. This can result in a decrease of treatment efficiency in the cation membrane AFT system when the NaCl concentration ratio (cathode/anode) is high. In contrast, the anion membrane allows only cathodic Cl^- and OH^- to pass through to the anodic half-cell. The increased NaCl concentration ratio (cathode/anode) is beneficial for Cl^- to compete with OH^- in movement across the membrane, exerting less effect on the anodic pH. Thus, the treatment efficiency should increase with the increase of NaCl concentration ratio (cathode/anode) in the anion membrane system.

In terms of treatment efficiency, the optimal NaCl concentration in the cation membrane AFT system is 0.04 M in the anodic half-cell and 0.08−0.12 M in the cathodic half-cell. For the
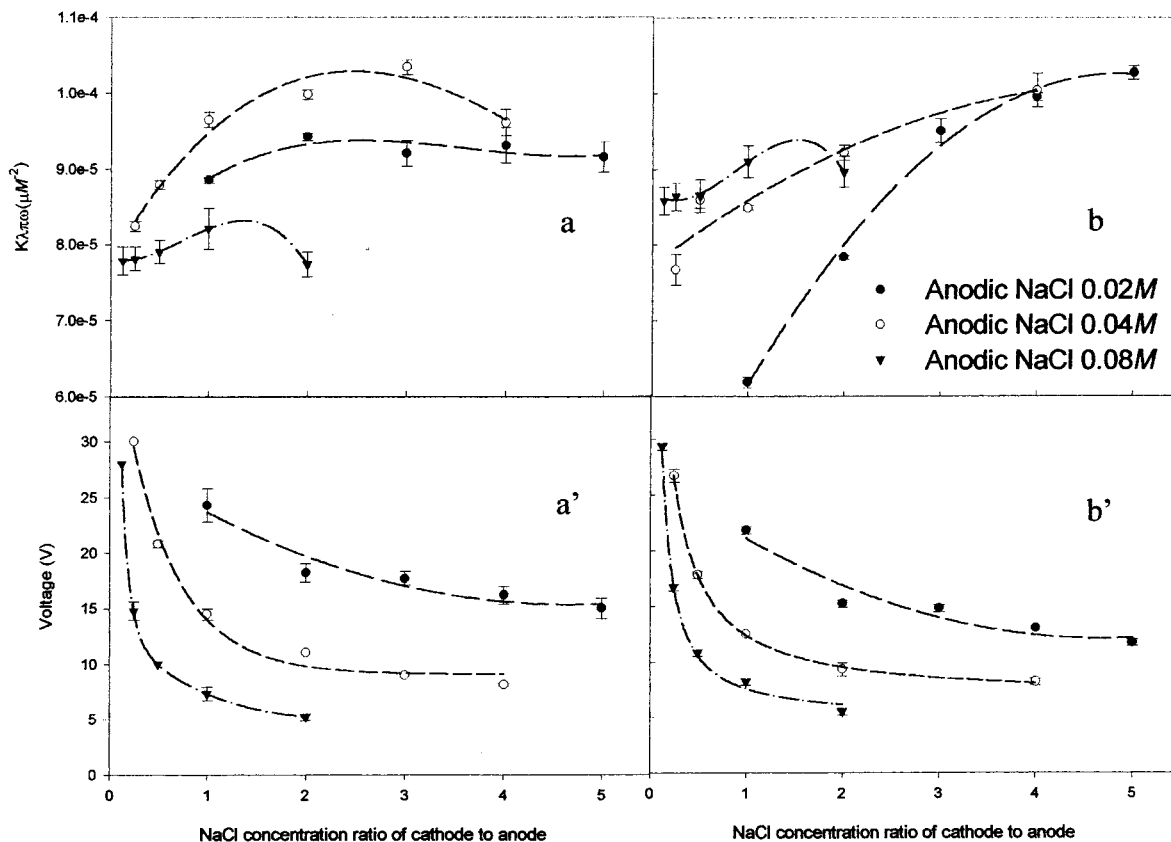
Figure 3. Changes in degradation rate ($K\lambda\pi\omega$) and electrolysis voltage with NaCl concentration in two half-cells: (a, a′) cation exchange membrane AFT; (b, b′) anion exchange membrane AFT.

anion membrane system, 0.02 M in the anodic half-cell and 0.08–0.10 M in the cathodic half-cell are the optimal NaCl concentrations. Because it is advisable to introduce the least amount of NaCl into the treatment system, the optimum treatment conditions for the experiments in this work include the anion membrane AFT with an anodic NaCl concentration of 0.02 M and a cathodic NaCl concentration of 0.08 M.

Effect of H_2O_2/Fe^{2+} Ratio. Degradation of carbaryl by the salt-bridge AFT and the anion membrane AFT with different H_2O_2/Fe^{2+} ratios can also be fitted by the AFT kinetic model very well (data not shown). All regression coefficients (r) are >0.99. Because the delivery rate of ferrous ion (ν_0) is fixed, $K\lambda\pi\omega$ can be used as a degradation rate parameter under different H_2O_2/Fe^{2+} ratios. For both anion membrane AFT and salt-bridge AFT, the degradation rate of carbaryl initially increased rapidly with the increase of H_2O_2/Fe^{2+} ratio (**Figure 4**). After the ratio reaches 15:1, the degradation rate becomes almost constant. However, when the ratio reaches 100:1 for the anion membrane AFT and 50:1 for the salt-bridge AFT, the degradation kinetics no longer obey the AFT model, and the degradation rate significantly decreases (data not shown). The excessive concentration of hydrogen peroxide may decrease its electrode potential. Hydrogen peroxide can compete with iron to be oxidized at the anode (eq 6) (21), decreasing the electrolysis current efficiency.

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \qquad (6)$$
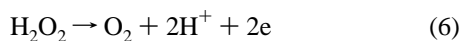
As also shown in **Figure 4**, the anion membrane appears to have a higher treatment efficiency than the salt-bridge AFT under the same operating conditions. The substitution of the ion exchange membrane for the salt-bridge results not only in
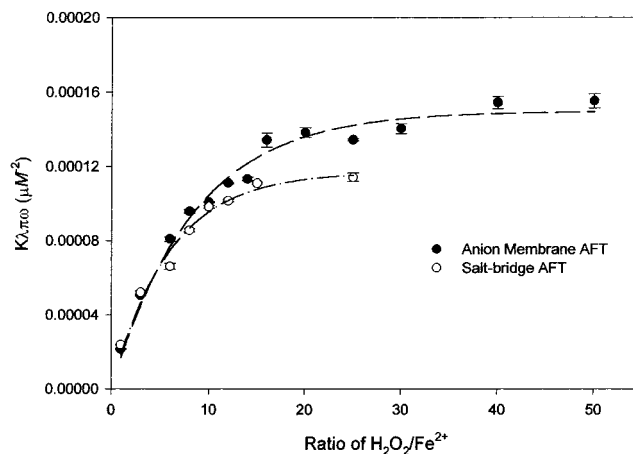

Figure 4. Effect of H_2O_2/Fe^{2+} ratio on carbaryl degradation rate by membrane AFT and salt-bridge AFT.

application convenience but also potentially in a higher treatment efficiency when a high ratio of H_2O_2/Fe^{2+} is applied.

Effect of Delivery Rates of Fenton Reagent. The degradation rate of carbaryl using the anion membrane AFT increases with the increase of Fenton reagent delivery rate (**Figure 5**). As shown by the regression coefficients in **Table 1**, the degradation kinetics obey the AFT model very well at all delivery rates. $K\lambda\pi\omega\nu_0^2$, the appropriate rate parameter for variable reagent delivery rates, increases with an increase in Fenton reagent delivery rates, resulting in an accelerated degradation of carbaryl. However, if the increase of Fenton reagent delivery rate were directly proportional to the degradation rate of carbaryl, the half-life of carbaryl ($t_{1/2}$) would be inversely proportional to the Fenton reagent delivery rate (ν_0).

Oxidation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 8, 2002 **2335**
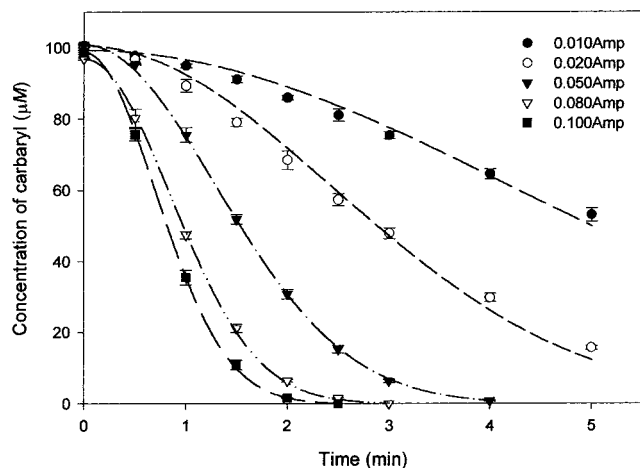
Figure 5. Degradation of carbaryl by anion membrane AFT at different delivery rates of Fenton reagent. Experimental data points are fitted by the AFT model.

Table 1. Regression Results of Carbaryl Degradation Kinetics at Different Delivery Rates of Fenton Reagent Using the AFT Model

electrolysis current (A)	delivery rate of Fe^{2+}, ν_0 ($\mu M \cdot min^{-1}$)	regression results
0.010	15.6	$\ln [C]_t/[C]_0 = -(0.0265 \pm 0.0009)t^2$, $r = 0.99$ $K\lambda\omega\pi = (2.19 \pm 0.07) \times 10^{-4}$ (μM^{-2})
0.020	31.1	$\ln [C]_t/[C]_0 = -(0.0765 \pm 0.0018)t^2$, $r = 0.99$ $K\lambda\omega\pi = (1.58 \pm 0.04) \times 10^{-4}$ (μM^{-2})
0.050	77.7	$\ln [C]_t/[C]_0 = -(0.304 \pm 0.001)t^2$, $r = 1.00$ $K\lambda\omega\pi = (1.06 \pm 0.003) \times 10^{-4}$ (μM^{-2})
0.080	125	$\ln [C]_t/[C]_0 = -(0.671 \pm 0.004)t^2$, $r = 0.99$ $K\lambda\omega\pi = (8.67 \pm 0.05) \times 10^{-5}$ (μM^{-2})
0.100	156	$\ln [C]_t/[C]_0 = -(1.019 \pm 0.011)t^2$, $r = 0.99$ $K\lambda\omega\pi = (8.43 \pm 0.09) \times 10^{-5}$ (μM^{-2})

Then $K\lambda\pi\omega$ should be constant under different delivery rates. This can be expressed as follows:

$$\ln(1/2) = -(1/2)k\lambda\pi\omega\nu_0^2 t_{1/2}^2 \tag{7}$$

Then

$$t_{1/2}\nu_0 = \sqrt{2 \ln 2 (K\lambda\pi\omega)^{-1}} = \text{constant} \tag{8}$$

To understand these results, the linear correlation between $K\lambda\pi\omega$ and ν_0 was analyzed, and it was found that $K\lambda\pi\omega$ significantly decreases with the increase of reagent delivery rate (eq 9), implying that the degradation rate of carbaryl is not directly proportional to the Fenton reagent delivery rate.

$$K\lambda\pi\omega = \frac{6.94 \times 10^{-4}}{\nu^{0.43 \pm 0.03}}, \qquad r = 0.99 \tag{9}$$

The higher the delivery rate, the lower the treatment efficiency will be.

This conclusion was also confirmed by comparing the anion membrane AFT with CFT. Because ferrous ion and hydrogen peroxide are added all at once during CFT, it can be regarded as a special kind of AFT with an extremely high Fenton reagent delivery rate. The degradation of carbaryl for 5 min of anion membrane AFT at 0.020 A under typical membrane AFT operating conditions is shown in **Figure 6**. The degradation of carbaryl by CFT with and without 0.02 M NaCl is also shown. The amount of Fenton reagent added in the CFT is the same as
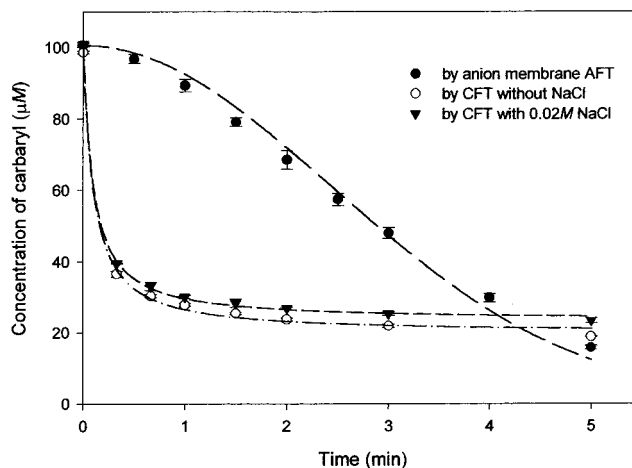
Figure 6. Degradation of carbaryl by anion membrane AFT and CFT with the same amount of Fenton reagent.

Table 2. Values of $K\lambda\pi\omega$ (μM^{-2}) at Different Temperatures and Activation Energies, E_a, of Carbaryl Degradation by Anion Membrane AFT

T (K)	$K\lambda\pi\omega$ (μM^{-2})	regression results
285.4	8.126 ± 0.060	$\ln(K\lambda\pi\omega) = -(3.303 \pm 0.507) - (1770 \pm 149)(1/T)$
292.4	9.745 ± 0.146	$r = 0.99$
297.9	10.821 ± 0.126	$E_a = 14.7 \pm 1.2$ kJ·mol^{-1}
302.8	11.589 ± 0.139	

that added during 5 min of membrane AFT. By comparing the residual carbaryl concentration, it appears that the treatment efficiency of CFT without NaCl is slightly higher than that with 0.02 M NaCl. This result is in accord with the reaction in eq 5. Although 0.02 M NaCl was present in the membrane AFT system, its treatment efficiency is still higher than both versions of CFT. This result indicates that a higher delivery rate of Fenton reagent results in a lower treatment efficiency. If time permits, a low delivery rate should be chosen to achieve high efficiency in practical applications of this membrane AFT technology.

Degradation at Different Temperatures. Hydroxyl radical reactions are usually very fast ($k = 10^7 - 10^{10}$ M^{-1} s^{-1}) (*22*), making it very difficult to investigate the effect of temperature kinetically. Because AFT is a controlled Fenton process and its kinetic model has been established, it is simple to estimate the effect of temperature on the Fenton treatment. Assuming that $\lambda\pi\omega$ is a constant parameter with variable temperature, then $K\lambda\pi\omega$ can be used as a parameter to signify K at different temperatures. Activation energy (E_a) can be obtained by using the Arrhenius equation

$$\ln k' = \ln A + \frac{E_a}{RT} \tag{10}$$

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

Our results show that the degradation rate of carbaryl increases with an increase in temperature (**Table 2**). Increasing treatment temperature also increases treatment efficiency. All degradation kinetics of carbaryl at four temperatures can be fitted by the AFT model quite well, and regression coefficients (r) are all >0.99 (data not shown). The activation energy (E_a) for degradation of carbaryl by the anion membrane AFT is estimated
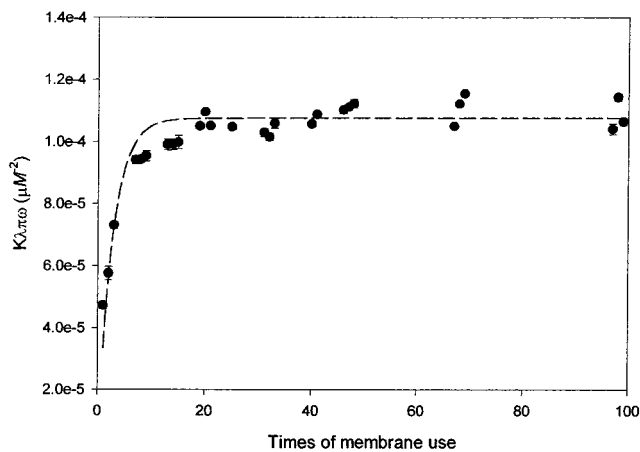
Figure 7. Changes in degradation rate of carbaryl with repeated use of anion membrane.
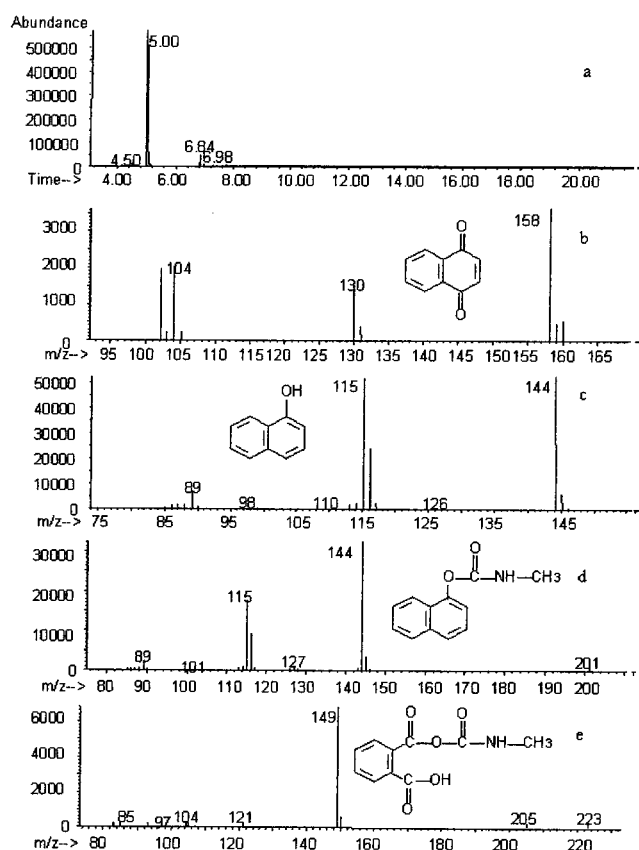

Figure 8. TIC and MS spectra of carbaryl degradation products.

to be 14.7 kJ·mol^{-1}. This value is in the same range as that found for diazinon with salt-bridge AFT (*19*).

Functional Stability of the Membrane with Repeated Use. A major advantage of the membrane AFT over the salt-bridge AFT is its convenience in practical application. Under these circumstances, the stability and reusability of the membrane may be an important concern. A repeat-use test of the anion membrane was investigated. As shown in **Figure 7**, the treatment efficiency increased rapidly for the first uses (~10) and soon became stable after that. No decrease of treatment efficiency was found with 100 repeated uses (each treatment time was 5−8 min), indicating that the ion exchange function of the membrane has been maintained during the repeated treatment processes. High and stable treatment efficiency can
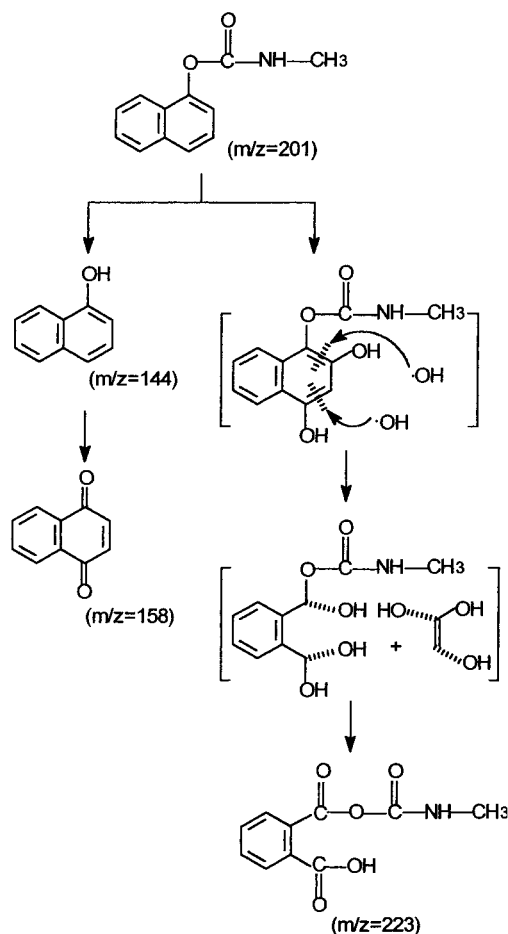

Figure 9. Degradation pathways of carbaryl by hydroxyl radical attack.

be achieved using such a membrane rather than the salt-bridge in the AFT system.

The functional stability of the membrane and the resulting high treatment efficiency demonstrate the advantage of membrane AFT over salt-bridge AFT, particularly because the salt bridge needs frequent replacement of the saturated electrolyte solution. The successful application of membrane technology to AFT brings it a major step closer to practical application. It is well-known that the hydroxyl radical is the essential strong oxidant in all Fenton treatments and all Fenton technologies focus on efficiently generating hydroxyl radicals and allowing them to react with pollutants efficiently. Thus, we believe that membrane AFT is effective and efficient when applied not only to carbaryl but also to many other kinds of organics.

Degradation Products. Degradation products formed after 3 min of treatment of carbaryl solution (at 0.050 A) by anion membrane AFT were determined using GC-MS. Four peaks were found in the total ion current (TIC) spectrum (**Figure 8a**). According to the MS spectrum (**Figure 8d**), the third peak (retention time = 6.84 min) can be attributed to the residual carbaryl. Interpretation of the MS spectrum (**Figure 8c**) suggests that the second peak (retention time = 5.00 min) in the TIC spectrum be attributed to 1-naphthol. This product has been found to be the main degradation product of carbaryl in water, soil, and some microorganism media (*23−26*). Confirmed by the MS spectrum (**Figure 8b**), the first peak in the TIC spectrum (retention time = 4.50 min) can be attributed to 1,4-naphthoquinone, which comes from the oxidation of 1-naphthol. This product has also been found in the TiO$_2$ photocatalytic degradation of carbaryl (*27*). By interpreting the MS spectrum (**Figure 8e**), we attributed the fourth peak in the TIC (retention time =

Oxidation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 8, 2002 **2337**

6.98 min) to a product formed by a partial breakdown of the naphthalene ring in the carbaryl molecule, (phthalic acid-*O*-)yl *N*-methylcarbamate.

It is possible that there were other, undetermined degradation products not found because of their evaporation and ionization properties in the GC-MS system, but those that were found show two possible oxidation pathways of carbaryl by the hydroxyl radical in the Fenton treatment (**Figure 9**). One path involves breaking off the carbamate branch; another involves direct breakdown of the naphthalene ring. The carbamate branch group is therefore not the only position attacked and not necessarily the first step for carbaryl degradation by the hydroxyl radical.

Conclusion. Degradation kinetics of carbaryl by ion exchange membrane AFT with different NaCl concentrations in both half-cells can be fitted by the AFT model quite well. The concentration of NaCl in both half-cells and its ratio can affect the treatment efficiency. The optimal NaCl concentrations for anion membrane AFT are 0.02 and 0.08 M, respectively, for the anodic and cathodic half-cell.

Compared with salt-bridge AFT, anion membrane AFT shows the same efficiency when the H_2O_2/Fe^{2+} ratio is less than 10:1 and higher efficiency when this ratio goes above 10:1. For membrane AFT, the lower the delivery rate of Fenton reagent and the higher the treatment temperature, the higher the treatment efficiency will be. The functional stability of the membrane during repeated use demonstrates the advantage of membrane AFT over salt-bridge AFT.

1-Naphthol, 1,4-naphthoquinone, and (phthalic acid-*O*-)yl *N*-methylcarbamate were identified by GC-MS as the degradation products of carbaryl after degradation by membrane AFT.

ABBREVIATIONS USED

AFT, anodic Fenton treatment; CFT, classic Fenton treatment; TIC, total ion current; HPLC, high-performance liquid chromatography; GC-MS, gas chromatography−mass spectrometry.

LITERATURE CITED

(1) Peris-Cardells, E.; Terol, J.; Mauri, A. R.; Guardia, M. de la; Pramauro, E. Continuous flow photocatalytic degradation of carbaryl in aqueous media. *J. Environ. Sci. Health* **1993**, *B28* (4), 431−445.

(2) Wang, Q.; Gan, J.; Papiernik, S. K.; Yates, S. R. Transformation and detoxification of halogenated fumigants by ammonium thiosulfate. *Environ. Sci. Technol.* **2000**, *34*, 3717−3721.

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

(4) Sedlak, D. L.; Andren, A. W. Oxidation of chlorobenzene with Fenton's reagent. *Environ. Sci. Technol.* **1991**, *25*, 777−782.

(5) 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.

(6) Tang, W. Z.; Huang, C. P. 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environ. Technol.* **1996**, *17*, 1371−1378.

(7) Pratap, K.; Lemley, A. T. Fenton electrochemical treatment of aqueous atrazine and metolachlor. *J. Agric. Food Chem.* **1998**, *46*, 3285−3291.

(8) Huston, P. L.; Pignatello, J. J. Degradation of selected pesticide active ingredients and commercial formulation in water by the photo-assisted Fenton reaction. *Water Res.* **1999**, *33*, 1238−1246.

(9) Bier, E. L.; Singh, J.; Li, Z.; Comfort, S. D.; Shea, P. J. Remediating RDX contaminated water and soil. *Environ. Toxicol. Chem.* **1999**, *18*, 1078−1084.

(10) Pignatello, J. J. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* **1992**, *26*, 944−951.

(11) Sun, Y.; Pignatello, J. J. Activation of hydrogen peroxide by iron(III) chelates for abiotic degradation of herbicides and insecticides in water. *J. Agric. Food Chem.* **1993**, *41*, 308−312.

(12) Saltmiras, D. A.; Lemley, A. T. Degradation of ethylene thiourea (ETU) with three Fenton treatment processes. *J. Agric. Food Chem.* **2000**, *48*, 6149−6157.

(13) 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.

(14) U.S. EPA. *Pesticides Industry Sales and Usage, 1996 and 1997 Market Estimates*; 733-R-99-001; Washington, DC, 1999.

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

(16) Siebert, D.; Eisenbrand, G. Induction of mitotic gene conversion in *Saccharomyces cervisiae* by N-nitrosated pesticides. *Mutat. Res.* **1974**, *22*, 121−126.

(17) Regan, J. D.; Setlow, R. B.; Francis, A. A.; Lijinsky, W. Nitrosocarbaryl: its effect on human DNA. *Mutat. Res.* **1976**, *38*, 293−302.

(18) Huckaba, C. E.; Keyes, F. G. The accuracy of estimation of hydrogen peroxide by potassium permanganate titration. *J. Am. Chem. Soc.* **1948**, *70*, 1640−1644.

(19) Wang, Q.; Lemley, A. T. Oxidation of diazinon by anodic Fenton treatment. *Water Res.* **2002**, in press.

(20) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O⁻) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17* (2), 513−886.

(21) Weast, R. C.; Astle, M. J.; Beyer, W. H. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1985; pp D152−D158.

(22) Walling, C. Fenton's reagent revisited. *Acc. Chem. Res.* **1975**, *8*, 125−131.

(23) Rajagopal, B. S.; Panda, S.; Sethunathan, N. Accelerated degradation of carbaryl and carbofuran in a flooded soil pretreated with hydrolysis products, 1-naphthol and carbofuran phenol. *Bull. Environ. Contam. Toxicol.* **1986**, *36*, 827−832.

(24) Gonzalez, V.; Ayala, J. H.; Afonso, A. M. Degradation of carbaryl in natural waters: enhanced hydrolysis rate in micellar solution. *Bull. Environ. Contam. Toxicol.* **1992**, *48*, 171−178.

(25) Sikka, H. C.; Miyazaki, S.; Lynch, R. S. Degradation of carbaryl and 1-naphthol by marine microorganisms. *Bull. Environ. Contam. Toxicol.* **1975**, *13*, 666−672.

(26) Kuo, W. S.; Regan, Sr., R. W. Degradation of carbaryl and 1-naphthol by spent mushroom compost microorganisms. *Water Sci. Technol.* **1992**, *26(9−11)*, 2081−2084.

(27) Pramauro, E.; Prevot, A. B.; Vincenti, M.; Brizzolesi, G. Photocatalytic degradation of carbaryl in aqueous solution containing TiO_2 suspension. *Environ. Sci. Technol.* **1997**, *31*, 3126−3131.