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

Huichun Zhang[1] and Ann T. Lemley *

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

[1] Current address: National Exposure Research Laboratory, U.S. Environmental Protection Agency, 960 College Station Road, Athens, GA 30605

Total 9 pages

One Text

Four Tables

Five Figures

**Text S1. Kinetic Modeling.** A semi-empirical kinetic model was previously developed by the authors (*1*) to describe the degradation kinetics of DEET in the FAFT system. In summary, (i) the reaction between •OH and DEET was regarded as second-order with a rate constant k of $2.76 \times 10^{-5}$ $\mu M^{-1} \cdot min^{-1}$ (*1*), i.e., the reaction rate of DEET at time t (min) is:

$$r = k[\bullet OH\ ][DEET] \tag{3}$$

(ii) the kinetic trend of •OH in FAFT can be best described by an exponential fit:

$$[\bullet OH] = [\bullet OH]_{ss}(1 - e^{-at}) \tag{4}$$

where $[\bullet OH]_{ss}$ is the steady state •OH concentration and parameter 'a' is the fitting parameter which relates to the initial generation rate of the hydroxyl radical; and (iii) the FAFT system can be treated as a continuous flow stirred tank reactor (CSTR); the mass balance of DEET in the system can be expressed as:

$$V\frac{dD}{dt} = Q \cdot D_0 - Q \cdot D - V \cdot r \tag{5}$$

where $D_0$ and D are DEET influent and effluent concentrations ($\mu M$), V is the reactor volume (mL), and Q is the flow rate in mL/min. Substituting eq. 3 and 4 into eq. 5, we obtain:

$$\frac{dD}{dt} = b(D_0 - D) - z(1 - e^{-at})D \tag{6}$$

where $b = \dfrac{Q}{V}$ $(min^{-1})$ which is the reciprocal of the FAFT hydraulic retention time, and $z = k[\bullet OH]_{ss}$.

We call this kinetic fitting approach the FAFT model.

Parameter b is always known for any given reactor volume and flow rate; parameter z and $[\bullet OH]_{ss}$ can be obtained by knowing the steady-state effluent concentration $D_{ss}$, i.e., when t $\rightarrow$ $\propto$, dD/dt = 0, then

$$z = b(D_0/D_{ss}-1) \tag{7}$$

2

$$[\bullet OH]_{ss} = z/k \qquad\qquad (8)$$

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 squared method in Sigma Plot. The fits were evaluated based on the correlation between the experimental data and the modeling data. $[\bullet OH]$ can be calculated based on eq 4. The removal efficiency (R %) of the parent compound is defined as $(1-D_{ss}/D_0) \times 100$ and will be used to compare treatment efficiencies under different FAFT conditions.

**Table S1**. Fitting parameters for the FAFT model at different $H_2O_2 : Fe^{2+}$ ratios ($b = 0.078$ min$^{-1}$). Reaction conditions (unless otherwise stated): 350-mL reactor; $[DEET]_0 = 200$ μM; flow rate $= 27.4 \pm 1.4$ mL/min; electrolysis $I = 0.05$ A; anodic $[NaCl] = 0.02$ M; cathodic $[NaCl] = 0.08$ M.

| $H_2O_2$:Fe(II) | z (min$^{-1}$) | a (min$^{-1}$) | $[OH]_{ss}$ (M) | R % |
|---|---|---|---|---|
| 1 | 0.21 | 0.18 | 7.6E-13 | 73.2 |
| 5 | 1.45 | 0.06 | 5.3E-12 | 94.9 |
| 10 | 1.63 | 0.07 | 5.9E-12 | 95.5 |
| 15 | 2.18 | 0.08 | 7.9E-12 | 96.6 |
| 20 | 2.10 | 0.02 | 7.6E-12 | 96.3 |

**Table S2**. Fitting parameters for the FAFT model at various NaCl concentrations in (a) anodic and (b) cathodic half-cells. Reaction conditions (unless otherwise stated): 100-mL reactor; $[DEET]_0 = 200$ μM; flow rate $= 8.2 \pm 0.2$ mL/min; electrolysis $I = 0.02$ A; input $H_2O_2 : Fe^{2+} = 10:1$; anodic $[NaCl] = 0.02$ M; cathodic $[NaCl] = 0.08$ M.

a) **Anodic**

| [NaCl] M | z (min$^{-1}$) | a (min$^{-1}$) | $[OH]_{ss}$ (M) | R % |
|---|---|---|---|---|
| 0.005 | 4.05 | 0.05 | 1.5E-11 | 98.0 |
| 0.01 | 3.15 | 0.07 | 1.1E-11 | 97.5 |
| 0.015 | 2.67 | 0.08 | 9.7E-12 | 97.0 |
| 0.02 | 2.67 | 0.08 | 9.7E-12 | 97.0 |

b) **Cathodic**

| [NaCl] M | z (min$^{-1}$) | a (min$^{-1}$) | $[OH]_{ss}$ (M) | R % |
|---|---|---|---|---|
| 0.08 | 6.46 | 0.13 | 2.3E-11 | 98.8 |
| 0.10 | 5.52 | 0.13 | 2.0E-11 | 98.5 |
| 0.12 | 6.66 | 0.11 | 2.4E-11 | 98.8 |
| 0.16 | 5.30 | 0.14 | 1.9E-11 | 98.5 |
| 0.20 | 5.58 | 0.14 | 2.0E-11 | 98.6 |

**Table S3**. Fitting parameters for the FAFT model for different DEET formulations. Reaction conditions: 100-mL reactor; $[DEET]_0 = 200$ μM; flow rate $= 8.2 \pm 0.2$ mL/min; electrolysis I $= 0.02$ A; input $H_2O_2 : Fe^{2+} = 10:1$; anodic $[NaCl] = 0.02$ M; cathodic $[NaCl] = 0.08$ M.

| % DEET | $z$ (min$^{-1}$) | $a$ (min$^{-1}$) | $[OH]_{ss}$ (M) | R % |
|---|---|---|---|---|
| 7 | 0.055 | 0.55 | 2.0E-13 | 40.3 |
| 25 | 0.8 | 0.1 | 2.9E-12 | 90.7 |
| 40 | 1.77 | 0.09 | 6.4E-12 | 95.0 |
| 100 | 4.12 | 0.07 | 1.5E-11 | 98.1 |

**Table S4**. Mechanism of Fe(II)-Initiated Chain Reactions.

| # | Reaction | $k$ (M$^{-1}$s$^{-1}$) | Ref. |
|---|---|---|---|
| 1 | $Fe(II) + H_2O_2 \Longrightarrow Fe(III) + \bullet OH + OH^-$ | 76 | 4 |
| 2 | $Fe(III) + H_2O_2 \Longrightarrow Fe(II) + HO_2\bullet/O_2^{\bullet -} + H^+$ | $2.0 \times 10^{-3}$ | 31 |
| 3 | $H_2O_2 + \bullet OH \Longrightarrow HO_2\bullet/O_2^{\bullet -} + H_2O$ | $3.3 \times 10^7$ | 31 |
| 4 | $Fe(III) + HO_2\bullet/O_2^{\bullet -} \Longrightarrow Fe(II) + O_2 + H^+$ | $1.4 \times 10^5$ | 30 |
| 5 | $Fe(II) + \bullet OH \Longrightarrow Fe(III) + OH-$ | $3.2 \times 10^8$ | 31 |
| 6 | $Fe(II) + HO_2\bullet/O_2^{\bullet -} \Longrightarrow Fe(III) + H_2O_2$ | $1.3 \times 10^6$ | 31 |
| 7 | $HO_2\bullet/O_2^{\bullet -} + HO_2\bullet/O_2^{\bullet -} \Longrightarrow H_2O_2 + O_2$ | $2.3 \times 10^6$ | 31 |
| 8 | $\bullet OH + HO_2\bullet/O_2^{\bullet -} \Longrightarrow H_2O + O_2$ | $7.1 \times 10^9$ | 31 |
| 9 | $\bullet OH + \bullet OH \Longrightarrow H_2O_2$ | $5.2 \times 10^9$ | 31 |

**Figure S1**. Structures of DEET and model amide compounds.

DEET

Benzadox (BDX)

Hexamide (HXD)

2-Methylbenzamide
(oMBD)

3-Methyl benzamide
(mMBD)

p-Toluamide
(pMBD)

N,N-Diethylnicotinamide
(DND)

N-Methyl-o-toluamide
(MTD)

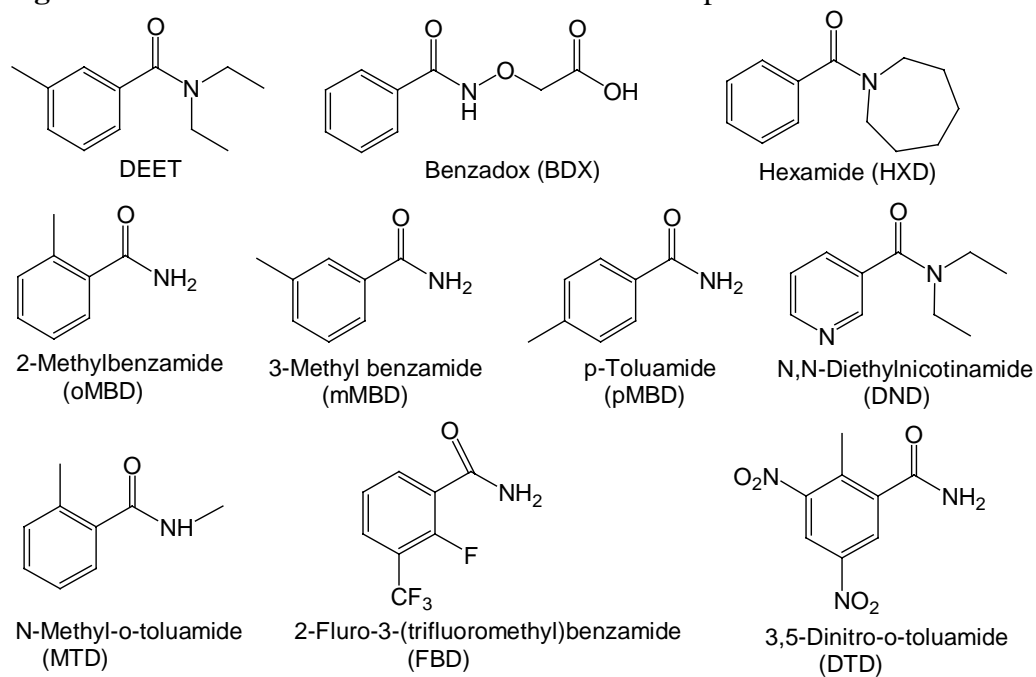2-Fluro-3-(trifluoromethyl)benzamide
(FBD)

3,5-Dinitro-o-toluamide
(DTD)

**Figure S2**. Effect of flow rate on DEET degradation. Symbols are the experimental data; lines are the model fits. Reaction conditions (unless otherwise stated): 350-mL reactor; input $H_2O_2 : Fe^{2+} = 10:1$, electrolysis current $I = 0.05$ A; anodic $[NaCl] = 0.02$ M; cathodic $[NaCl] = 0.08$ M.
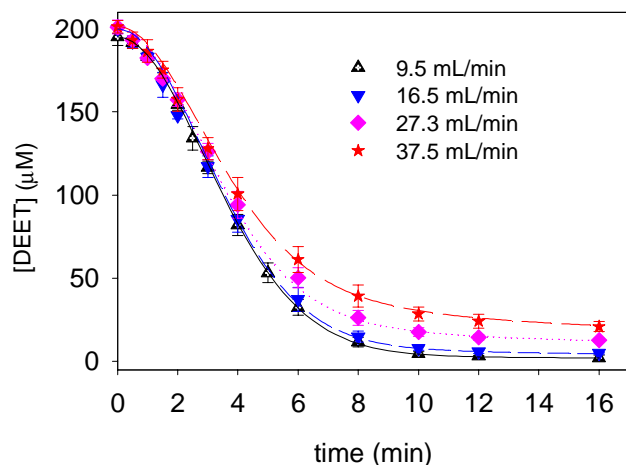


**Figure S3**. Calculated $[\bullet OH]$ in FAFT at (a) various Fe(II) delivery rates and (b) $H_2O_2 : Fe^{2+}$ ratios. Reaction conditions (unless otherwise stated): 350-mL reactor; $[DEET]_0 = 200$ μM; flow rate $= 27.4 \pm 1.4$ mL/min; electrolysis $I = 0.10$ A; input $H_2O_2 : Fe^{2+} = 10:1$; anodic $[NaCl] = 0.02$ M; cathodic $[NaCl] = 0.08$ M.
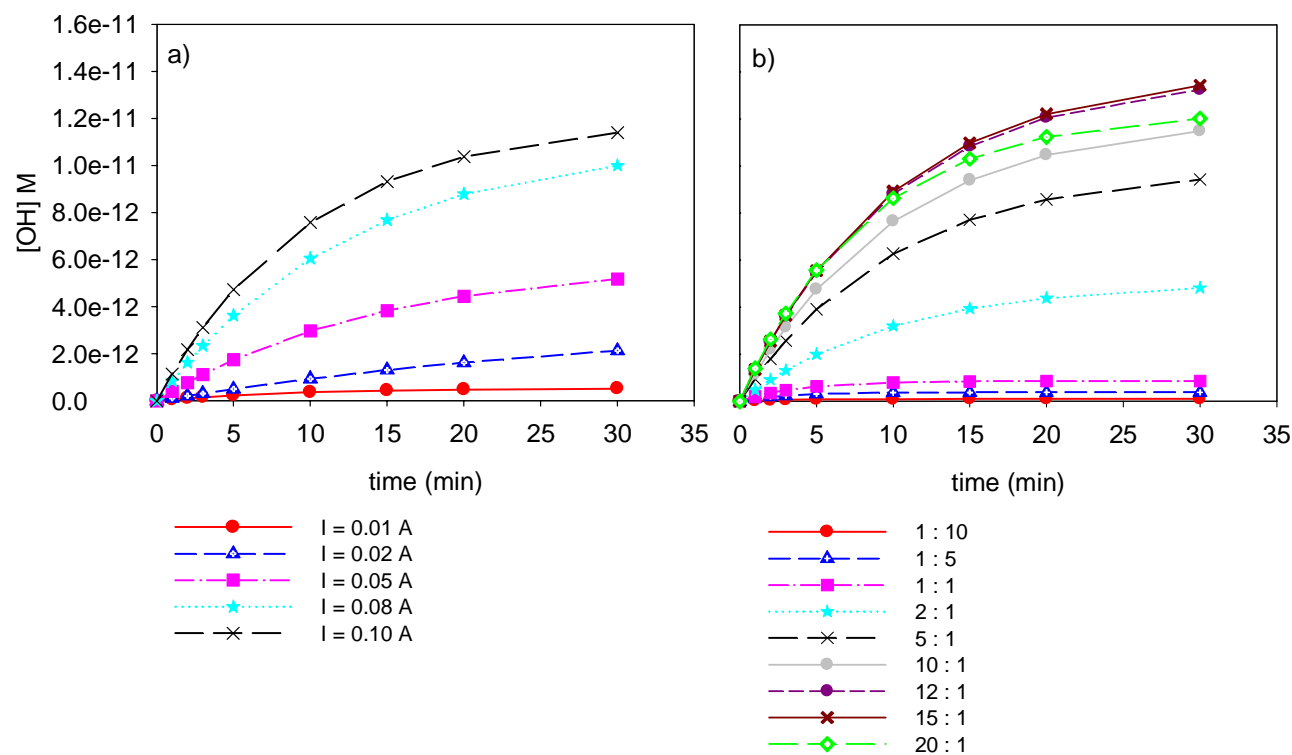
**Figure S4**. Effect of NaCl concentration on the electrolysis voltage of a) cathode and b) anode at three different reaction times. Reaction conditions (unless otherwise stated): 100-mL reactor; $[DEET]_0 = 200 \ \mu M$; flow rate $= 8.2 \pm 0.2$ mL/min; electrolysis I = 0.02 A; input $H_2O_2 : Fe^{2+} = 10:1$; anodic [NaCl] = 0.02 M; cathodic [NaCl] = 0.08 M.
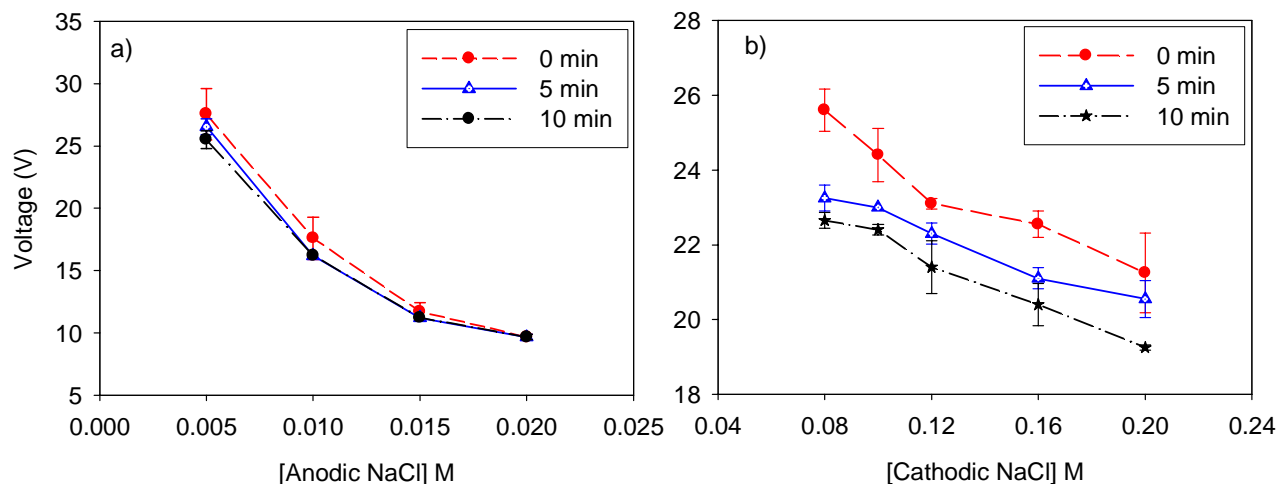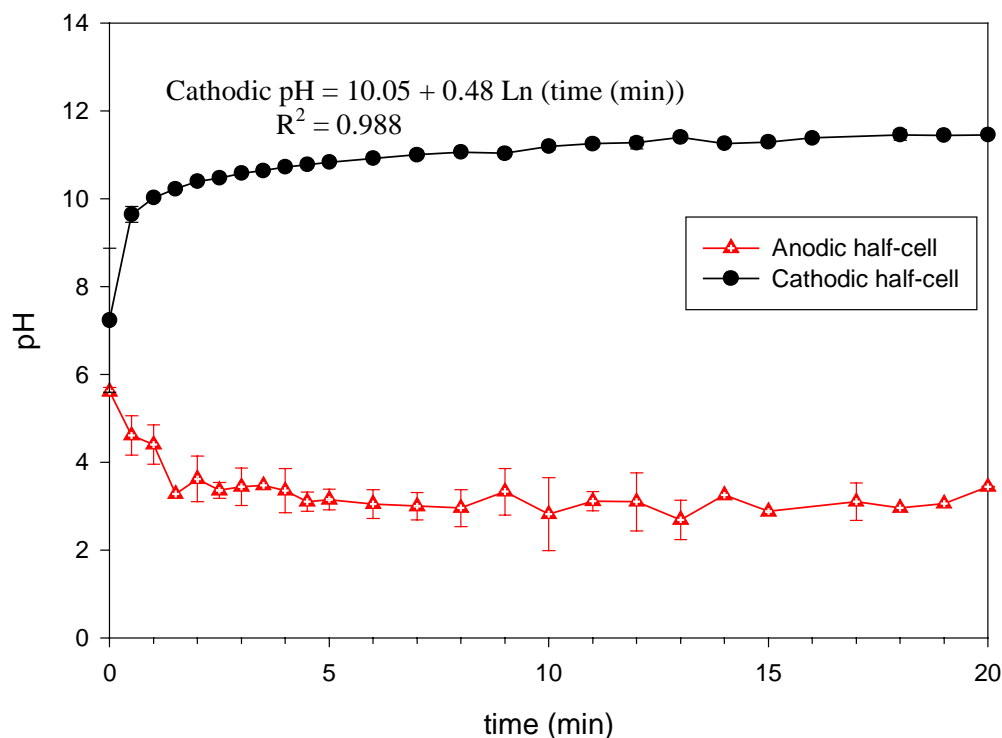


**Figure S5**. Time course of pH in anodic & cathodic half cells in FAFT. Reaction conditions: 350-mL reactor with a fixed cathodic volume; flow rate $= 27.4 \pm 1.4$ mL/min; input $H_2O_2 : Fe^{2+} = 10:1$, electrolysis current I = 0.05 A; anodic [NaCl] = 0.02 M; cathodic [NaCl] = 0.08 M.

**Reference:**

(1)     Zhang, H.; Lemley, A. T. Reaction mechanism and kinetic modeling of DEET degradation by flow-through anodic Fenton treatment (FAFT). *Environ. Sci. Technol.* **2006,** 40, 4488-4494.