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Summary of Advanced Oxidation and Reduction Processes Work at the Brook Byers Institute for Sustainable Systems

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Sep 5th 2018

Advanced Oxidation Processes Introduction

- Advanced oxidation processes (AOPs) yield various **highly reactive radicals** (e.g. HO•, SO_4^{-}•, Cl•) at room temperate and pressure.

- These electrophilic radicals are capable of destructing nearly all organic contaminants in the aqueous phase.

Organic contaminants → (Radicals) → CO_2, H_2O

Complex radical chain reactions

- Research Directions:

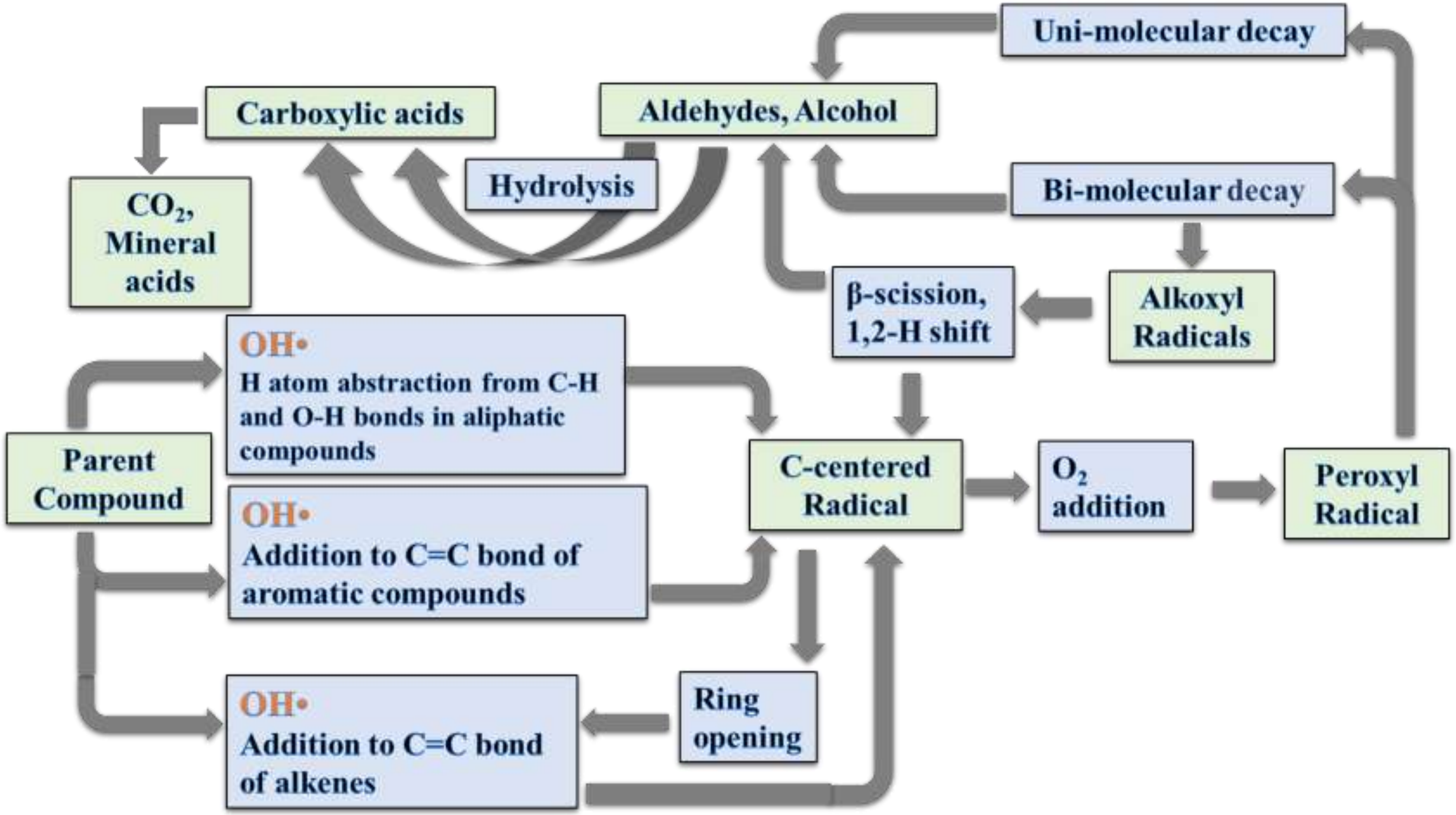
Technologies
- Chemical based
- UV based
- Electrochemical based

Models
- Interpret AOPs mechanisms
- Optimize AOPs operation conditions to reduce toxicity
- Predict AOPs performances

General Reaction Rules in AOP's

***Exampl**e*

General reaction mechanisms that HO• initiates based on past experimental studies



Stefan and Bolton, 1998; 1999; 1999; Stefan et al., 1996; 2000; Cooper et al., 2009; Li et al., 2004; 2007; von Sonntag and Schuchmann, 1984; Schuchmann and von Sonntag, 1979

Our Work on AOP Technologies

No.1	AOPs technologies names	AOPs technologies reactions
1	O_3/NOM	$O_3 + NOM \rightarrow HO\bullet + byproducts$
2	O_3/H_2O_2	$2O_3 + H_2O_2 \rightarrow 2HO\bullet + 3O_2$
3	O_3/Activated Carbon	$O_3 + Activated\ Carbon \rightarrow HO\bullet + byproducts$
4	Fentons	$Fe^{2+} + H_2O_2 \rightarrow HO\bullet + Fe^{3+} + OH^-$
5	Fenton/RGO α−FeooH	$RGO = Fe^{II} + H_2O_2 \rightarrow HO\bullet + Fe^{III}OH + H_2O$
6	Peroxymonosulfate/Ascorbic Acid	$HSO_5^- + H_2A \rightarrow SO_4^-\bullet + H^+ + A^- + H_2O$
7	Peroxymonosulfate/CoFeNi	$HSO_5^- + Co(II) \rightarrow SO_4^-\bullet + Co(III) + OH^-$
8	UV/H_2O_2	$H_2O_2 + h\nu \rightarrow 2HO\bullet$
9	UV/TiO_2	$TiO_2 + h\nu + OH^- + O_2 \rightarrow HO\bullet + O_2^-\bullet + TiO_2$
10	Solar light/TiO_2 /H_2O_2	$TiO_2 + H_2O_2 + e^- \rightarrow HO\bullet + OH^- + TiO_2$
11	UV/Persulfate	$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^-\bullet$
12	UV/HOCl	$HOCl + h\nu \rightarrow HO\bullet + Cl\bullet$

* TiO_2 is a **photocatalyst**.

* Developed photocatalysts for AOPs: $CaCO_3$-Fe_2O_3 nanorod, Fe-TiO_2, $Co_3(PO_4)_2/Ag_3PO_4$

* Designed **solar photoreactor** for photocatalysts (e.g. TiO_2 based compound parabolic collector reactor)

New Project

Common components in water matrix include: Cl^-, HCO_3^-,CO_3^{2-}NOM,bromide.

Also investigated:

- bromate **formation** and **migration** in O_3 AOPs technologies
- the **impacts** of Cl^-, HCO_3^-,CO_3^{2-} NOM on AOPs technologies

W Zhang et al., 2018

Our Work on AOP Technologies

Electrochemical Oxidation Processes

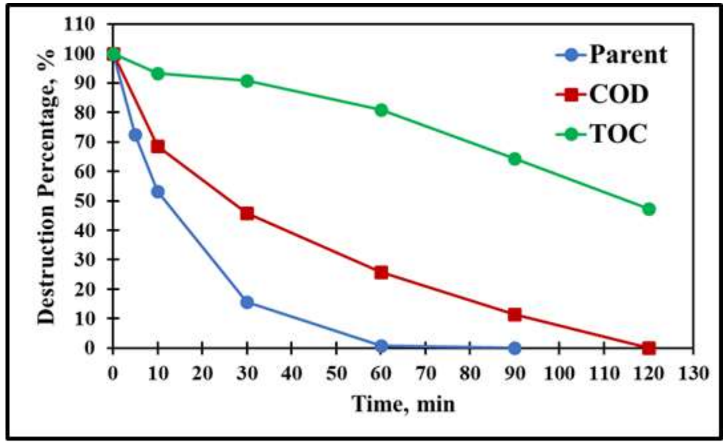
No.1	Developed Electrodes
1	TiO_2 nanotubes/SnO_2-Sb/PbO_2 anode
2	Blue TiO_2 nanotubes/SnO_2-Sb anode
3	Fe_2O_3-GQDs/NF-TiO_2 anode
4	Activated Carbon electrode
5	Al-Doped PbO_2 anode
6	Fe0/TiO_2(cathode), bio-anode

Electrode reactions:

Anode reaction: $H_2O \rightarrow$ **HO·**$+H^+ + e^-$

Cathode reaction: $2H^+ + 2e^- \rightarrow H_2$

Electron Efficiency



Equation:

$$\eta_C = \frac{32}{12} \cdot \left(\frac{n}{4x}\right) \cdot \frac{d(TOC)}{d(COD)}$$

- x, number of carbon atoms in organic
- n, number of electrons transferred from anode in a balanced chemical reaction;

Exp: $C_{18}H_{20}FN_3O_4 + 41H_2O \rightarrow 18CO_2 + F^- + 3NO_3^- + 102H^+ + 98e^-$

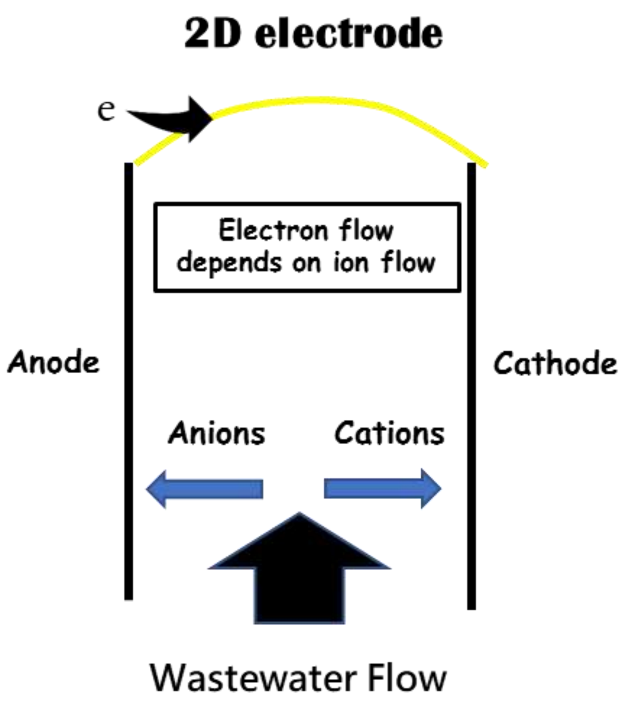
For 20 mg/L ofloxacin using EAOP with current density 30 mA/cm²

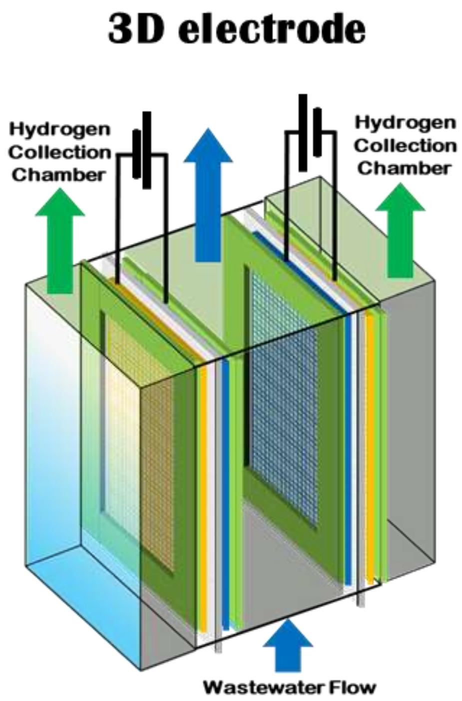
- 100% **Parent compound** destroyed in 1 hour;
- 100% **COD** destroyed in 2 hours;
- 52.6% **TOC** destroyed in 2 hours.

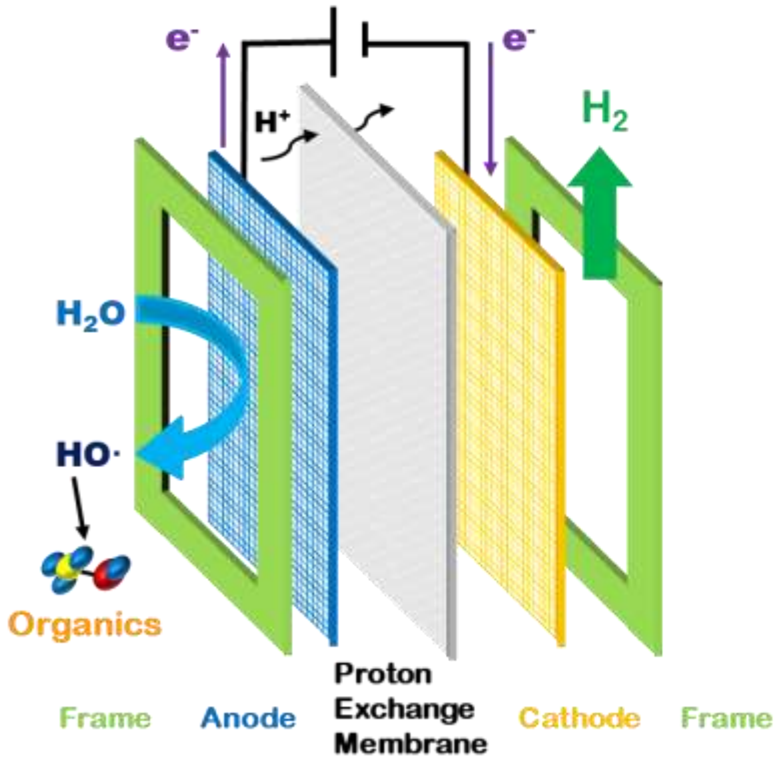
The electron efficiency is **88.45%** (88.45% electrons cause effective oxidation)

Our Work on AOP Technologies

Electrochemical Oxidation Processes: from 2-Dimensional to 3-Dimensional



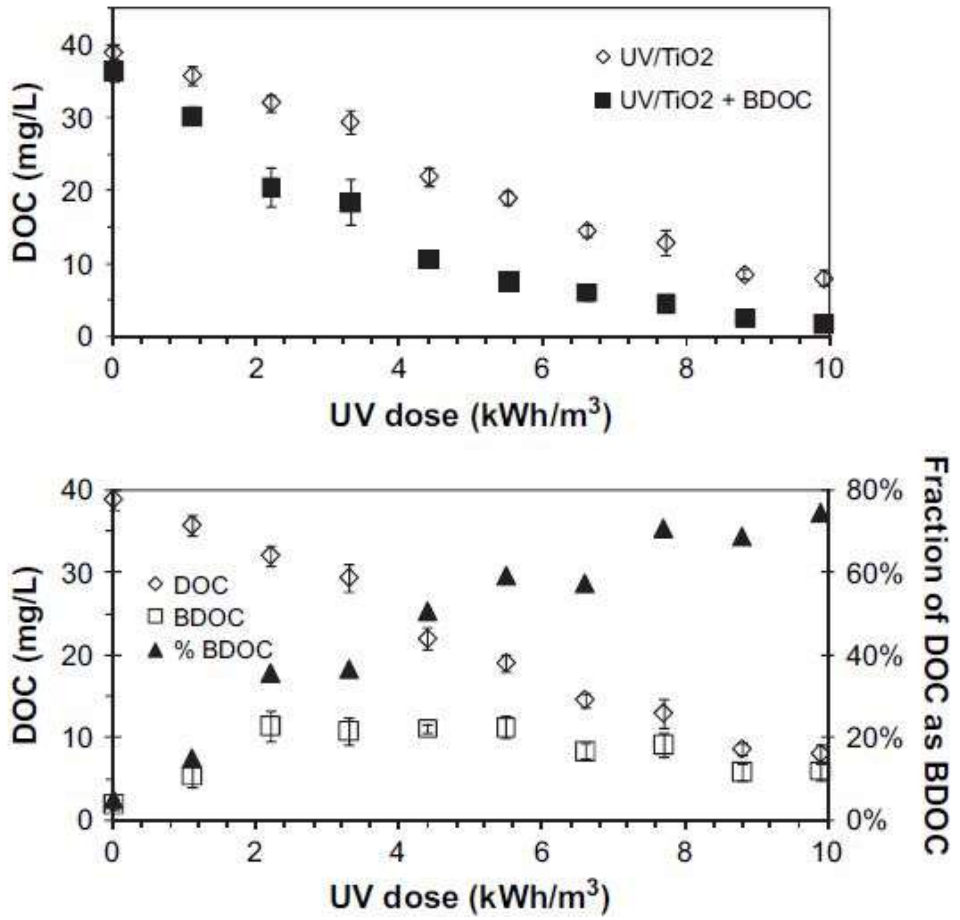




- Lower cell voltage, lower EE/O
- No additional electrolyte required to enhance efficiency
- Higher electron efficiency (3D as high as 106.7%, where 2D is 86.6% in a case study)

Our Work on AOP Technologies

Combined AOPs with **Biological Processes**



Effect of dual treatment (UV/TiO_2 followed by biodegradation in BDOC reactors) of RO retentate at pH 5 with 2 g/L of TiO2

UV/TiO_2 With Biological Treatment for Reverse Osmosis Retentate

- Lower power can be used when combined with downstream biodegradation.
- Essentially incorporating biological treatment can **reduce power requirements by 20% to 50%** depending upon what find DOC concentration you are targeting.

Westerhoff et al., 2009.

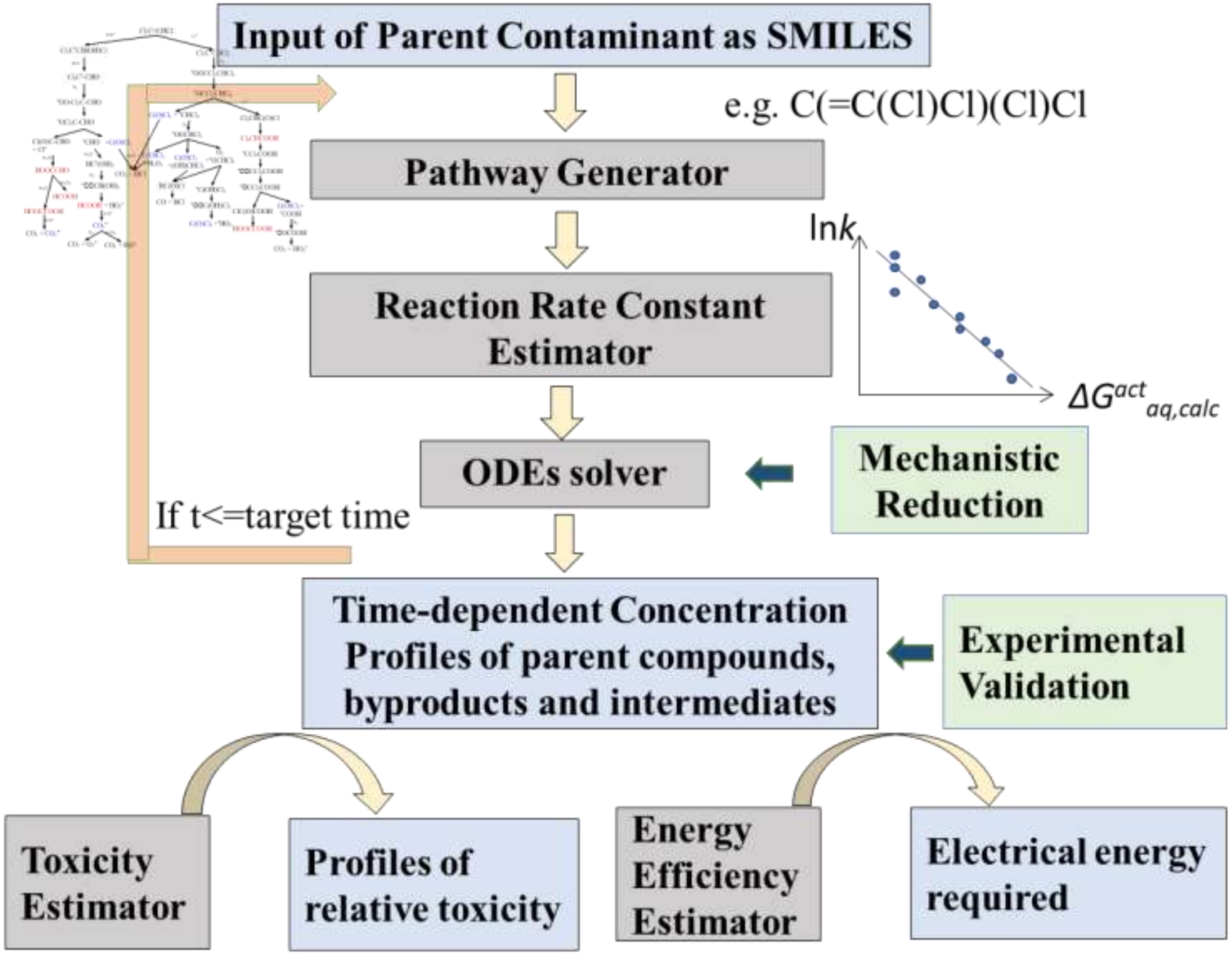
Process Models & Methodologies

- **Reaction Pathway Generator (Graph Theory)**

- **Rate Constants Estimator (Group Contribution Method, Free Energy Linear Relationship, Genetic Algorithm)**

- **Ordinary Differential Equations (ODEs) Generator and Solver (Gear's Algorithm or Monte Carlo algorithm)**

***Kinetic Monte Carlo Solver can solve 1 million ODEs on PC within 30 minutes**

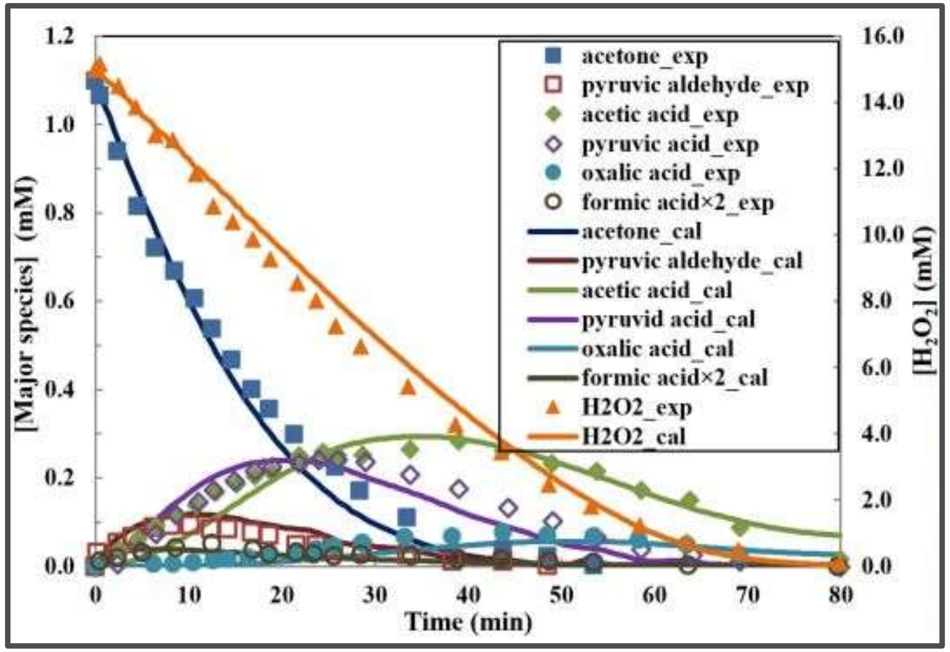


Modeling Results

Examples

Acetone degradation in UV/H_2O_2 processes

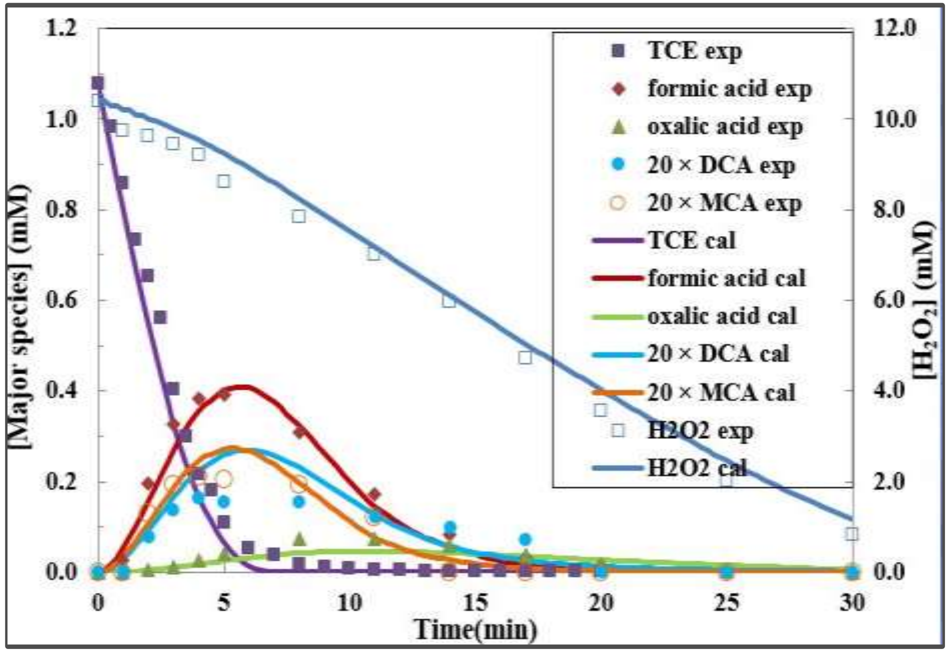
Predicted concentration profiles of acetone and stable byproducts



X Guo et al., 2014;2015

TCE degradation in UV/H_2O_2 processes

Predicted concentration profiles of TCE and stable byproducts



X Guo et al., 2014;2015

Modeling Results for Newest Project - Benzoic Acid Derivatives Degradation in UV/HOCl Processes

Primary Radicals

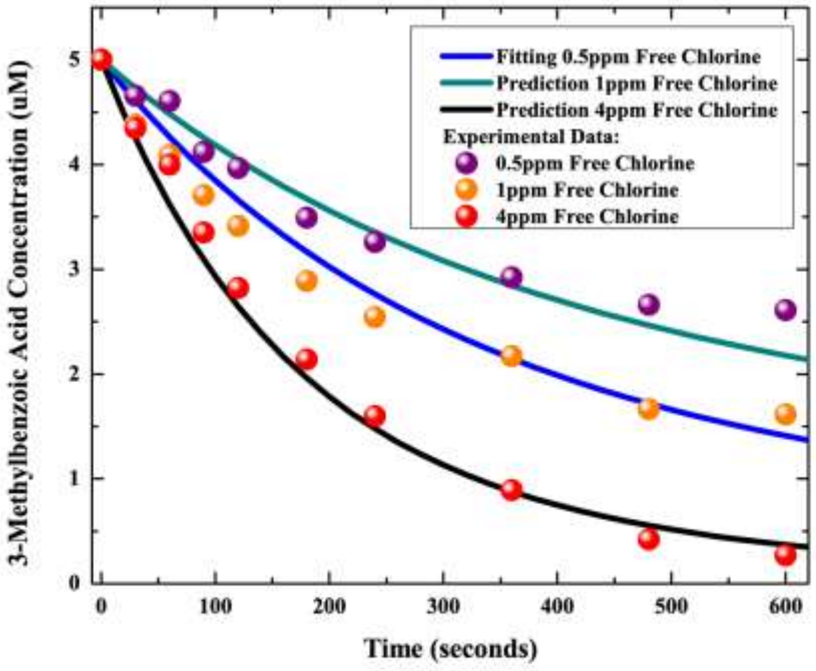
HO• Cl•

Secondary Radicals

Cl_2^{-}• ClO• **(dominant contribution)**

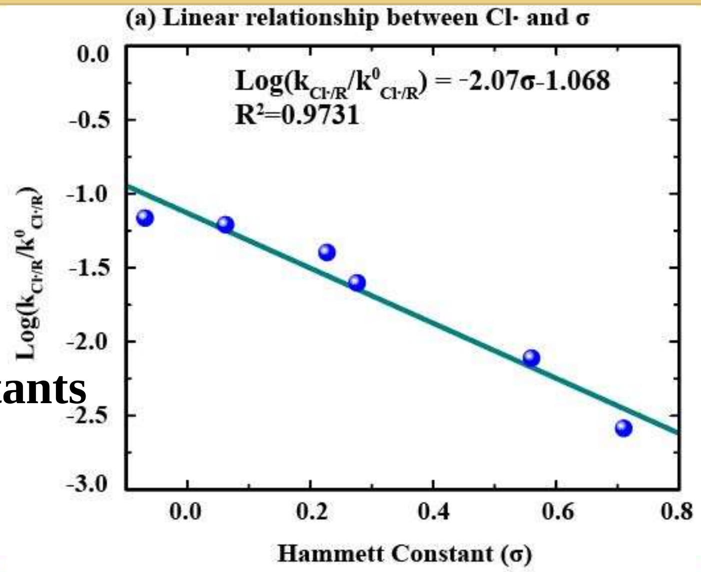
Kinetic Behavior

(e.g. 3-Methylbenzoic acid)

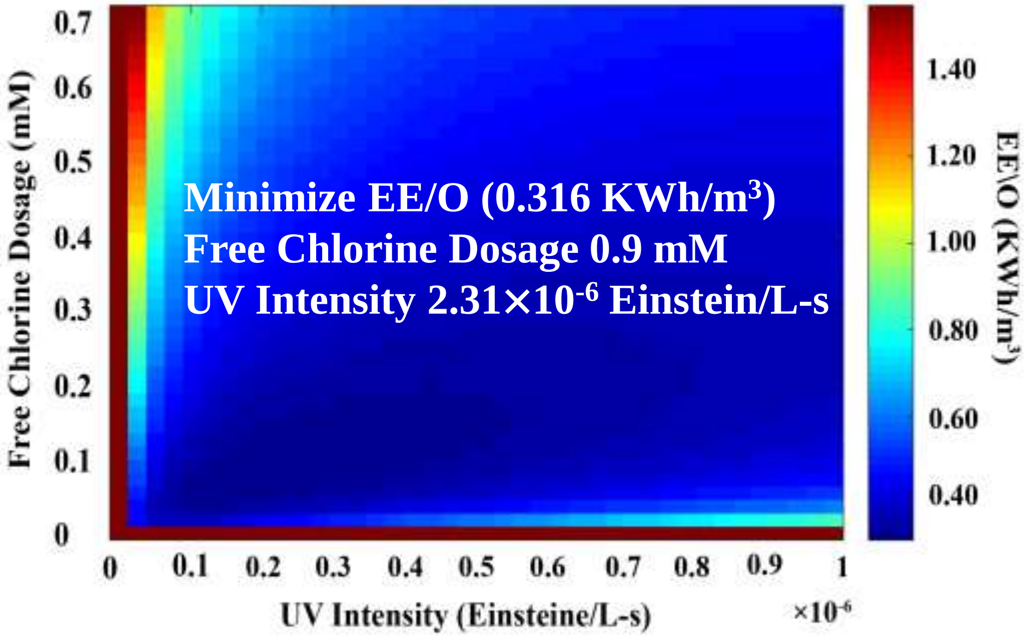


Quantity Structure Activity Relationship

(e.g. Linear relationship between the **reactivity of Cl·** and **hammett constants** for benzoic acid derivatives)



Energy Efficiency



Experimental Condition:

[R]= 5×10^{-6}M, pH=7.2

Advanced Reduction Processes Introduction

- Advanced reduction processes (ARPs) yield **highly reactive reducing radicals** (e.g. aqueous electron e^-_{aq}) at room temperature and pressure

Activating Method (e.g. UV, E-Beam, Ultrasound, Microwave) + **Reducing Agent** (e.g. sulfite, dithionite, sulfide, ferrous iron → **Reductant Radicals**

- These reducing free radicals donate an unpaired electron to reduce organic contaminants in the aqueous phase.

Reduction

Reducing radicals → Organic contaminants (e.g. perfluorooctanoic acid (PFOA))

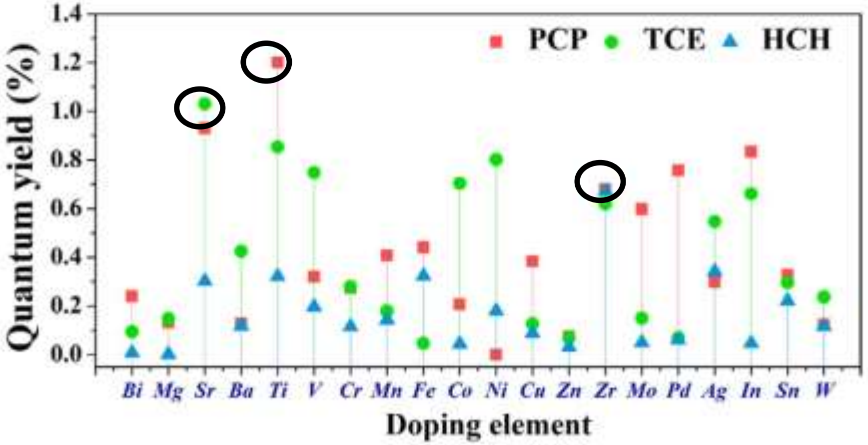
cannot be oxidized by some oxidizing radicals (e.g. HO·, Cl·)

Our Work on ARP Technologies

Materials Work

❖ Developed **photocatalysts** for ARPs:

- Ti-β-Bi_2O_3 **reduce** → Pentachlorophenol
  Removal efficiency: 95.2%
- Sr-β-Bi_2O_3 **reduce** → Trichloroethylene
  Removal efficiency: 97.4%
- Zn-β-Bi_2O_3 **reduce** → Hexachlorocyclohexane
  Removal efficiency: 90.3%



- Au-Cu_2O nanowire **reduce** → Triclosan
  Removal efficiency: 96.5%

J Niu et al. 2015

Modeling Work

❖ Determining the **reactivity** of e_{aq}^-: $k_{e_{aq}^-}$

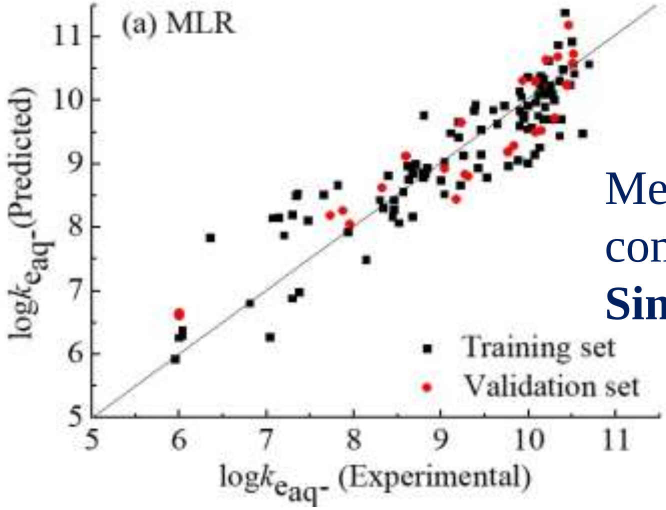
⇩ Develop

Quantitative structure-activity relationship (QSAR)

e.g. MLR-based QSAR model for aliphatic compounds

$\log k_{e_{aq}^-} = 9.383 - 0.823\ E_{LUMO} + 0.269\ nCconj - 1.324\ CATS2D\_03\_AA + 0.705\ F02[C\text{-}S] - 0.412 GATS1p - 0.631 Mor11e + 0.371\ MATS4m$

⇩ ke_{aq}^- prediction vs. experimental results



Mechanism of organic compounds reduction by e^-_{aq}:
Single electron transfer

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