

Evaluation of the Performance of Flow-through Anodic Fenton Treatment in Amide Compound Degradation

HUICHUN ZHANG[†] AND ANN T. LEMLEY*

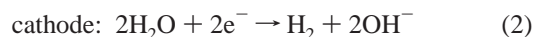
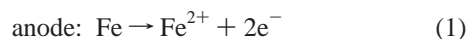
Graduate Field of Environmental Toxicology, TXA, MVR Hall, Cornell University,
 Ithaca, New York 14853-4401

A flow-through anodic Fenton treatment (FAFT) system based on the batch AFT technology was previously developed to degrade pesticides in aqueous solution. As one of a series of benchtop and pilot-scale studies in process optimization, the goal of the reported work is to evaluate the performance of the FAFT system under various operating conditions, which is critical to bringing this technology into practical general use in the field. For this purpose, the removal efficiency of the parent pesticide and the concentration of the hydroxyl radical in FAFT were calculated on the basis of a previously developed FAFT kinetic model and used for the evaluation. *N,N*-Diethyl-3-methylbenzamide (DEET), an insect repellent, was used as a chemical probe. Experimental data showed that the key to a high treatment efficiency is to operate the FAFT system to achieve a maximum $\cdot\text{OH}$ production with a minimum input of energy and chemicals. For the anodic half-cell, the system should be operated under flow-through conditions with a self-developed optimum pH of 3.0, a relatively high flow rate, and the initial effluent recycled within 6–10 min to the FAFT system for further treatment; for the cathodic half-cell, it should have a fixed volume and be entirely replaced by another batch of cathodic solution only when the pH reaches a very high value. The delivery rate of the ferrous iron should be maintained at an electrolytic current between 0.01 and 0.02 A; the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ should be between 5:1 and 10:1. NaCl was found to be the best electrolyte, with concentrations of 0.01–0.02 and 0.08 M in the anodic and cathodic half-cells, respectively. The FAFT system was successfully applied to degrade various model amide compounds and DEET formulations, which suggests the likelihood of extending this approach to other pesticide-containing wastewaters.

KEYWORDS: FAFT; DEET; kinetic model; pesticide formulation; QSAR

INTRODUCTION

Pesticide-contaminated wastewaters with high concentrations of pesticides and inactive ingredients need an environmentally sound and cost-effective on-site treatment technology to eliminate potential contamination of the aqueous environment. Among various cleanup technologies, the advanced oxidation process (AOP) using the highly reactive hydroxyl radical generated via the Fenton reaction has been widely recognized as an effective technology (1–4). In particular, our laboratory has systematically studied anodic Fenton treatment (AFT) technology at the benchtop scale (5–14). The treatment system is divided into two half-cells and separated via an anion exchange membrane. Ferrous iron is delivered into the anodic half-cell by electrolysis from an iron anode (eq 1). Hydrogen peroxide is constantly added to the anodic half-cell by a peristaltic pump. In the cathodic half-cell, water is reduced to H_2 on a graphite cathode (eq 2).



AFT has been proven to be effective at treating high-concentration pesticide-containing solutions with a broad spectrum of target pollutants due to the following features: high and stable treatment efficiency, ease of operation, self-optimal acidic condition development (pH \sim 3) for Fenton treatment, controlled constant reagent delivery and ease of handling, and no need to add ferrous solutions or pure oxygen. A kinetic model was developed for batch AFT and was found to fit AFT degradation kinetics for a variety of pesticides and their mixtures (8–13). The coexistence of other organic ingredients in pesticide commercial products can lower the oxidation rate of the target pesticide (6, 7, 9), and the presence of humic acid slows pesticide degradation and shifts the reaction kinetics from the AFT model to the first-order model, mainly due to the buffering capacity of the humic acid, which keeps the reaction slurry at nearly neutral pH (13). In related work a weak interaction between ferric iron and several triazinone/triazine herbicides was

* To whom correspondence should be addressed. E-mail: atl2@cornell.edu.

[†] Present address: National Exposure Research Laboratory, U.S. Environmental Protection Agency, 960 College Station Rd., Athens, GA 30605.

proposed and incorporated into the kinetic model to better fit the data (14). In addition to effectively degrading the parent pollutants, AFT treatment can also remove chemical oxygen demand (COD) from the wastewater, improve biodegradability, and reduce the toxicity of the effluent (11).

Batch AFT systems have been optimized with respect to the most appropriate electrolyte to use (9), the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, the reagent delivery rate, the initial pesticide concentration, the temperature (8), and the membrane versus salt-bridge to separate two half-cells (10). On the basis of the established batch AFT, the authors have developed a flow-through AFT system (FAFT) (15). Reaction mechanisms were proposed and employed to model the degradation kinetics of various active compounds such as Fe^{2+} , Fe^{3+} , H_2O_2 , the parent pollutant, and its reaction intermediates. With a fundamental understanding of the system, a simple semiempirical FAFT kinetic model was then developed to track the kinetic trends of the parent pollutant and the active oxidant—the hydroxyl radical. To scale up and eventually apply the FAFT technology to actual pesticide wastewater treatment, which may involve a series of benchtop and pilot-scale studies, the FAFT system first needs to be evaluated for its performance under various operating conditions at a benchtop scale. Although the model based on the detailed reaction mechanisms would better serve this purpose, the requirement of many parameters that are not readily available (such as the rate constants of the reaction intermediates and the concentrations of various species) makes its extensive application in wastewater treatment impractical. We chose to use the semiempirical kinetic model as a tool because (i) it can provide the treatment efficiency of the parent compound, which can be correlated with the operating conditions, and this can provide guidance for further studies on systems at the same or larger scales; and (ii) the concentration of the hydroxyl radical can be predicted, and thus we can reasonably estimate the treatment efficiency of other organic pollutants (including their oxidation intermediates) on the basis of their second-order rate constant for reaction with $\cdot\text{OH}$ and the obtained $\cdot\text{OH}$ concentration.

N,N-Diethyl-3-methylbenzamide (DEET) is the most effective insect repellent applied on the skin to act against a wide range of blood-sucking arthropods (16, 17). An insect repellent containing $\leq 10\%$ DEET for children and no more than 30% DEET for adults was recommended for use against mosquitoes carrying West Nile virus (18). In total, about one-third of the U.S. population uses DEET (19). DEET has a direct effect on the nervous system in laboratory animals with signs including ataxia, seizures, and death (20). Extensive and repeated topical application of DEET has resulted in human poisoning, including two deaths (21). DEET has been detected in urine samples from treated rats (22). Additionally, DEET was among the most frequently detected compounds and was found in 74.1% of 54 water samples from U.S. streams with a maximum concentration of 1.1 $\mu\text{g}/\text{L}$ (23, 24). In a recent USGS study (25), DEET was detected in 25% of stream and raw water samples, with the highest level at 0.5 $\mu\text{g}/\text{L}$, and in finished water samples with the highest level at 0.066 $\mu\text{g}/\text{L}$. The likely sources for DEET contamination include improper disposal and container rinsing associated with its frequent use (26). For these reasons DEET was selected in this study as a probe to investigate the FAFT system. The main purpose of this work was to evaluate the performance of the FAFT system under various operating conditions including pH, flow rate, initial DEET concentration, delivery rate of the ferrous iron, ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, electrolytes and their concentrations, reactor setup, and effect of inactive ingredients in formulated pesticide. Because Fenton chemistry

in the FAFT system is complex, it is not practical, from the wastewater treatment perspective, to measure every single species in the system to evaluate the system performance or to optimize the process. Rather, it is useful to choose compound or compounds the degradation of which can represent the general trend in treatment efficiency. We chose to calculate the removal efficiency of the parent compound and the concentration of the hydroxyl radical for each condition by fitting the experimental data to the previously developed FAFT model. Because (1) DEET oxidation intermediates resemble DEET in their structures (15) and (2) $\cdot\text{OH}$ is the active oxidant in the FAFT system and its concentration determines the overall removal of all organic pollutants, the removal efficiency of DEET oxidation intermediates is expected to be similar to that of DEET and will not be discussed in detail. The correlations between the above two parameters and the operating conditions were established when applicable.

MATERIALS AND METHODS

Chemicals. DEET (98%) was purchased from Chem Services (West Chester, PA). Model amide compounds including benzodiox (BDX), 2-methylbenzamide (oMBD), 3-methylbenzamide (mMBD), *p*-toluamide (pMBD), *N,N*-diethylnicotinamide (DND), *N*-methyl-*o*-toluamide (MTD), 2-fluoro-3-(trifluoromethyl)benzamide (FBD), and 3,5-dinitro-*o*-toluamide (DTD) (see Figure S1 in the Supporting Information for structure information) were all purchased from Sigma-Aldrich (St. Louis, MO) at $>98\%$ purity. Hexamide (HXD) was obtained from Interbioscreen (Russia). Acetonitrile (HPLC grade), hydrogen peroxide, methanol (HPLC grade), phosphoric acid, AlCl_3 , CaCl_2 , MgCl_2 , NaCl , Na_3PO_4 , and water (HPLC grade) were obtained from Fisher (Fair Lawn, NJ) at certified grade unless otherwise specified. DEET formulations were received as a gift from Repel. All chemicals were used directly without further purification.

Membrane. Anion exchange membrane (ESC-7001) was purchased from Electrosynthesis (Lancaster, NY). The electrical resistance in 1 M NaCl solution at 25 °C is 8 $\text{ohm}\cdot\text{cm}^{-2}$.

Degradation of DEET by FAFT. The reaction setup is similar to that described previously (15). Briefly, all experiments were carried out in two 350-mL or 100-mL glass half-cells that served as anodic and cathodic half-cells. These two half-cells were separated by an anion exchange membrane. Anodic and cathodic half-cell influents (DEET solution with NaCl and NaCl aqueous solution, respectively) were pumped into respective half-cells at a constant rate varying from 8.2 to 37.5 mL/min. Effluent from each half-cell was separately collected for further analysis. Each of the two half-cells was stirred using a magnetic stirring bar. A 2 cm \times 10 cm \times 0.2 cm iron plate and a 1 cm (i.d.) \times 10 cm (l) graphite rod were used as anode and cathode, respectively. The electrolysis current was controlled at 0.01–0.10 A to vary the Fe^{2+} delivery rate. Hydrogen peroxide solution of 0.311 M was delivered into the anodic half-cell at different rates to maintain the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio in the range from 0.1:1 to 20:1. Pumping of influents into FAFT half-cells was started and reaction was initiated by turning on the power supply when the first drop of hydrogen peroxide entered the anodic half-cell. Reactions were maintained at room temperature (23 ± 2 °C). At given time intervals, 1 mL of anodic effluent was collected and added to a 2-mL HPLC vial containing 100 μL of methanol (to quench the subsequently generated hydroxyl radicals) for HPLC analysis. Treatments were repeated for a total of three replicates.

Analysis of pH, DEET, and Model Amides. pH values in each half-cell were monitored by an Acument AB15 pH-meter. Decrease in the concentration of DEET or model amides was monitored by a reverse-phase high-performance liquid chromatography (HPLC) system with a Restek Ultra C18 column (4.6 \times 250 mm, 5 μm) and a diode array UV–vis detector (1100, Agilent Technology). The detector wavelength was set at 220–265 nm for DEET and amides. The mobile phase consisted of acetonitrile and water (60:40, pH adjusted to 3 using phosphoric acid).

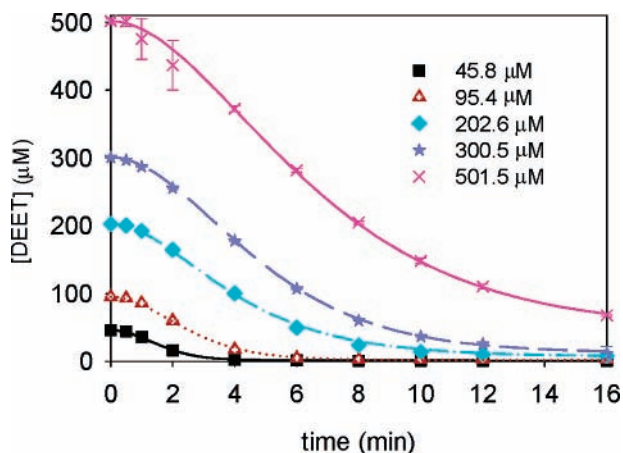


Figure 1. Effect of DEET initial concentration on DEET degradation. Symbols are the experimental data; lines are the model fits. Reaction conditions (unless otherwise stated): 350-mL reactor; flow rate = 27.4 ± 1.4 mL/min; input H₂O₂/Fe²⁺ = 10:1, electrolysis current *I* = 0.05 A; anodic [NaCl] = 0.02 M; cathodic [NaCl] = 0.08 M.

Kinetic Data Analysis. A semiempirical kinetic model was previously developed by the authors (15) to describe the degradation kinetics of DEET in the FAFT system (see a detailed description in text S1 in the Supporting Information). In summary, degradation of the parent pollutant and generation of the hydroxyl radical are governed by the equations

$$\frac{dD}{dt} = b(D_0 - D) - z(1 - e^{-at})D \quad (3)$$

$$[\cdot\text{OH}] = [\cdot\text{OH}]_{\text{ss}}(1 - e^{-at}) \quad (4)$$

where D_0 and D are DEET influent and effluent concentrations (μM); $b = Q/V$ (min^{-1}) – the reciprocal of the FAFT hydraulic retention time, where V is the reactor volume (mL) and Q is the flow rate in mL/min; $z = k[\cdot\text{OH}]_{\text{ss}}$, where k [$2.76 \times 10^5 \mu\text{M}^{-1} \text{min}^{-1}$ (15)] is the second-order rate constant between $\cdot\text{OH}$ and DEET and $[\cdot\text{OH}]_{\text{ss}}$ is the steady state $\cdot\text{OH}$ concentration; and parameter a is the fitting parameter that relates to the initial generation rate of the hydroxyl radical.

Parameter b is always known for any given reactor volume and flow rate; parameter z and $[\cdot\text{OH}]_{\text{ss}}$ can be obtained by knowing the steady-state effluent concentration D_{ss}

$$z = b(D_0/D_{\text{ss}} - 1) \quad (5)$$

$$[\cdot\text{OH}]_{\text{ss}} = z/k \quad (6)$$

By comparing the modeling results with the actual DEET degradation data, parameter a can be obtained for any given b and z values based on the best fitting results by using the least-squares method in Sigma Plot. The fits were evaluated on the basis of the correlation between the experimental data and the modeling data. $[\cdot\text{OH}]$ can be calculated from eq 4. The removal efficiency (R , %) of the parent compound is defined as $(1 - D_{\text{ss}}/D_0) \times 100$ and will be used to compare treatment efficiencies under different FAFT conditions.

RESULTS AND DISCUSSION

Effect of DEET Initial Concentration and Flow Rate. Degradation of DEET in FAFT was monitored by varying DEET initial concentration (45.8–501.5 μM) while keeping other conditions identical. All data can be fitted well with the FAFT model (Figure 1). Previous work (15) has reported that degradation of DEET under different flow rates (9.5–37.5 mL/min) can also be fitted with the model (Figure S2). As the fitting parameters show in Table 1, both higher initial concentration and higher flow rate led to a lower $[\cdot\text{OH}]_{\text{ss}}$ and a lower R .

Table 1. Fitting Parameters for the FAFT Model at Various (a) Initial Concentrations or (b) Flow Rates Based on the Experimental Data in Figures 1 and S2

(a) $b = 0.078 \text{ min}^{-1}$					
C (μM)	z (min^{-1})	a (min^{-1})	$[\text{OH}]_{\text{ss}}$ (M)	R (%)	removal ($\mu\text{mol}/\text{min}$)
45.8	3.93	0.16	$1.4\text{E}-11$	98.1	1.2
95.4	3.13	0.09	$1.1\text{E}-11$	97.6	2.5
202.6	2.56	0.05	$9.3\text{E}-12$	97.0	5.4
300.5	2.10	0.04	$7.6\text{E}-12$	96.4	7.9
501.5	1.23	0.04	$4.5\text{E}-12$	94.0	12.9

(b)						
Q (mL/min)	b	z (min^{-1})	a (min^{-1})	$[\text{OH}]_{\text{ss}}$ (M)	R (%)	removal ($\mu\text{mol}/\text{min}$)
9.5	0.027	2.61	0.05	$9.5\text{E}-12$	99.0	1.8
16.5	0.047	1.87	0.08	$6.8\text{E}-12$	97.6	3.2
27.3	0.078	1.63	0.07	$5.9\text{E}-12$	95.5	5.2
37.5	0.107	1.20	0.10	$4.3\text{E}-12$	91.8	6.9

Table 2. Fitting Parameters for the FAFT Model at (a) Various Fe(II) Delivery Rates and (b) Different H₂O₂/Fe²⁺ Ratios Based on the Experimental Data in Figure 3 ($b = 0.078 \text{ min}^{-1}$)

(a)				
I (A)	z (min^{-1})	a (min^{-1})	$[\text{OH}]_{\text{ss}}$ (M)	R (%)
0.01	0.15	0.11	$5.4\text{E}-13$	65.8
0.02	1.00	0.03	$3.6\text{E}-12$	92.8
0.05	1.63	0.07	$5.9\text{E}-12$	95.5
0.08	3.12	0.08	$1.1\text{E}-11$	97.6
0.10	3.34	0.10	$1.2\text{E}-11$	97.7

(b)				
H ₂ O ₂ /Fe(II)	z (min^{-1})	a (min^{-1})	$[\text{OH}]_{\text{ss}}$ (M)	R (%)
0.1	0.03	0.30	$1.0\text{E}-13$	26.1
0.2	0.11	0.33	$3.8\text{E}-13$	54.4
1	0.24	0.26	$8.6\text{E}-13$	75.3
2	1.40	0.10	$5.1\text{E}-12$	94.7
5	2.74	0.10	$9.9\text{E}-12$	97.2
10	3.34	0.10	$1.2\text{E}-11$	97.7
12	3.85	0.10	$1.4\text{E}-11$	98.0
15	3.90	0.10	$1.4\text{E}-11$	98.0
20	3.41	0.12	$1.2\text{E}-11$	97.8

However, a linear relationship was observed between the molar amount of DEET degraded ($\mu\text{mol}/\text{min}$) and D_0 or Q :

$$\text{removal amount} = (0.12 \pm 0.07) + (0.026 \pm 0.001) \times D_0 \quad R^2 = 0.999 \quad (7)$$

$$\text{removal amount} = (0.17 \pm 0.12) + (0.18 \pm 0.01) \times Q \quad R^2 = 0.999 \quad (8)$$

Using the obtained $[\cdot\text{OH}]_{\text{ss}}$ and the value of parameter a , the concentration or the molar amount of $\cdot\text{OH}$ at any time was calculated (Figure 2). Although a higher $\cdot\text{OH}$ concentration was found in FAFT operated at lower DEET initial concentration (Figure 2a), the increase in $[\cdot\text{OH}]$ with decreasing D_0 was much smaller than the decrease in D_0 itself. For example, there is a 10-fold increase in D_0 from 45.6 to 501.5 μM , but $[\cdot\text{OH}]$ increased only about 4.9-fold. Also, the amount of $\cdot\text{OH}$ generated ($\mu\text{mol}/\text{min}$) increased with increasing flow rate (Figure 2b). More available $\cdot\text{OH}$ will degrade DEET oxidation intermediates at a faster rate and thus lead to a higher treatment efficiency of the system (similar discussion applies to the

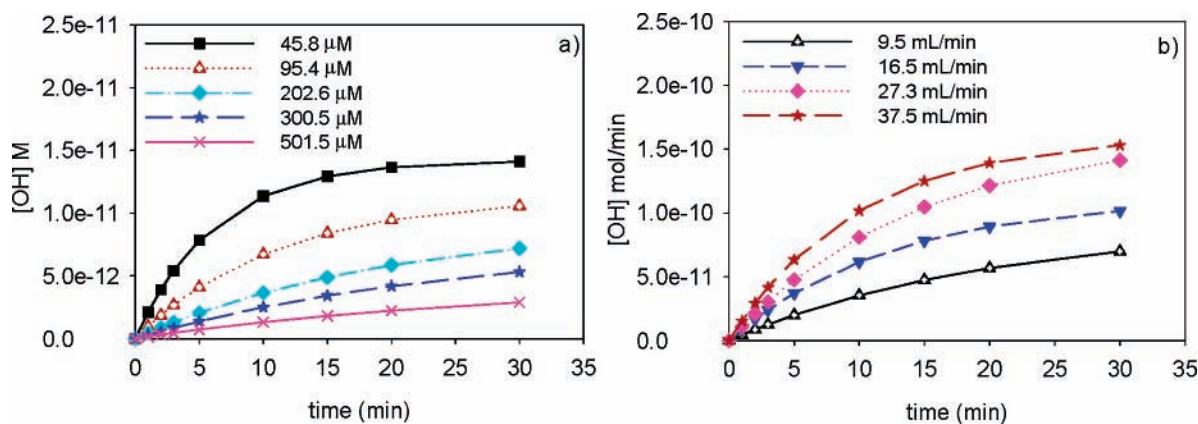


Figure 2. Calculated $[\cdot\text{OH}]$ in FAFT at various (a) DEET initial concentrations and (b) flow rates based on the experimental data in Figures 1 and S2.

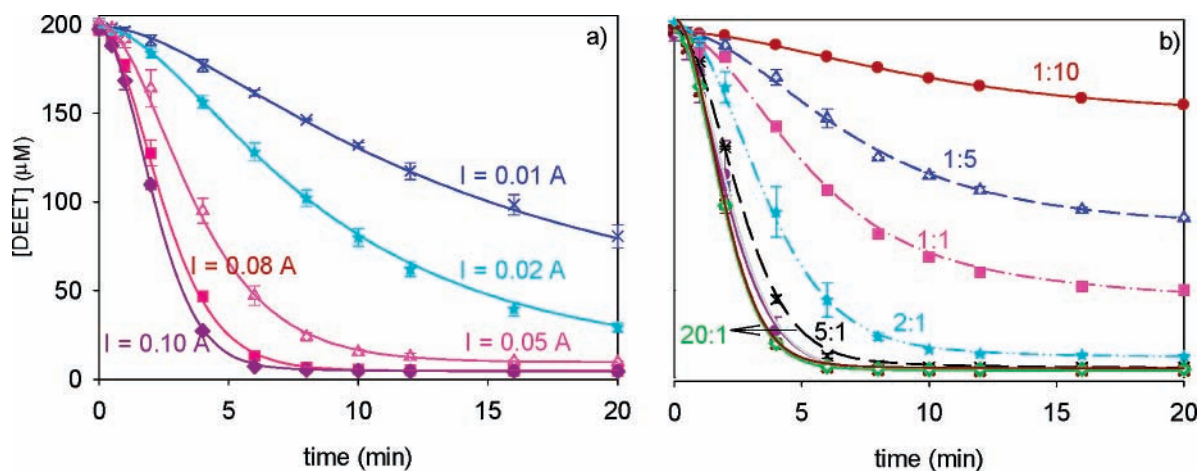


Figure 3. Effect of (a) Fe(II) delivery rate and (b) $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio on DEET degradation. Symbols are the experimental data; lines are the model fits. Reaction conditions (unless otherwise stated): 350-mL reactor; $[\text{DEET}]_0 = 200 \mu\text{M}$; flow rate = $27.4 \pm 1.4 \text{ mL/min}$; electrolysis $I = 0.10 \text{ A}$; input $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 10:1$; anodic $[\text{NaCl}] = 0.02 \text{ M}$; cathodic $[\text{NaCl}] = 0.08 \text{ M}$.

sections below). The above results indicate that the FAFT system is more efficient at treating high-concentration pesticide-containing wastewater at a high flow rate.

Effect of Fe^{2+} Delivery Rate and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ Ratio. Degradation of DEET under different Fe^{2+} delivery rates or $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios was further investigated, and the experimental data can also be fitted by the FAFT model well (Figure 3). As the fitting parameters show in Table 2a, R increased drastically, from 65.8 to 92.8%, when the electronic current I increased from 0.01 to 0.02 A, and increased by only 4.9% when I increased from 0.02 to 0.10 A. Similarly, there was a large increase in R (from 26.1 to 97.2%) when the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio increased from 1:10 to 5:1 but a small increase (from 97.2 to 98.0%) when the ratio changed from 5:1 to 12:1 (Table 2b). Further increase in the ratio up to 20:1 caused a slight decrease in R to 97.8%. A similar trend was observed when the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio was varied between 1:1 and 20:1 while the electronic current at I was fixed at 0.05 A (15; Table S1). The change in the above removal efficiencies can be explained by the calculated $\cdot\text{OH}$ concentrations at different delivery rates or $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios at any reaction time (Figure S2). To achieve the maximum removal efficiency with the minimum amount of input in both energy and chemicals, it is recommended to employ a Fe(II) delivery rate between 0.02 and 0.05 A and a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio between 5:1 and 10:1, which agrees with the findings for the batch AFT system (10).

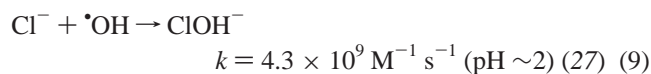
Effect of Electrolyte in Anodic Half-Cell. In previous work on the treatment of diazinon in batch AFT (9), different salts, including NaCl, KCl, Na_2SO_4 , and NaNO_3 , were used as

Table 3. Fitting Parameters for the FAFT Model Using Different Electrolytes in the Anodic Half-Cell^a

	z (min^{-1})	a (min^{-1})	$[\text{OH}]_{\text{ss}}$ (M)	R (%)	voltage at 0 min (V)
NaCl	6.46	0.13	$2.3\text{E}-11$	98.8	8.3 ± 0.7
CaCl_2	2.01	0.12	$7.3\text{E}-12$	96.1	9.3 ± 0.4
MgCl_2	2.25	0.11	$8.2\text{E}-12$	96.5	6.8 ± 0.1
AlCl_3	1.00	0.30	$3.6\text{E}-12$	92.4	6.6 ± 0.4
Na_3PO_4	0.0065	1.70	$2.4\text{E}-14$	7.3	11.7 ± 0.8

^a Reaction conditions (unless otherwise stated): 100-mL reactor; $[\text{DEET}]_0 = 200 \mu\text{M}$; flow rate = $8.2 \pm 0.2 \text{ mL/min}$; electrolysis $I = 0.02 \text{ A}$; input $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 10:1$; anodic electrolyte concentration = 0.02 M; cathodic $[\text{NaCl}] = 0.08 \text{ M}$ ($b = 0.082 \text{ min}^{-1}$).

electrolytes, and it was found that NaCl and KCl were equally effective, Na_2SO_4 slightly decreased the treatment efficiency, and NaNO_3 significantly impeded diazinon oxidation. On the basis of these results, the effect of additional electrolytes including CaCl_2 , MgCl_2 , AlCl_3 , and Na_3PO_4 was compared with that of NaCl in the FAFT system. The DEET degradation kinetics in the presence of any of the electrolytes can be fitted by the FAFT model very well (data not shown) with the treatment efficiency following the order $\text{NaCl} > \text{MgCl}_2 \approx \text{CaCl}_2 > \text{AlCl}_3 \gg \text{Na}_3\text{PO}_4$ (Table 3). The lower efficiency associated with MgCl_2 , CaCl_2 , and AlCl_3 is most likely due to the consumption of the hydroxyl radical by the additional chloride ions



as suggested by the corresponding lower levels of calculated [$\cdot\text{OH}$] (data not shown). The extremely low efficiency when using Na_3PO_4 as the electrolyte may be related to the strong chelating ability of the phosphate ion (i.e., $\text{H}_2\text{PO}_4^{2-}$) toward Fe^{2+} and Fe^{3+} with chelating constants ($\log K$) of 2.70 and 5.43, respectively (28). Note that the pH is around 3 in the anodic half-cell, and thus $\text{H}_2\text{PO}_4^{2-}$ is the predominant species of the phosphate ions ($\text{p}K_a$ for H_3PO_4 is 2.14). In addition, the phosphate scavenging effect may also account for the negative effect observed. Electrolysis voltage was also monitored for the FAFT system using the above electrolytes. The presence of divalent and trivalent ions yielded a slightly lower voltage than that of NaCl, and the highest voltage was observed when Na_3PO_4 was used as the electrolyte (Table 3). Overall, NaCl is the most economical and efficient electrolyte to use in the FAFT system.

Effect of NaCl Concentration in Anodic and Cathodic Half-Cells. Previous work on batch AFT studied the effect of NaCl concentration in the range of 0.02–0.08 M in the anodic half-cell and 0.008–0.16 M in the cathodic half-cell with the NaCl concentration ratio of cathode to anode varying between 0.1:1 and 5:1 (10). The results suggested that the optimum NaCl concentrations for the anodic and cathodic half-cells were 0.02 and 0.08–0.10 M, respectively. In an attempt to further lower the NaCl concentration in both half-cells (and hence lower the operational cost), NaCl concentration was varied between 0.005 and 0.02 M and between 0.08 and 0.20 M in the anodic and cathodic half-cells, respectively. Similar degradation kinetics and DEET removal efficiencies (between 97.0 and 98.8%) were observed for all of the NaCl concentrations studied, and the FAFT model fitting parameters are shown in Table S2. The data suggest that the change in NaCl concentration within the studied range did not significantly change the concentration of the hydroxyl radical and hence the treatment efficiency. The pH value in the cathodic half-cell at 10 min of treatment time, however, decreased from 11.61 to 11.55 as cathodic NaCl concentration increased from 0.08 to 0.20 M. Slower pH increment in the cathodic half-cell can allow the cathodic solution to be used for a longer time (see below for more discussion). On the other hand, electrolysis voltage decreased with increasing NaCl concentration in either half-cell (Figure S3). Because high voltages may cause undesirable oxidation of the parent pollutant and reaction intermediates in the anodic half-cell, the optimum NaCl level should be 0.01–0.02 and 0.08 M for the anodic and cathodic half-cells, respectively, to maintain a reasonable voltage without sacrificing treatment efficiency or consuming too much electrolyte.

Effect of Reactor Setup. To convert batch AFT into a FAFT system, the reactor setup requires optimization. First, the initial FAFT effluent still contains a large amount of parent pollutant and its degradation intermediates, which might cause problems for the follow-up treatment. There are two suggested approaches to solve this problem: (1) treat the wastewater in the batch AFT mode in the initial period and then switch to the FAFT mode at a certain time once the pollutant in the reactor reaches an acceptable level (i.e., batch to flow-through) and (2) treat the wastewater in the FAFT mode from the beginning, but instead of discharging the initial effluent, recycle the effluent into the FAFT system for further treatment until the effluent pollutant reaches an acceptable level (i.e., cycle to flow-through). The above two scenarios were tested at the switch times of 6 and 10 min. In batch AFT, DEET concentration in the reactor

reached zero at ~ 10 min. After switching the batch model to the flow-through mode at 6 or 10 min, effluent DEET concentration increased from 1.2 or 0 μM to a steady-state concentration of $\sim 5.0 \mu\text{M}$ within 25–40 min. When the switch from cycle to flow-through mode was made at 6 or 10 min, effluent DEET concentration changed from 3.8 or 2.7 μM to a steady-state concentration of 3.4 or 3.0 μM within 20–40 min. Overall, a larger volume of wastewater can be treated by the FAFT system through the cycle to flow-through mode than through the batch to flow-through mode while achieving a similar steady-state effluent concentration.

Another decision about the FAFT system is whether the cathodic half-cell should also be operated in a flow-through mode. If the answer is yes, it means consumption of a large quantity of water containing a fairly high concentration of salt and generation of salty and alkaline wastewater, which needs further treatment (see results below). Two FAFT systems were set up to determine the optimum operating condition, one with a normal flow rate through the cathodic half-cell and the other with a fixed cathodic volume without any input or output volume. Degradation of DEET was monitored in both systems for up to 20 min, and it was found that DEET degradation kinetics could be fitted by the FAFT model for both systems and similar treatment efficiencies were achieved in both (data not shown). The only difference was that the pH value increased at a much smaller rate in the flow-through system than in the other system (see eq 2 and Figure S4). Because it is much cheaper to treat a small volume of highly alkaline wastewater than to treat a large volume of a less alkaline one, it is recommended to fix the volume in the cathodic half-cell until it reaches a point where the pH is too high, and then the entire solution can be replaced by another batch of NaCl solution. The following experiments were all conducted with a fixed cathodic volume.

Effect of pH on DEET Degradation. In addition to measuring pH values in the cathodic half-cell as detailed above, pH values were also monitored in the anodic half-cell (Figure S4) and were found to quickly decrease from 5.6 ± 0.2 to 3.16 ± 0.23 within 1.5–2 min and then stay at that value throughout the treatment time (up to 3 h). It is well-known that the optimal pH for the Fenton reaction is ~ 3 , so the FAFT system (similar to batch AFT) has a major advantage of a self-developing optimal pH within a short period of time. Because FAFT and batch AFT systems all showed an S-shaped kinetic curve with a low rate of degradation in the beginning (< 1 min) followed by a relatively high rate until reaching either a steady state in FAFT or zero parent pollutant concentration in AFT, it appears that the nonoptimal pH in the anodic half-cell in the beginning of the reaction could be one of the reasons for the observed S-shaped curve (note the synchronous development between pH and DEET degradation). To test this hypothesis, the pH in both the anodic half-cell and anodic influent was adjusted to 3.0 and DEET degradation in FAFT was monitored (data not shown). Interestingly, the initial reaction rates after pH adjustment were not significantly faster than those of the normal FAFT. Thus, other factors, particularly the concentration of $\cdot\text{OH}$ as discussed above, contribute to the S-shaped kinetic curve.

Application of the FAFT System. Previous work by the authors (15) showed that the degradation of various model amide compounds in FAFT can be fitted by the FAFT model well, with the fitting parameters shown in Table 4. To verify the obtained removal efficiencies, it would be helpful to show that these R values agree with the corresponding second-order $\cdot\text{OH}$ rate constants of amides. Applying the competition kinetics as

Table 4. Fitting Parameters for the FAFT Model for the Degradation of Different Model Amide Compounds in FAFT^a

	<i>z</i> (min ⁻¹)	<i>a</i> (min ⁻¹)	[OH] _{ss} (M)	<i>R</i> (%)	<i>k</i> _{OH} (M ⁻¹ s ⁻¹)	EA (eV)	EA _{ring} (eV)
BDX	3.12	0.2	1.1E-11	97.4	4.2E+09	-0.17	0.23
DEET	6.46	0.13	2.30E-11	98.8	4.6E+09	0.1	0.21
HXD	5.18	0.12	1.9E-11	98.4	5.2E+09	0.11	0.23
MTD	4.06	0.16	1.5E-11	98.0	4.5E+09	0.17	0.2
oMBD	8.43	0.1	3.1E-11	99.0	4.6E+09	0.2	0.2
mMBD	7.09	0.15	2.6E-11	98.9	4.0E+09	0.21	0.21
pMBD	6.69	0.15	2.4E-11	98.8	5.0E+09	0.21	0.21
DND	0.56	1.2	2.0E-12	87.2	7.0E+08	0.31	0.41
FBD	1.33	0.55	4.8E-12	94.2	9.0E+08	0.64	0.64
DTD	0.13	10	4.7E-13	62.1	3.0E+08	1.36	1.36

^a Reaction conditions (unless otherwise stated): 100-mL reactor; [amide]₀ = 200 μM; flow rate = 8.2 ± 0.2 mL/min; electrolysis *I* = 0.02 A; input H₂O₂/Fe²⁺ = 10:1; anodic [NaCl] = 0.02 M; cathodic [NaCl] = 0.08 M (*b* = 0.082 min⁻¹).

discussed earlier (8, 11) and selecting DEET as the reference compound, the rate constants for the model amides were obtained as shown in **Table 4**. Not surprisingly, the order of measured rate constants agrees very well with the order of calculated removal efficiencies for the amides, that is, the smaller the rate constant, the lower the removal efficiency. A quantitative structure–activity relationship (QSAR) can be applied to understand the different reactivities among the amides. Because •OH is a highly electrophilic species, electron affinity (EA) can be an adequate descriptor for the reactivity of the amides because it represents the energy difference associated with the gain of an electron (29), which should correlate with the ease or difficulty of the reaction with •OH. In other words, compounds with electron-withdrawing groups have higher electron affinity values and react with •OH more slowly. The estimated EA values for different amides are shown in **Table 4**, and a linear relationship was obtained for the correlation between log *R* and EA:

$$\log R = -(0.14 \pm 0.02)EA + (2.01 \pm 0.01) \quad R^2 = 0.81 \quad (10)$$

To further compare the reactivity of •OH toward either the aromatic ring or the aliphatic side chain in each amide, the electron affinity of the aromatic ring (EA_{ring}) within each amide was estimated (**Table 4**), and a similar linear relationship was obtained:

$$\log R = -(0.16 \pm 0.02)EA_{\text{ring}} + (2.03 \pm 0.01) \quad R^2 = 0.91 \quad (11)$$

The better correlation of log *R* versus EA_{ring} (i.e., higher *R*²) indicates that •OH mainly reacts with the aromatic ring, with the reactivity being affected by the properties of the ring substituents (i.e., electron-withdrawing groups inhibit the reaction and vice versa).

Pesticide wastewater typically contains active pesticides and other inactive ingredients, many of which are organic compounds that can compete with pesticides for the available hydroxyl radicals in the FAFT system. To evaluate the effect of the inactive ingredients on the degradation of DEET in FAFT, commercially available DEET formulations containing 7–100% DEET were oxidized in the FAFT system. All of the DEET degradation kinetics can be fitted well by the FAFT model (see Table S3 for the fitting parameters). Obviously, higher inactive ingredient contents yielded lower treatment efficiency:

$$R = (99.59 \pm 2.99) \times (1 - e^{-(0.082 \pm 0.010)[\% \text{DEET}]}) \quad R^2 = 0.98 \quad (12)$$

Overall, the above data indicate that the FAFT system can be applied to the treatment of pesticide wastewaters containing a mixture of organic compounds.

A well-accepted reaction mechanism (Table S4) for the Fenton process has been previously developed (30–32) and was proved to be operative in the FAFT system by the authors (15). Briefly, the hydroxyl radical is the active oxidizing agent generated by a chain reaction involving Fe²⁺, Fe³⁺, H₂O₂, and radicals such as HO₂• and O₂•⁻. In addition to oxidizing organic pollutants, •OH can be consumed through reaction with itself and all of the above species except Fe³⁺. The effects on the system treatment efficiency of changing operating conditions that are reported in this work can be explained either by the availability of more organic compounds to react with •OH (e.g., increasing DEET initial concentration or flow rate, comparing the cycle to flow-through mode with the batch to flow-through mode) or by less available •OH after consumption by competing reactions with nonorganic species such as Fe²⁺ or H₂O₂ (e.g., increasing electrolysis current or H₂O₂/Fe²⁺ ratio, the use of CaCl₂, MgCl₂, or AlCl₃ instead of NaCl as the electrolyte). In the cases when a higher concentration of NaCl was employed in either the anodic or cathodic half-cell, Cl⁻ should compete for •OH (eq 9) and thus yield lower treatment efficiency. However, a similar *R* was observed with various concentrations of NaCl in either the anodic or cathodic half-cell. Note that anion exchange membranes allow only anions such as Cl⁻ and OH⁻ to flow from the cathodic half-cell to the anodic half-cell, and hence an increase in [NaCl] in the cathodic half-cell should also increase [NaCl] in the anodic half-cell. Although the exact role of Cl⁻ in the FAFT system warrants further study, Wang and Lemley (10) believed that the higher potential at lower NaCl concentrations may lead to more oxidative reactions occurring and hence lower the electrolysis current efficiency to generate ferrous iron. The above two factors may neutralize each other so that the overall treatment efficiency of the parent pollutant is not affected.

The current study evaluated the performance of the previously developed flow-through AFT system, another step forward toward its application in treating small-scale, high-concentration pesticide wastewaters. The effects of various operating conditions on the treatment efficiency obtained in this study can be applied to estimate treatment efficiencies under other operating conditions. The successful application of the FAFT system to the degradation of model amides and DEET formulations indicates the likelihood of extending this approach to other pesticide-containing wastewaters. Regardless of the type of organic compounds present, the key to high treatment efficiency is to operate the FAFT system to achieve a maximum •OH production with a minimum input of energy and chemicals. The FAFT effluent from the anodic half-cell is acidic and contains a large amount of Fe³⁺ and DEET oxidation intermediates; the effluent from the cathodic half-cell is alkaline (pH > 10). Further study is necessary to treat these effluents until their final discharge.

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Supporting Information Available: Degradation kinetics of DEET in the FAFT system. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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