The Application of Advanced Oxidation Processes (AOPs) and Development of Electrochemical Advanced Oxidation Processes (EAOPs)

From Bench to Pilot Scale

American Chemistry Society Annual Meeting, Boston, Aug 21th 2018

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Advanced Oxidation processes (AOPs) that produce hydroxyl radicals (HO·) at ambient temperature and atmospheric pressure are promising water treatment technology.

HO· radicals are highly reactive electrophiles, that react rapidly and non-selectively with the electron-rich sites of compounds.

HO· radicals are capable of mineralizing organic compounds into carbon dioxide CO₂ and water H₂O.
Introduction – What are AOPs? 2/2

- According to Bolton and Carter (Bolton and Cater, 1994), the following general pattern of oxidation is observed for AOPs.

- The most significant observed by-products are the carboxylic acids, due to the fact that the second order rate constants for these compounds are much lower than those for most organics. However, if adequate reaction time is provided, all by-products (>99% as measured by a TOC mass balance) are destroyed.

- Oxidized Pollutants are more biodegradable. We will show a practical application.
# AOPs Investigated

<table>
<thead>
<tr>
<th>No.</th>
<th>AOPs technologies names</th>
<th>AOPs technologies reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O₃/NOM</td>
<td>O₃ + NOM → HO•+byproducts</td>
</tr>
<tr>
<td>2</td>
<td>O₃/H₂O₂</td>
<td>2O₃ + H₂O₂ → 2HO•+3O₂</td>
</tr>
<tr>
<td>3</td>
<td>O₃/Activated Carbon</td>
<td>O₃ + Activated Carbon → HO•+byproducts</td>
</tr>
<tr>
<td>4</td>
<td>Fentons</td>
<td>Fe²⁺ + H₂O₂ → HO•+Fe³⁺ + OH⁻</td>
</tr>
<tr>
<td>5</td>
<td>Fenton/RGO α–FeooH</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Peroxymonosulfate/Ascorbic Acid</td>
<td>HSO₅⁻ + H₂A → SO₄⁻•+H⁺ + A⁻ + H₂O</td>
</tr>
<tr>
<td>7</td>
<td>Peroxymonosulfate/CoFeNi</td>
<td>HSO₅⁻ + Co(II) → SO₄⁻•+Co(III) + OH⁻</td>
</tr>
<tr>
<td>8</td>
<td>UV/H₂O₂</td>
<td>H₂O₂ + hν → 2HO•</td>
</tr>
<tr>
<td>9</td>
<td>UV/TiO₂</td>
<td>TiO₂ + hν + OH⁻ + O₂ → HO•+O₂⁻•+TiO₂</td>
</tr>
<tr>
<td>10</td>
<td>Solar light/TiO₂ /H₂O₂</td>
<td>TiO₂ + H₂O₂ + e⁻ → HO•+OH⁻ + TiO₂</td>
</tr>
<tr>
<td>11</td>
<td>UV/Persulfate</td>
<td>S₂O₈²⁻ + hν → 2SO₄⁻</td>
</tr>
<tr>
<td>12</td>
<td>UV/HOCl</td>
<td>HOCl + hν → HO•+Cl⁻</td>
</tr>
</tbody>
</table>

## Electrochemical AOPs

**Anode:** H₂O → HO• + e⁻ + H⁺
Principals of Electrochemical AOPs

Direct Oxidation
(Direct Electron Transfer on Anode)

&

Indirect Oxidation
(Oxidants Generated on Anode)

Electrochemical Advanced Oxidation

Organic Compounds $\xrightarrow{\text{OH}^\cdot \text{H}_2\text{O}}$ Intermediates (Aldehydes, Carboxylic Acids) $\xrightarrow{\text{OH}^\cdot \text{H}_2\text{O}}$ CO$_2$ + H$_2$O

Electrochemical Oxidation

Anode $\xrightarrow{\text{Pollutants}}$ Oxidation

Cathode $\xrightarrow{\text{Reduction}}$

Power Supply $\xrightarrow{e^-}$
Hydroxyl Radical Generation for 2D Electrode

We use semiconductors as anode materials

\[ \text{Anode} \rightarrow h_{vb}^{+} + e_{cb}^{-} \]
\[ h^{+} + H_2O \rightarrow HO \cdot +H^{+} \]

Electron flow depends on ion flow

Wastewater Flow
Three-Dimensional EAOP System

Anode $\rightarrow h_{vb}^+ + e_{cb}^-$

$e + H^+ \rightarrow 1/2H_2$

$\text{Cathode}$

$\text{Anode} \rightarrow h_{vb}^+ + e_{cb}^-$

$h^+ + H_2O \rightarrow HO \cdot +H^+$

Schematic of the three-dimensional electrode system. The anode material is a wire mesh of blue-TiO$_2$ nanotubes combined with SnO$_2$-Sb.
Electrochemical Oxidation Processes: **2-Dimensional** and **3-Dimensional Electrodes**

3D Electrode:
- Lower cell voltage, lower EE/O
- Works with low ionic strength
# Band Gap Engineering

## Loss Electron Oxidation (LEO)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Oxidation Potential vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H_2O \rightarrow 4H^+ + 4e^- + O_2$</td>
<td>$E^0 = -1.23 , V$</td>
</tr>
<tr>
<td>$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$</td>
<td>$E^0 = -1.77 , V$</td>
</tr>
<tr>
<td>$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$</td>
<td>$E^0 = -2.01 , V$</td>
</tr>
<tr>
<td>$H_2O + O_2 \rightarrow O_3 + 2H^+ + 2e^-$</td>
<td>$E^0 = -2.07 , V$</td>
</tr>
<tr>
<td>$SO_4^{2-} \rightarrow SO_4^- + e^-$</td>
<td>$E^0 = -2.60 , V$</td>
</tr>
<tr>
<td>$H_2O \rightarrow HO \cdot +H^+ + e^-$</td>
<td>$E^0 = -2.74 , V$</td>
</tr>
</tbody>
</table>

## Gain Electron Reduction (GER)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reduction Potential vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H^+ + 2e^- \rightarrow H_2$</td>
<td>$E^0 = 0.00 , V$</td>
</tr>
<tr>
<td>$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$</td>
<td>$E^0 = 0.62 , V$</td>
</tr>
</tbody>
</table>

Anode $\rightarrow$ $h_{vb}^+ + e_{cb}^-$

$h^+ + H_2O \rightarrow HO \cdot +H^+$

Ideally, we want every electron to create one HO·!
Multi-Layered Semiconductor Anode: Mixed Metal Oxide electrode (MMO)

Base substrate for Anode 1 and 2: Ti (2~3 mm thick)

**Anode 1:** TiO$_2$ Nanotubes/SnO$_2$-Sb/PTFE-PbO$_2$
**Inner Layer:** TiO$_2$ Nanotube array
**Intermediate layer:** -SnO$_2$-Sb (Sb$_2$O$_4$)
**Outer Layer:** PTFE-PbO$_2$

**Anode 2:** Blue TiO$_2$ Nanotubes/Aged SnO$_2$-Sb
**Inner Layer:** Blue TiO$_2$ Nanotube array
**Outer Layer:** -SnO$_2$-Sb (Sb$_2$O$_4$)

TiO$_2$ band gap: rutile 3.0 eV, anatase 3.2 eV, blue 3.3 eV
SnO$_2$ band gap: rutile 3.6 eV; PbO$_2$ 1.6 eV (good for higher current densities)
SEM Characterization of Layers, Anode #1

Anode #1: TiO$_2$ Nanotubes/SnO$_2$-Sb/PTFE-PbO$_2$

SEM of (a). TiO$_2$-Nanotubes Substrate, (b). SnO$_2$-Sb intermediate layer, (c). PTFE/PbO$_2$ electrode
Half-Coated, Non-Aged vs. Fully Coated, Aged, Anode #2

Anode #2. Blue TiO$_2$ Nanotubes/Aged SnO$_2$-Sb

Half coated surface (coated only 5 times which still expose some nanotubes surface) with non-aging sol-gel (exhibit less compact morphology and large crystal size).

Fully coated aged SnO$_2$-Sb layer (15 times coating) shows compact crystals configuration and smaller size which improved surface area and surface reaction sites.

The estimated life time of Blue TiO$_2$ nanotubes and Aged SnO$_2$-Sb is 2189 and 4794 h at operational current densities of 10 and 5 mA/cm$^2$
Characterization: Voltammetry

Linear sweep voltammetry (LSV) of the #1, #2 anode, BDD for a 0.5 M H₂SO₄ solution (pH = 0). Scan rate is 10 mV/s. The standard reduction potentials (pH=0) for O₂, H₂O₂, O₃ and HO· are +1.23 V, +1.77 V, +2.07 V and +2.74 V.
\[
\frac{d[BA]}{dt} = k_{BA,HO} \times [BA] \times [HO]_{ss}
\]

\[= k_{BA}[BA]\]

\[[HO]_{ss} = \frac{k_{BA}}{k_{BA,HO}}\]

\[k_{BA,HO} = 5.9 \times 10^9 L/(mol\cdot s)\]

The steady state hydroxyl radical concentration is estimated from 1 mM benzoic acid degradation in a 30 mM NaClO₄ at 5 mA/cm². \([HO\cdot] = k_{BA}/k_{HO}\)

Hydroxyl Radicals Production Comparison

Anode material #2: 7.43 × 10⁻¹⁴ mol/L

Anode material #1: 4.77 × 10⁻¹⁴ mol/L

Actual industrial used anode: Ti/PbO₂

Pilot treatment results will show in a minute

These blue NTA are unstable because they are not coated with SnO₂ – Sb.
The stoichiometric equation for benzoic acid is given as

\[ C_7H_6O_2 + 12H_2O \rightarrow 7CO_2 + 30H^+ + 30e^- \]

We define the electron efficiency to be

\[ EE = \frac{32}{12} \cdot \frac{n}{4x} \cdot \frac{d(TOC)}{d(COD)} \]

Where TOC in mg (c)/L and COD in mg (O_2)/L, n is the number of electrons transfer from the anode for a complete oxidation reaction and x is the number of carbon atoms in the organic contaminants.

According to the equation and calculation, the electron efficiency for 2D and 3D systems in this case are

\[ EE(2D) = 0.866 (86.6\%) \text{ and } EE(3D) = 1.067 (106.7\%) \]
Mass Transfer Impact of EAOPs

We used Differential Column Batch Reactor (DCBR) in experiments

Investigate & optimize electrode spacing & fluid velocity
Mass Transfer Impact: Electrode Spacing for 2D Electrode

(a) ofloxacin destruction by #1 anode for various electrode spacing (b) pseudo-first-order rate constants (c) EE/O. Anode surface area 10 cm², electrode spacing 1 cm, fluid velocity 0.033 m/s, initial ofloxacin concentration 20 mg/L, voltage 3.5-8.6 V, electrolyte concentration is 0.05 M Na₂SO₄, pH value 6.25 and temperature is 25 °C.
Mass Transfer Impact: Fluid Velocity

(a) ofloxacin destruction on #1 anode for various fluid velocity (b) pseudo-first-order rate constants (c) EE/O. Anode surface area 10 cm², electrode spacing 1 cm, fluid velocity 0.033 m/s, initial ofloxacin concentration 20 mg/L, voltage 3.5-8.6 V, electrolyte concentration is 0.05 M Na₂SO₄, pH value 6.25 and temperature is 25 °C.
Mass Transfer Impact: Effectiveness Factor

Plain channel:

\[
\Omega = \frac{r_{obs}}{r_{max}} = \frac{k_{obs}[R]}{k_{max}[R]}
\]

\[
\Omega = \frac{k_f \cdot \theta}{k_f \cdot \theta + (k_{Max}) \cdot d}
\]

Sherwood number:

\[
Sh = \frac{k_f \cdot d}{D_l} = 3.3 \cdot \left( \frac{d}{l} \cdot Re \cdot Sc \right)^{\frac{1}{3}}
\]

Reynolds number:

\[
Re = \frac{\rho \cdot u \cdot d}{\mu}
\]

Schmidt number:

\[
Sc = \frac{\mu}{\rho \cdot D_l}
\]

Effectiveness factor in different fluid velocity and the best fitted model. #1 anode surface area 10 cm², electrode spacing 1 cm, electrolyte 0.05 M Na₂SO₄ solution, current density 30 mA/cm², initial ofloxacin concentration 20 mg/L, voltage 6.3-6.4 v, pH value 6.25, temperature 25 °C.

\(\Omega = 0.436\) means more than 56% oxidation rate reduced by mass transfer!
Many AOP follow a pseudo-first order rate. EE/O is useful because if EE/O is .5kW/hr-order then if you supply .5, 1, 1.5 kW/m³ then you will 90, 99, 99.9 % destruction of the parent compound. Note COD and TOC have a much slower rate. Byproducts are less toxic and more biodegradable.
EE/O in Conventional AOPs

Conventional AOP Example: EE/O in UV/H₂O₂

\[
EE/O = \frac{P \times t}{V \times \log \left( \frac{C_0}{C} \right)} + \frac{C_{H_2O_2} \times 0.0022 \text{lb} \times E_{H_2O_2}}{\log \left( \frac{C_0}{C} \right)}
\]

- \(P\): total lamp power in kW;
- \(t\): irradiation time, s;
- \(V\): the reactor volume, m³;
- \(C_0\): the initial concentration of benzene, M;
- \(C\): the final concentration of benzene, M;
- \(P_{UV}\): UV intensity, Einstein/L-s
- \(E_{H_2O_2}\): energy used to produce H₂O₂, 4.9 kWh/lb

\[
[H_2O_2]_0, [HCO_3]_0, [NO_3]_0, [NO_2]_0: \text{initial concentration of } H_2O_2, \text{M}
\]
\[
[R]_0: \text{initial concentration of target contaminant }, \text{M}
\]
\[
L: \text{effective pathlength, cm}^{-1}
\]
\[
\epsilon_{H_2O_2}, \epsilon_R \text{ and } \epsilon_R: \text{molar absorption coefficients for } H_2O_2, \text{target contaminant and NOM, respectively}
\]
\[
A = (\epsilon_{H_2O_2} [H_2O_2]_0 + \epsilon_R [R]_0 + \epsilon_{NOM} [NOM]_0) L
\]
\[
k_1, k_2, k_3 \text{ and } k_4: \text{second order rate constants between (i) } HO \cdot \text{ and } H_2O_2, \text{M}^{-1}\text{s}^{-1};\text{(ii) } HO \cdot \text{ and } HCO_3^-, \text{M}^{-1}\text{s}^{-1}; \text{(iii) } HO \cdot \text{ and } \text{NOM, } (\text{mg/L})^{-1}\text{s}^{-1}; \text{(iv) } HO \cdot \text{ and target contaminant, M}^{-1}\text{s}^{-1}\text{, respectively}
\]

\[
EE/O = \frac{2.303 \times P \times (k_1[H_2O_2]_0 + k_2[HCO_3^-]_0 + k_3[NOM]_0 + k_4[R]_0) \times (\epsilon_{H_2O_2} [H_2O_2]_0 + \epsilon_R [R]_0 + \epsilon_{NOM} [NOM]_0)}{P_{UV} \times k_4 \times \epsilon_{H_2O_2} [H_2O_2]_0 \times (1 - 10^{-A}) \times V}
+ 34 \text{ gram/L} \times [H_2O_2]_0 \times 0.0022 \text{ lb/gram} \times E_{H_2O_2} \times 1000 \text{ L/m}^3
\]

- Target contaminant concentrations, oxidant dosage, NOM determine the EE/O of conventional AOPs
EE/O in EAOPs

EE/O = \frac{v \times j \times A \times V \times t}{V \times \log \left( \frac{C_0}{C} \right)} = \frac{v \times j \times A \times t}{\log \left( \frac{C_0}{C} \right)}

v, voltage, \text{V}  
\begin{align*}
  j, \text{current density, } \frac{\text{mA}}{\text{cm}^2} \\
  A, \text{surface area per volume, } \frac{\text{m}^2}{\text{m}^3} \\
  V, \text{volume, } \text{m}^3 \\
  C, \text{concentration, } \frac{\text{mol}}{\text{m}^3} \\
  k_s, \text{surface reaction rate, } \text{s}^{-1} \\
  k_{obs}, \text{observed reaction rate, } \text{s}^{-1} \\
  \Omega, \text{effectiveness factor}
\end{align*}

EE/O = \frac{v \times j \times A}{0.434 \times (k_s) \times \Omega}

\Omega = \frac{k_{obs}}{k_s}

- Target contaminants concentration dose does not effect EE/O in EAOPs
- EE/O is a constant under same operational conditions
Water Streams Conductivity Guide

Conductivity, µS/cm

- Seawater
- Industrial Wastewater
- Surface Water
- Potable Water In The US
- Tap Water
- Distilled Water
- Ultrapure Water

0.1  1  10  100  1000  10000  100000  100000
Degradation of 1 mmol/L benzoic acid in a 470 mL differential column batch reactor, pH controlled ~6.8, surface water used, has a low conductivity 112 µs/cm, controlled current density is 30 mA/cm², 2D anode size is 10 cm², 3D used 80 meshed Ti gauze has surface area 7.18 cm²/10 cm², DCBR operated at Re 194, Sc 2727, Sh 194, $k_f \times 10^{-6}$ m/s, $D_l 9 \times 10^{-6}$ cm²/s
EE/O Analysis in EAOPs

<table>
<thead>
<tr>
<th>Electrolyte Concentration</th>
<th>BA concentration</th>
<th>Voltage</th>
<th>Current Density</th>
<th>EE/O</th>
<th>Voltage</th>
<th>Current Density</th>
<th>EE/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/L</td>
<td>mg/L</td>
<td>V</td>
<td>mA/cm²</td>
<td>kWh/m³</td>
<td>V</td>
<td>mA/cm²</td>
<td>kWh/m³</td>
</tr>
<tr>
<td>Surface Water+BA</td>
<td>~0.0004 (113 µS/cm)</td>
<td>24 (0.2 mM)</td>
<td>60</td>
<td>10.5</td>
<td>15.2</td>
<td>10.5</td>
<td>8.68</td>
</tr>
<tr>
<td>Surface Water+BA</td>
<td>0.0004</td>
<td>122 (1 mM)</td>
<td>60</td>
<td>10.5</td>
<td>5.3</td>
<td>30.4</td>
<td>2.90</td>
</tr>
<tr>
<td>Industrial Water+BA</td>
<td>0.1 (16210 µS/cm)</td>
<td>24</td>
<td>7.3</td>
<td>30.4</td>
<td>5.3</td>
<td>30.4</td>
<td>2.90</td>
</tr>
<tr>
<td>Industrial Water+BA</td>
<td>0.1</td>
<td>122</td>
<td>8</td>
<td>30.4</td>
<td>5.3</td>
<td>30.4</td>
<td>2.90</td>
</tr>
</tbody>
</table>

- Ionic strength is important in EAOPs, NOM is not.
- Initial concentration, \( C_0 \), does not effect EE/O (at least for the concentrations we tested).
- Accordingly, the pseudo – first surface rate constant is same for different influent concentrations and the same operational conditions for the conditions we tested.
- We expect to see the reaction rate to decrease with high \( C_0 \) because at high concentrations all the reactions site on the anode will be occupied, preventing the oxidation rate from increasing (Langmuir-Hinshelwood Hougen Watson kinetics, confirmation needed).
Conventional AOPs vs. EAOPs Modeling 1/3

A case study to compare EEOs for:

UV/H₂O₂, H₂O₂/O₃, UV/HOCl, UV/Persulfate, UV/TiO₂

EAOPs (two-dimensional and three-dimensional)

Simulation Conditions:
[\text{HCO}_3^-] = 3 \text{ mM}; [\text{NOM}] = 2 \text{ mg/L}; [\text{Cl}^-] = 0.001 \text{ M};
pH = 7; k_{BA} = 5.9 \times 10^{-9} \text{ L/(mol·s)}

Same 2.2 W input energy gives UV light intensity = 1.64 \times 10^{-6} \text{ Einstein s}^{-1} \text{ L}^{-1};
Initial Concentrations [R] (Benzoic Acid in this case) = 20, 200, 2000 mg/L;

Quantum yield:
UV/H₂O₂ = 0.5, UV/HOCl = 0.9, UV/Persulfate = 0.7,
UV/TiO₂ = 0.04 (light transmission efficiency = 0.4);

Chemical production energy:
H₂O₂ = 4.9 kWh/lb, persulfate = 4.9 kWh/lb, HOCl = 5.1 kWh/lb, O₃ = 5 kWh/lb;

Note: TiO₂ and electrodes production energies are not included in simulation

EAOPs assumptions & parameters:
J = 30 mA/cm², 2D anode size A = 10 cm², 3D anode size A= 7.18 cm² (80 meshed Ti gauze)
Sc = 2727, Sh = 194, D_l = 9 \times 10^{-6} \text{ cm}^2/\text{s}, d = 1 \text{ cm}

Note: pumping energy is small compare to electricity and neglected in simulation

Q = 20 mL/min, Re = 18.51, k_f = 2.35 \times 10^{-6} \text{ m/s}
Q = 500 mL/min, Re = 462.96, k_f = 6.88 \times 10^{-6} \text{ m/s}
Q = 2000 mL/min, Re = 2037.04, k_f = 1.13 \times 10^{-5} \text{ m/s (Re < 2100 in laminar flow)}
# Conventional AOPs vs. EAOPs Modeling 2/3

**Minimal EE/O (kWh/m³)**

<table>
<thead>
<tr>
<th>AOPs</th>
<th>Minimal EE/O (kWh/m³)</th>
<th>Optimal Oxidant/Catalyst Dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/TiO₂</td>
<td>10.38</td>
<td>[TiO₂] = 300 mg/L</td>
</tr>
<tr>
<td>UV/Persulfate</td>
<td>1.28</td>
<td>[Persulfate] = 1.17 g/L</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>0.90</td>
<td>[H₂O₂] = 0.204 g/L</td>
</tr>
<tr>
<td>UV/HOCl</td>
<td>3.67</td>
<td>[HOCl] = 0.14 g/L</td>
</tr>
<tr>
<td>H₂O₂/O₃</td>
<td>0.015</td>
<td>[H₂O₂] = 0.0206 mg/L</td>
</tr>
</tbody>
</table>

**Optimal EE/O (kWh/m³)**

<table>
<thead>
<tr>
<th>AOPs</th>
<th>Optimal Oxidant/Catalyst Dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/TiO₂</td>
<td>[TiO₂] = 300 mg/L</td>
</tr>
<tr>
<td>UV/Persulfate</td>
<td>[Persulfate] = 1.6 g/L</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>[H₂O₂] = 0.612 g/L</td>
</tr>
<tr>
<td>UV/HOCl</td>
<td>[HOCl] = 0.26 g/L</td>
</tr>
<tr>
<td>H₂O₂/O₃</td>
<td>[H₂O₂] = 0.028 mg/L</td>
</tr>
</tbody>
</table>

**Ion Strength Increase**

<table>
<thead>
<tr>
<th>Electrolyte (Na₂SO₄)</th>
<th>2D-EAOP EE/O (kWh/m³)</th>
<th>3D-EAOP EE/O (kWh/m³)</th>
<th>2D-EAOP EE/O (kWh/m³)</th>
<th>3D-EAOP EE/O (kWh/m³)</th>
<th>2D-EAOP EE/O (kWh/m³)</th>
<th>3D-EAOP EE/O (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0M</td>
<td>37.02</td>
<td>37.02</td>
<td>35.45</td>
<td>35.45</td>
<td>34.04</td>
<td>34.04</td>
</tr>
<tr>
<td>0.001M</td>
<td>64.66</td>
<td>42.05</td>
<td>60.15</td>
<td>22.60</td>
<td>56.34</td>
<td>21.36</td>
</tr>
<tr>
<td>0.005M</td>
<td>37.81</td>
<td>20.69</td>
<td>35.59</td>
<td>19.37</td>
<td>33.67</td>
<td>18.24</td>
</tr>
<tr>
<td>0.01M</td>
<td>26.76</td>
<td>15.52</td>
<td>25.04</td>
<td>14.48</td>
<td>23.57</td>
<td>13.60</td>
</tr>
<tr>
<td>0.1M</td>
<td>4.69</td>
<td>12.94</td>
<td>4.55</td>
<td>12.07</td>
<td>4.43</td>
<td>11.32</td>
</tr>
</tbody>
</table>

**Mass Transfer Increase**

- **Re = 18.51**
- **Re = 462.96**
- **Re = 2037.04**
### Conventional AOPs vs. EAOPs Modeling 3/3

**[R]₀ = 20 mg/L**

~ 16 mg/L TOC

<table>
<thead>
<tr>
<th>AOPs</th>
<th>Minimal EE/O (kWh/m³)</th>
<th>Optimal Oxidant/Catalyst Dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/TiO₂</td>
<td>10.38</td>
<td>[TiO₂]=300 mg/L</td>
</tr>
<tr>
<td>UV/Persulfate</td>
<td>1.28</td>
<td>[Persulfate]=1.17 g/L</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>0.90</td>
<td>[H₂O₂]=0.204 g/L</td>
</tr>
<tr>
<td>UV/HOCl</td>
<td>3.67</td>
<td>[HOCl]=0.14 g/L</td>
</tr>
<tr>
<td>H₂O₂/O₃</td>
<td>0.015</td>
<td>[H₂O₂]=0.0206 mg/L</td>
</tr>
</tbody>
</table>

**For low concentration treatment objectives, EAOPs may not be as good as compared to conventional AOPs.**

**Conventional UV/H₂O₂ and H₂O₂/O₃ are the best conventional AOPs for BA.**

<table>
<thead>
<tr>
<th>Electrolyte (Na₂SO₄)</th>
<th>2D-EAOP EE/O (kWh/m³)</th>
<th>3D-EAOP EE/O (kWh/m³)</th>
<th>2D-EAOP EE/O (kWh/m³)</th>
<th>3D-EAOP EE/O (kWh/m³)</th>
<th>2D-EAOP EE/O (kWh/m³)</th>
<th>3D-EAOP EE/O (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0M</td>
<td>37.02</td>
<td>35.45</td>
<td>56.34</td>
<td>34.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001M</td>
<td>64.66</td>
<td>20.69</td>
<td>33.67</td>
<td>18.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005M</td>
<td>37.81</td>
<td>15.52</td>
<td>23.57</td>
<td>13.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>26.76</td>
<td>12.94</td>
<td>20.04</td>
<td>11.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1M</td>
<td>4.69</td>
<td>12.07</td>
<td>4.43</td>
<td>11.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Re = 18.51**

**Mass Transfer Increase**

**Re = 462.96**

**Re = 2037.04**

**Ion Strength Increase**
Conventional AOPs vs. EAOPs Modeling 3/3

- For high concentration treatment objectives, EAOPs are more energy efficient.

- 3D-EAOP saves more energy than 2D because it requires lower applied voltage.

- 3D-EAOP works better than 2D in low ion strength treatment.

---

For the given conditions:

- \([R]_0 = 2000 \text{ mg/L}\)
- \(\sim 1379 \text{ mg/L TOC}\)

<table>
<thead>
<tr>
<th>Electrolyte (Na$_2$SO$_4$)</th>
<th>2D-EAOP EE/O (kWh/m$^3$)</th>
<th>3D-EAOP EE/O (kWh/m$^3$)</th>
<th>2D-EAOP EE/O (kWh/m$^3$)</th>
<th>3D-EAOP EE/O (kWh/m$^3$)</th>
<th>2D-EAOP EE/O (kWh/m$^3$)</th>
<th>3D-EAOP EE/O (kWh/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0M</td>
<td>37.02</td>
<td>35.45</td>
<td>34.04</td>
<td>31.34</td>
<td>33.67</td>
<td>31.12</td>
</tr>
<tr>
<td>0.001M</td>
<td>64.66</td>
<td>60.15</td>
<td>56.34</td>
<td>53.14</td>
<td>53.67</td>
<td>52.84</td>
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<tr>
<td>0.005M</td>
<td>37.81</td>
<td>35.59</td>
<td>33.67</td>
<td>31.84</td>
<td>32.67</td>
<td>31.72</td>
</tr>
<tr>
<td>0.01M</td>
<td>26.76</td>
<td>25.04</td>
<td>23.57</td>
<td>22.34</td>
<td>22.57</td>
<td>22.12</td>
</tr>
<tr>
<td>0.1M</td>
<td>4.69</td>
<td>4.55</td>
<td>4.43</td>
<td>4.32</td>
<td>4.37</td>
<td>4.31</td>
</tr>
</tbody>
</table>

Re = 18.51  Re = 462.96  Re = 2037.04

Mass Transfer Increase

Ion Strength Increase
Limiting Current in Different Conditions

\[ j_{\text{lim}} = n \times F \times k_f \times C_{\text{salt}} \]

<table>
<thead>
<tr>
<th>Electrolyte Concentration</th>
<th>Q</th>
<th>Q</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2SO4</td>
<td>ml/min</td>
<td>ml/min</td>
<td>ml/min</td>
</tr>
<tr>
<td>20</td>
<td>500</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>Re</td>
<td>Re</td>
<td></td>
</tr>
<tr>
<td>18.52</td>
<td>462.96</td>
<td>1851.85</td>
<td></td>
</tr>
<tr>
<td>kf</td>
<td>kf</td>
<td>kf</td>
<td></td>
</tr>
<tr>
<td>m/s</td>
<td>m/s</td>
<td>m/s</td>
<td></td>
</tr>
<tr>
<td>2.35405E-06</td>
<td>6.88E-06</td>
<td>1.09E-05</td>
<td></td>
</tr>
<tr>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
</tr>
<tr>
<td>mol/L</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>0.001</td>
<td>0.68</td>
<td>1.99</td>
<td>3.16</td>
</tr>
<tr>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
</tr>
<tr>
<td>mol/L</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>0.005</td>
<td>3.41</td>
<td>9.96</td>
<td>15.81</td>
</tr>
<tr>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
</tr>
<tr>
<td>mol/L</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>0.01</td>
<td>6.81</td>
<td>19.92</td>
<td>31.63</td>
</tr>
<tr>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
</tr>
<tr>
<td>mol/L</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>0.05</td>
<td>34.07</td>
<td>99.62</td>
<td>158.14</td>
</tr>
<tr>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
<td>jlim</td>
</tr>
<tr>
<td>mol/L</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>0.1</td>
<td>68.14</td>
<td>199.24</td>
<td>316.27</td>
</tr>
</tbody>
</table>
Full Scale Reactor Design

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent concentration</td>
<td>$C_0$</td>
<td>mg/L</td>
<td>20</td>
</tr>
<tr>
<td>Effluent concentration</td>
<td>$C_e$</td>
<td>mg/L</td>
<td>0.2</td>
</tr>
<tr>
<td>Flow rate</td>
<td>$Q$</td>
<td>m³/day</td>
<td>1000</td>
</tr>
<tr>
<td>Pseudo first order rate constant</td>
<td>$k$</td>
<td>/min</td>
<td>0.042</td>
</tr>
<tr>
<td>Size of reactor</td>
<td>$V_{\text{Required}}$</td>
<td>m³</td>
<td>38 m³</td>
</tr>
<tr>
<td>Detention time</td>
<td>$\tau$</td>
<td>min</td>
<td>54.8</td>
</tr>
<tr>
<td>Electrode spacing</td>
<td>$d$</td>
<td>cm</td>
<td>1</td>
</tr>
<tr>
<td>Fluid velocity</td>
<td>$u$</td>
<td>m/s</td>
<td>0.033</td>
</tr>
<tr>
<td>Electrolyte Na$_2$SO$_4$ Concentration</td>
<td></td>
<td>M</td>
<td>0.05</td>
</tr>
<tr>
<td>Current density</td>
<td>$J$</td>
<td>mA/cm$^2$</td>
<td>30</td>
</tr>
</tbody>
</table>

Assuming a Plug Flow Reactor (PFR) to be Confirmed with CFD
Full Scale Reactor Design

Rough Design of Reactor (top view):

Influent

Effluent

10.5 meters long

10 meters electrodes

10 meters

1.5 cm

95 cm

Reactor Channel

2 meters deep
The total costs (capital costs + energy costs) as a function of different electrode spacing for different theoretical reaction rate. In here, the treatment objective is 99% removal, flow rate is 1000 m³/day and the fluid velocity is 0.0116 m/s. The flow channel has eddy promoter and its electrode spacing and obstacle distance ratio is 1/3. The electricity price is $0.0512/kWh and the pumping power is 8.53 kW. The electrode price is $300/m² and its lifetime is 2000 h.
The total costs (capital costs + energy costs) as a function of different electrode spacing for different theoretical reaction rate. In here, the treatment objective is 99% removal, flow rate is 1000 m$^3$/day and the fluid velocity is 0.0116 m/s. The flow channel has eddy promoter and its electrode spacing and obstacle distance ratio is 1/3. The electricity price is $0.0512$/kWh and the pumping power is 8.53 kW. The electrode price is $300$/m$^2$ and its lifetime is 2000 h.
Computer-based First-Principles Kinetic Model

* 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

- Input of Parent Contaminant as SMILES
- e.g. C(=C(Cl)Cl)(Cl)Cl

- Pathway Generator

- Reaction Rate Constant Estimator

- ODEs solver

- If $t \leq$ target time

- Mechanistic Reduction

- $\Delta G_{aq,calc}^{act}$

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

- Time-dependent Concentration Profiles of parent compounds, byproducts and intermediates

- Toxicity Estimator

- Profiles of relative toxicity

- Energy Efficiency Estimator

- Electrical energy required

- Experimental Validation
Complexity of Reaction Pathway

Example
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
Predicted Concentration Profiles of Trichloroethene (TCE) and Stable-byproducts in UV/H₂O₂ AOP

Comparison of concentration profiles of major species for experimental data (Li, Stefan, Crittenden, 2007 ES&T 41, 1696-1703) and simulation results

<table>
<thead>
<tr>
<th>Initial concentration of TCE</th>
<th>1.08 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration of O₂</td>
<td>2.2 mM</td>
</tr>
<tr>
<td>Initial concentration of H₂O₂</td>
<td>10.4 mM</td>
</tr>
<tr>
<td>Initial pH</td>
<td>5.9</td>
</tr>
<tr>
<td>Wave length of UV</td>
<td>200~300 nm</td>
</tr>
<tr>
<td>Light intensity</td>
<td>7.79×10⁻⁶ Einstein/L·s</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Completely mixed batch reactor</td>
</tr>
<tr>
<td>Reaction time</td>
<td>30 min</td>
</tr>
</tbody>
</table>

Reaction rate constants are obtained from group contribution method (Minakata et al., 2009 ES&T 43, 6220-6227) and literature including:

Li et al., 2009 ES&T 43, 2831-2837.
Li et al., 2007 ES&T 41, 1696-1703.

The photolysis of TCE was added manually because it is not included in this version of the pathway generator.
Comparison of number averaged molecular weight (MW) for experimental data (Vijayalakshmi et. al., *J. Appl. Polym. Sci.* 2006, 100, 3997-4003) and on-the-fly KMC model

The KMC model used a population number of $10^8$/L to represent a concentration of 1mol/L.

Time evolvement of the number of generated reactions for the degradation of PAM during the UV/TiO$_2$ process.

References


References


25. Xing, Linlin; Xie, Yongbing; Cao, Hongbin; Minakata, Daisuke; Zhang, Yi; Crittenden, John C.; “Activated carbon-enhanced ozonation of oxalate attributed to HO• oxidation in bulk solution and surface oxidation: Effects of the type and number of basic sites,” *Chemical Engineering Journal*, 2014, 245, 71-79.


References


