Treatment of Refractory Industrial Wastewater Using Chemical Oxidation and Biological Treatment

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John Crittenden¹, Xin Guo¹, Xiaoyang Meng¹, Jiuhui Qu², Huachun Lan², Jinming Luo¹,², Junfeng Niu³, Ruzhen Xie⁴ Duo Li⁵, Qian Feng⁶

¹Brook Byers Institute for Sustainable Systems, School of Civil and Environmental Engineering, Georgia Institute of Technology; ²Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences; ³State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University; ⁴College of Architecture and Environment, Sichuan University; ⁵CrittendenTech, Beijing and Atlanta; ⁶College of Environment Hohai University
Oxidation and Biological Treatment Synergies

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

- Organic pollutant $\rightarrow$ Aldehydes $\rightarrow$ Carboxylic acids $\rightarrow$ Carbon Dioxide and mineral acids

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.

Waste water becomes more biodegradable!
Electrochemical Processes
Electrochemical Oxidation Technology

Principles of Electrochemical Oxidation:

- The generation of hydroxyl radical (HO\(\cdot\)), reduction potential at 2.8 V.
- The mineralization of pollutants to \(\text{CO}_2\) and \(\text{H}_2\text{O}\).
Electrochemical degradation kinetics of Ofloxacin and electrical energy analysis on TiO₂ – based SnO₂ (Sb)/FR – PbO₂ electrode

Molecular Structure of Ofloxacin
Molar mass: 361.368 g/mol.

FR: Polytetrafluoroethylene Resin

SEM of (a). TiO₂ - Nano Tubes Substrate, (b). SnO₂ - Sb intermediate layer, (c). TiO₂ - based SnO₂(Sb)/FR - PbO₂ electrode
Band Gap Engineering

Objective:
Hydroxyl radical (HO·) production by electrochemical oxidation

Procedures:
1. Use DFT calculation to calculate the Projected Density Of States (PDOS) of potential material options and their band gaps.
2. Convert PDOS results (vacuum scale) to normal hydrogen electrode (NHE) scale and compare with the reduction potential of hydroxyl radical (HO·), 2.8 V (pH = 0).
3. Make the anode to create HO· and minimize byproducts, e.g., O₂, O₃, H₂O₂.

\[
\text{Anode} \rightarrow h^+ + e_{cb}
\]

\[
h^+ + H_2O \rightarrow HO\cdot + H^+
\]
## Band Gap Engineering

### Half reactions:

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$</td>
<td>-1.23</td>
</tr>
<tr>
<td>$H_2O_2$</td>
<td>$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$</td>
<td>-1.77</td>
</tr>
<tr>
<td>$O_3$</td>
<td>$O_2 + H_2O \rightarrow O_3 + 2H^+ + 2e^-$</td>
<td>-2.07</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>$2SO_4^{2-} \rightarrow S_2O_8^{2-} + e^-$</td>
<td>-2.43</td>
</tr>
<tr>
<td>$HO$</td>
<td>$H_2O \rightarrow HO^\bullet + H^+ + e$</td>
<td>-2.80</td>
</tr>
<tr>
<td>$h^+$</td>
<td>$h^+ + e \rightarrow Anode$</td>
<td>&gt;3.00</td>
</tr>
</tbody>
</table>
Band Gap Engineering

Linear Sweep Voltammetry of the TiO$_2$ – based SnO$_2$ (Sb)/FR – PbO$_2$ electrode:
In 0.5 M H$_2$SO$_4$ solution, scan rate: 10 mV/s
Geometry optimization for electrodes
(1) PbO₂,
(2) La-PbO₂,
(3) Gd-PbO₂
O: red balls,
Pb: gray balls,
La: blue ball,
Gd: green ball

Projected density of states of surface Pb atom on (a) PbO₂ (110),
(b) La-PbO₂ (110) and (c) Gd-PbO₂ (110) planes
XRD Results: All Peaks are Beta-PbO₂

X-ray diffraction patterns of (a) PbO₂, (b) La-Gd co-doped PbO₂

Doped PbO₂ have greater crystalinity. Size=34.42 nm and more active sites.

Crystal size=60.97 nm
the ratio of $\text{Pb}^{2+}/\text{Pb}^{4+}$ for La-Gd-PbO$_2$ electrode was 3.53, which was slightly larger than that of PbO$_2$ (2.78), More redox couples for Doped PbO$_2$

XPS separation spectrum of Pb 4f in PbO$_2$ electrode and La-Gd-doped PbO$_2$ electrode
Differential Column Batch Reactor

- The solution flows through the reactor.
- Due to recirculation of the solution, the reactor acts like a batch reactor.
- Reaction models can be used for fitting the kinetic curves and evaluating the mass transfer coefficients.
Differential Column Batch Reactor
Relationship between current density and pseudo first order rate constant on Ofloxacin:
Anode surface area = 10 cm², electrode spacing = 1 cm, fluid velocity = 0.033 m/s, voltage = 3.5 – 7.5 V, 
electrolyte = 0.05 M Na₂SO₄ solution, Ofloxacin concentration = 20 mg/L, pH = 6.25, T = 25 °C
Energy Efficiency

\[ EE/O = \frac{U \cdot J \cdot A \cdot (\frac{t}{60})}{V \cdot \log\left(\frac{C_{in}}{C_{out}}\right)} \]

U, voltage (V)
J, current density (A/m²)
A, electrode area (m²)
t, reaction time (min)
V, reactor volume (m³)

EE/O in Ofloxacin destruction vs. pseudo first order rate constants for current in the range of 5 – 50 mA/cm².
Various Variable: Electrolyte Concentration

Ofloxacin destruction under different electrolyte concentration:
Anode surface area = 10 cm², electrode spacing = 1 cm, fluid velocity = 0.033 m/s, current density = 30 mA/cm², voltage = 4.2 – 23.1 V, Ofloxacin concentration = 20 mg/L, pH = 6.25, T = 25 °C
Ofloxacin destruction under different electrode spacing:
Anode surface area = 10 cm², fluid velocity = 0.033 m/s, current density = 30 mA/cm², voltage = 5 – 12.8 V, electrolyte = 0.05 M Na₂SO₄ solution, Ofloxacin concentration = 20 mg/L, pH = 6.25, T = 25 °C
Impact of Fluid Velocity on Reactor Performance

Ofloxacin destruction under different fluid velocity:
Anode surface area = 10 cm², electrode spacing = 1 cm, current density = 30 mA/cm², voltage = 6.3 – 6.4 V, electrolyte = 0.05 M Na₂SO₄ solution, Ofloxacin concentration = 20 mg/L, pH = 6.25, T = 25 ℃
Flow Past a Flat Plate
## 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>2</td>
</tr>
<tr>
<td>Flow rate</td>
<td>$Q$</td>
<td>m$^3$/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>m$^3$</td>
<td>38 m$^3$</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>
<tr>
<td>Pseudo first order rate constant</td>
<td>$k$</td>
<td>/min</td>
<td>0.042</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):

1. 10.5 meters long
2. 10 meters electrodes
3. 1 meter
4. Reactor Channel
5. 2 meters deep
6. 10 meters
7. 5 cm
8. 95 cm
9. 1 meter
10. 5 cm
90% Ofloxacin destruction under different electrode spacing:
current density = 30 mA/cm², voltage = 5 – 12.8 V, electrolyte = 0.05 M Na₂SO₄ solution, Ofloxacin concentration = 20 mg/L, pH = 7, T = 25 °C
Electrochemical Oxidation Technology

**Ti/\(\text{SnO}_2\)-Sb-Ce**

1. The surface of electrode: porous, long life, high efficiency
2. Wide applications: high efficiency of ammonia removal and detoxification
3. Environmental friendly and no secondary pollution
4. Easy to operate with high degree of automation
5. Small footprint
6. No sludge

**Ti/\(\text{SnO}_2\)-Sb/Ce-PbO\(_2\)**
Electrochemical Oxidation Technology Case
Coking Waste Water

Capacity: 3600 m³/day

<table>
<thead>
<tr>
<th></th>
<th>Influent</th>
<th>Effluent</th>
<th>OpEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>90 ~ 180</td>
<td>&lt; 50</td>
<td>5 ~ 8 kWh/m³</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>4.8</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>Total CN⁻ (mg/L)</td>
<td>0.85</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.35</td>
<td>7.8</td>
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</tr>
</tbody>
</table>
**CASE STUDY: RO CONCENTRATE**

**Chemical Plant**  
**Capacity:** 600 m³/day

<table>
<thead>
<tr>
<th></th>
<th>Influent</th>
<th>Effluent</th>
<th>OpEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>360-400</td>
<td>&lt; 50</td>
<td>15 kWh/m³</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>1.86</td>
<td>&lt; 0.5</td>
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<tr>
<td>TOC</td>
<td>110-137</td>
<td>&lt; 17</td>
<td></td>
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<tr>
<td>pH</td>
<td>8.7</td>
<td>8.0</td>
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</tbody>
</table>
CASE STUDY: RO CONCENTRATE

Chemical Plant
Capacity: 1200 m³/day

<table>
<thead>
<tr>
<th></th>
<th>Influent</th>
<th>Effluent</th>
<th>OpEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>60</td>
<td>&lt; 30</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
<td>8.1</td>
<td>4 kWh/m³</td>
</tr>
</tbody>
</table>
## CASE STUDY: COKING WASTE WATER REUSE

**Chemical Plant in Hebei**

**capacity:** 800m³/day

<table>
<thead>
<tr>
<th></th>
<th>Influent</th>
<th>Effluent</th>
<th>OpEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>120~150</td>
<td>&lt; 50</td>
<td>6 kWh/m³</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>5.2</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>Total CN⁻ (mg/L)</td>
<td>0.08</td>
<td>&lt; 0.01</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>9.12</td>
<td>7.2</td>
<td></td>
</tr>
</tbody>
</table>
Full Scale Reactor in the Field
Coking and Char Waste Water Treatment

COD: influent ~150 mg/L
effluent < 50 mg/L

Flow rate: 432 cu. meters/day
## BENCH SCALE: REFINERY RO CONCENTRATE

Daqing Petrochemical Plant, China

<table>
<thead>
<tr>
<th></th>
<th>Influent</th>
<th>Effluent</th>
<th>OpEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>128</td>
<td>&lt; 50</td>
<td>6 kWh/m³</td>
</tr>
<tr>
<td>pH</td>
<td>8.12</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>
BENCH SCALE: ABS PRODUCED WATER

Daqing Petrochemical Plant, China

ABS Plastics (Acrylonitrile - Butadiene - Styrene)

<table>
<thead>
<tr>
<th></th>
<th>COD (mg/L)</th>
<th>OpEx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td>Electro Coagulation</td>
<td>&lt;1300</td>
<td>2kWh/m³</td>
</tr>
<tr>
<td>Electro Oxidation</td>
<td>&lt;1000</td>
<td>5kWh/m³</td>
</tr>
</tbody>
</table>

Ready for Biological Treatment?
Electrochemical Destruction of Acrylonitrile waste water

Fe$^{2+}$ online generation, high catalytic activity and increased HO· production
APPLICATIONS OF ELECTROCHEMICAL PROCESS

More than 50 successful installation for treatment of industrial waste water in China.

Waste water treated 50,000,000 m³/year; COD emission reduction 17800 tons, Heavy metal emission reduction 1736 tons, water saved 110,000,000 m³.
Pilot Test on Treatment of Acrylonitrile Waste Water

Influent COD 460mg/L, Effluent COD < 80 mg/L

1-chemical tank; 2-Feed water tank (after biological treatment); 3-Multi-phase separation; 4-Electrical Control System; 5-three stage electro chemical process; 6-Operation Desk; 7-Multi-phase separation; 8-equalization tank; 9-Biological Treatment

Pilot-scale: 1.0 m³/h
Pilot Test on Treatment of Acrylonitrile Waste Water

Multi-Phase Separation
Adding FeCl₃
Effluent pH = 2.9-3.1

Three stage electrochemical process
(Electro-Fenton)

Multi-Phase Separation
Use NaOH control pH to 6.8
Adding PAM as flocculant
Effluent pH around 7

Aerobic biological treatment
Pilot Test on Treatment of Acrylonitrile Waste Water

COD (mg/L) vs. Time (d)

- **First coagulation tank effluent**
- **First stage multi-phase separation**
- **Second stage multi-phase separation**
- **Aerobic treatment tank**

The graph shows the COD levels over time for different treatment stages in the pilot test.
# Pilot Test on Treatment of Acrylonitrile Waste Water

<table>
<thead>
<tr>
<th>Subject</th>
<th>Dosage</th>
<th>Price</th>
<th>Cost (USD / T)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron salt</td>
<td>0.6 kg</td>
<td>0.5 USD / kg</td>
<td>0.3</td>
<td>95 % FeCl3</td>
</tr>
<tr>
<td>Acid</td>
<td>25 mL</td>
<td>0.2 USD / kg</td>
<td>0.01</td>
<td>98 % H2SO4</td>
</tr>
<tr>
<td>Alkali</td>
<td>0.54 kg</td>
<td>0.1 USD / kg</td>
<td>0.04</td>
<td>Ca(OH)2</td>
</tr>
<tr>
<td>Electrode</td>
<td>/</td>
<td>/</td>
<td>0.3</td>
<td>3 month period</td>
</tr>
<tr>
<td>Electricity cost</td>
<td>/</td>
<td>0.2 USD / Kwh</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

**Diagram**

1. Composite flocculant
2. Sand filtration tank
3. Multi-phase catalytic tower
4. Aeration filter tank
5. Treatment: Backwash tank
6. Treated water

- Waste water
- Based on water quality
- Fe$^{2+}$
- Alkali
- UV
- Ozone generator
Photo-Catalytic (UV/TiO2) Oxidation
Process Flow Diagram for UV/TiO2

Source

Compressed Air

Racks

DO Control

Air Flow Controller

Compounded Air

Catalyst Recovery Unit

Discharge
Photo-Cat Capacity

Municipal

Lab

0.25 - 1 MGD

30 MGD

Industrial

DL: 5-50 kW

DDL: 10-100 kW

Multi-Pallet: >200 kW
Maintenance Free UV Quartz

- No Cleaning or Replacement
- No Wipers
No Quartz or Catalyst Fouling

35,000 hours continuous use
Turbidity, TDS Insensitive

- Unaffected by:
  - Turbidity, Dissolved Solids
  - Dissolved Metals, Opaque fluids
CFD and Light Penetration and HO Concentration Modeling

Fluence w/sq m

HO concentration

Y(m) Z(m)

0 0.5 1

0 0.5 1.5

100 200 300 400 500 600 700 800 900 1000 1100 1200

5E-09 1E-08 1.5E-08 2E-08 2.5E-08 3E-08 3.5E-08 4E-08 4.5E-08 5E-08
Lower power can be used when combined with downstream biodegradation (i.e., sand filter).

Essentially incorporating bio can reduce power requirements by 20% to 50% depending upon what final DOC concentration you are targeting.

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

Westerhoff, Moon, Minakata, Crittenden. Wat Res. 2009, 43, 3992-3998.
# World Oil Reserves

<table>
<thead>
<tr>
<th>Country</th>
<th>Reserves (bbl)</th>
<th>Share of World %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saudi Arabia</td>
<td>264,600,000,000</td>
<td>19.00%</td>
</tr>
<tr>
<td>Canada</td>
<td>175,200,000,000</td>
<td>12.58%</td>
</tr>
<tr>
<td>Iran</td>
<td>137,600,000,000</td>
<td>9.88%</td>
</tr>
<tr>
<td>Iraq</td>
<td>115,000,000,000</td>
<td>8.26%</td>
</tr>
<tr>
<td>Kuwait</td>
<td>104,000,000,000</td>
<td>7.47%</td>
</tr>
<tr>
<td>United Arab Emirates</td>
<td>97,800,000,000</td>
<td>7.02%</td>
</tr>
<tr>
<td>Venezuela</td>
<td>97,770,000,000</td>
<td>7.02%</td>
</tr>
<tr>
<td>Russia</td>
<td>74,200,000,000</td>
<td>5.33%</td>
</tr>
<tr>
<td>Libya</td>
<td>47,000,000,000</td>
<td>3.38%</td>
</tr>
<tr>
<td>Nigeria</td>
<td>37,500,000,000</td>
<td>2.69%</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>30,000,000,000</td>
<td>2.15%</td>
</tr>
<tr>
<td>Qatar</td>
<td>25,410,000,000</td>
<td>1.82%</td>
</tr>
<tr>
<td>China</td>
<td>20,350,000,000</td>
<td>1.46%</td>
</tr>
<tr>
<td>United States</td>
<td>19,120,000,000</td>
<td>1.37%</td>
</tr>
</tbody>
</table>

The Alberta Oil Sands
Oil Sands Surface Mining & Slurries
Oil Sands SAGD
Steam Assisted Gravity Drainage Process
Oil Sands Processing

- Oil Sands
- Bitumen Flotation Plant
- Tailings Pond
- Froth Treatment Plant
- Bitumen to Upgrader
Oil Sands + Water = Crude Oil

- Oil Sands
- Bitumen
- Synthetic Crude
UV/TiO$_2$, Photo-Cat OFS

Oil Sands Wastewater → CF-CMS ↓ Sand ↓ Oil ↓ Bitumen

→ OILS ↓ Naptha

→ AOP+ ↓ Toxicity ↓ NVTOC

Reuse Water
OILS Product Streams

No Waste Generated
UV/TiO$_2$, Photo-Cat OFS

Before

After
# Tailings Water Toxicity Removal

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw</th>
<th>CF-CMS</th>
<th>Photocatalytic (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Post</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microtox Toxicity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IC₅₀ (5min, 15°C)</td>
<td>3.9%</td>
<td>14.5%</td>
<td>86.0% &gt;100% &gt;100%</td>
</tr>
<tr>
<td>IC₅₀ (15min, 15°C)</td>
<td>3.1%</td>
<td>13.0%</td>
<td>86.1% &gt;100% &gt;100%</td>
</tr>
<tr>
<td>BOD-₅ (mg/L)</td>
<td>35</td>
<td>31</td>
<td>19 17 12</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>260</td>
<td>220</td>
<td>180 180 170</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>69.2</td>
<td>63.4</td>
<td>57.3 58.7 60</td>
</tr>
<tr>
<td>Low Level TSS (mg/L)</td>
<td>14</td>
<td>3</td>
<td>NA NA NA</td>
</tr>
<tr>
<td>UV Transmittance</td>
<td>13%</td>
<td>21%</td>
<td>31% 33% 40%</td>
</tr>
<tr>
<td>Napthenic Acids (mg/L)</td>
<td>30</td>
<td>29</td>
<td>12 7.8 3.4</td>
</tr>
<tr>
<td>VOCs Detected</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>4</td>
<td>NA</td>
<td>2 &lt;1 &lt;1</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>6</td>
<td>NA</td>
<td>2 &lt;1 &lt;1</td>
</tr>
<tr>
<td>Advantages</td>
<td>Disadvantages</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>---------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Long stability and can be preserved prior to use of H$_2$O$_2$.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• H$_2$O$_2$+UV → 2HO•</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Poor UV light absorption of H$_2$O$_2$</td>
<td></td>
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</tr>
<tr>
<td>• Special reactors required for UV illumination</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Need to deal with the H$_2$O$_2$ Residual</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**H₂O₂/UV**

**Low Pressure UV system (UV/H₂O₂)**

**Trojan Tech Performance:**
- 24 reactors
- H₂O₂ 10 mg/L
- Chemical 600lb/d
- 21300 kWh/d
- Total Cost $3029/d

**Median Pressure UV system (UV/H₂O₂)**

**Trojan Tech Performance:**
- 10 reactors
- H₂O₂ 10 mg/L
- Chemical 600lb/d
- 10800 kWh/d
- Total Cost $11699/d

---

**Lamp Configuration**
<table>
<thead>
<tr>
<th><strong>Advantages</strong></th>
<th><strong>Disadvantages</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Suitability for waters with poor UV light transmission</td>
<td>• Stripped volatile organics</td>
</tr>
<tr>
<td>• Special reactors requirement for UV illumination</td>
<td>• Expensive and inefficient to produce O₃</td>
</tr>
<tr>
<td>• (2\text{O}_3+\text{H}_2\text{O}_2 \rightarrow 2\text{HO}^-+3\text{O}_2)</td>
<td>• Need to remove gaseous O₃ Residues</td>
</tr>
<tr>
<td></td>
<td>• Difficulty of maintenance (O₃/H₂O₂ dosages)</td>
</tr>
<tr>
<td></td>
<td>• Low pH is detrimental</td>
</tr>
<tr>
<td></td>
<td>• When only ozonation is used, bromate formation is of concern if source water contains bromide ion.</td>
</tr>
</tbody>
</table>
HiPOx (H₂O₂/O₃)
Performance: 180-200 gallons/minute
Treating 1, 4-Dioxane industrial wastewater as high as 65 ppm
Applied Process Technologies, Inc
# List of Other AOPs

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ElectroOxidation</strong></td>
<td>Modified TiO₂ coating PbO₂ electrode generate HO• from water.</td>
</tr>
<tr>
<td></td>
<td>[ H₂O \rightarrow HO•+H⁺+e⁻ ]</td>
</tr>
<tr>
<td><strong>Ultrasonic/Ozone Oxidation</strong></td>
<td>Increases the mass transfer efficiency of ozone to destroy bacteria and revitalize contaminated water for reuse. Submerged electrodes create a secondary oxidation process with production of hydroxyl radicals.</td>
</tr>
<tr>
<td><strong>Ferrate</strong></td>
<td>FeO₄²⁻ oxidizes contaminants and is reduced to Fe³⁺, which acts as coagulant and finally flocculent.</td>
</tr>
<tr>
<td><strong>Persulfate Oxidation</strong></td>
<td>S₃O₈²⁻ oxidizes contaminants and is reduced to SO₄⁻•, which attack some non-degradable chemicals by HO•, like PFOA.</td>
</tr>
<tr>
<td></td>
<td>[ S₃O₈²⁻ \xrightarrow{Δ} 2SO₄⁻• ]</td>
</tr>
<tr>
<td></td>
<td>[ \text{Fe(0)} + S₂O₈²⁻ \rightarrow SO₄⁻•+Fe³⁺ ]</td>
</tr>
<tr>
<td><strong>Zero Valant Iron</strong></td>
<td>In the presence of O₂, Low pH, and Fe⁰, hydroxyl radical can be created in water. This formation is similar with Fenton reaction.</td>
</tr>
<tr>
<td></td>
<td>[ 2H⁺ + O₂ + Fe⁰ \rightarrow H₂O₂ + Fe²⁺ ]</td>
</tr>
<tr>
<td></td>
<td>[ HO•+HO⁻ + Fe³⁺ ]</td>
</tr>
<tr>
<td><strong>FBR Fenton (Fenton IV)</strong></td>
<td>Using a fluidized bed reactor (FBR) to introduce a secondary catalyst, iron oxyhydroxide (FeOOH), to the process.</td>
</tr>
<tr>
<td></td>
<td>[ H₂O₂ + Fe²⁺ \rightarrow HO•+HO⁻+Fe³⁺ ]</td>
</tr>
<tr>
<td></td>
<td>[ \rightarrow \text{Fe(OH)}₃ ]</td>
</tr>
<tr>
<td><strong>ElectroCoagulation</strong></td>
<td>Fe²⁺ and Fe³⁺ are released from iron blades where direct current is applied. Particles neutralization and precipitation occur.</td>
</tr>
</tbody>
</table>
Summary

- There are many challenging industrial waste waters in China.
- New Standards are forcing heavy industries in China to implement chemical oxidation to meet lower COD standards.
- A promising approach involves a combination of oxidation and biological treatment.
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• College of Architecture and Environment, Sichuan University colleagues.
• CrittendenTech, Beijing and Atlanta.
• College of Environment, Hohai University
References

- Stefan and Bolton, 2002.