Introduction

World Population

Fonte: U.S. Census Bureau (www.census.gov)
World Population

Increase in World Population

Desire to Increase Life Quality

Intensification of Agricultural and Industrial Development

WATER POLLUTION

TREATMENT TECHNOLOGIES
Biological Treatment

Pollutants Degradation Through the Action of Microorganisms

UNSUITABLE TO TREAT EFFLUENTS PRESENTING HIGH TOXICITY, HIGH CONCENTRATED OR NON-BIODEGRADABLE ORGANIC COMPOUNDS
Incineration

Destruction of pollutants by combustion

ONLY ECONOMICALLY RECOMMENDED TO THE TREATMENT OF VERY CONCENTRATED EFFLUENTS (COD > 300 g/L)
Wet Air Oxidation (WAO/CWAO)

IDEAL TO THE TREATMENT OF EFFLUENTS WITH A CONCENTRATION CONSIDERED TOO HIGH FOR BIOLOGICAL TREATMENT AND SIMULTANEOUSLY TOO LOW FOR INCINERATION
- **Wet Air Oxidation (WAO)**

  \[ \text{RH} + \text{O}_2 \xrightarrow{T, P} \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + \text{R’COOH}^* \quad \Delta H << 0 \]

  - Low Biodegradability
  - Toxic Contaminants
  - High Concentration

- **R’COOH* : Residual Oxidation Intermediates**
  - Low Molecular Weight Carboxylic Acids
Oxidizing Agent: Oxidizing Potential

- Oxidizing Agent: O₂
- Oxidizing Potential: low when compared with other oxidizing agents

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>E⁰ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluor (F₂)</td>
<td>3.03</td>
</tr>
<tr>
<td>Hydroxyl Radical (HO•)</td>
<td>2.80</td>
</tr>
<tr>
<td>Atomic Oxygen (O)</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H₂O₂)</td>
<td>1.77</td>
</tr>
<tr>
<td>Hydroperoxyl Radical (HOO•)</td>
<td>1.70</td>
</tr>
<tr>
<td>Chlorine dioxide (ClO₂)</td>
<td>1.50</td>
</tr>
<tr>
<td>Hypochlorous acid (HClO)</td>
<td>1.49</td>
</tr>
<tr>
<td>Chlorine (Cl₂)</td>
<td>1.36</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Oxidizing Agent: Solubility

- Up to 100°C the solubility of O$_2$ in aqueous media decreases with T
- Above 100°C the solubility of O$_2$ in aqueous media increases with T
- The solubility of O$_2$ in aqueous media increases with P

Hydrometallurgy, 48 (1998), 327-342
WAO: Typical Conditions

- **Temperature:** 125-320°C
  - Increased $O_2$ solubility and reaction rate

- **Total Pressure:** 50-200 bar
  - To maintain the system in liquid phase and to increase $O_2$ availability
  - Higher pressures when air is used (less expensive)
WAO: Process

- COD ∈ [10-100 g/L]
- Residence Time: 15-120 min
- COD Removal: 75-90%

Zimpro® Wet Oxidation: www.usfilter.com
WAO: Process

Zimpro® Wet Oxidation: www.usfilter.com

Energy Recovery
COD > 20 g/L
WAO Reactions

\[ \text{RH} + \text{O}_2 \rightarrow \text{RO-OH} \]
\[ \text{RO-OH} \rightarrow \text{RO}^* + \text{HO}^* \]
\[ \text{RO-OH} + \text{RH} \rightarrow \text{RO}^* + \text{R}^* + \text{H}_2\text{O} \]
\[ \text{R}^* + \text{O}_2 \rightarrow \text{RO-O}^* \]
\[ \text{RO-O}^* \rightarrow \text{R'}^* + \text{CO}_2 \]
\[ \text{R}^* + \text{HO}^* \rightarrow \text{ROH} \]
\[ \text{R}^* + 2\text{HO}^* \rightarrow \text{R’COOH} \]
Combined Process

RH + O₂ → CO₂ + H₂O

Acetic Acid + O₂

Low Biodegradability
Easy Oxidation

High Biodegradability
Difficult Oxidation

WAO + Biological Treatment
WAO: Commercialization

- **Zimpro® (1950’s)**
  Pioneering Company: Zimpro Products (US Filter → Vivendi → Siemens Water Technologies, Germany (since 2003))

- **First Unit Commercialized**
  Treatment of wastewater from pulp industry

- **Zimpro Units Commercialized**
  - Sludge treatment: 105
  - Treatment of industrial effluents: 41
  - Activated carbon regeneration: 16
  - Other applications: 5

**IN TOTAL OVER 200 WAO UNITS WERE COMMERCIALIZED FOR INDUSTRIAL AND MUNICIPAL APPLICATIONS**
Process PACT & Sludge Treatment

Process PACT
(powdered activated carbon treatment)
WAO + Biological Treatment

Regeneration of Activated Carbon
Destruction of Sludge
Treatment of Industrial Effluents

WAO for propylene oxide/styrene monomer production effluents
Zimpro® wet air oxidation at Repsol YPF, Tarragona Spain (2000)
www.water.siemens.com
WAO: Commercialization

- **Kenox® (1980’s)**
  Kenox Technology Corporation
  Canada
  → Merichem Company (since 2015)

- **VerTech® (1970’s)**
  Providentia Environment Solutions
  Holland (since 2008)

Kenox Technology Corporation’s Wet Air Oxidation (WAO) process technology
http://www.merichem.com/wet-air-oxidation-wao

Treatment of Highly Polluted Industrial Wastewaters (Chemical, Pharmaceutical ...), Spent Caustics (Petrochemical) and Sludges
## WAO vs CWAO

<table>
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<tr>
<th>non catalytic</th>
<th>catalytic</th>
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<tbody>
<tr>
<td>125 to 320 °C</td>
<td>100 to 220 °C</td>
</tr>
<tr>
<td>50 to 200 bar $P_T$</td>
<td>5 to 50 bar $P_T$</td>
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Lower Energetic and Investment Costs
Higher Oxidation Efficiency

DEVELOPMENT OF SUITABLE CATALYSTS
Homogeneous Catalysts

- **Catalysts**
  - Cu(SO₄), FeCl₂, ...

- **Loprox® (1990’s)**
  - Bayer Technology Services
  - Germany (10 units installed)

- **Wetox® (2010)**
  - Viclink
  - New Zealand

**Pre-treatment of Highly Polluted Industrial Wastewater, Spent Caustic Streams and Sludge Treatment**

*Loprox® at Bayer HealthCare, La Felguera Spain (1993) [www.bayertechnology.com]*
Homogeneous Catalysts

- **Catalysts**
  - \( \text{Cu(SO}_4\text{)}, \text{FeCl}_2, \ldots \)

Metallic Ions Present in the Treated Solution

Additional Separation Step
Catalyst Recycling?
Heterogeneous Catalysts: Transition Metals

- Catalysts
  - Co:Bi (5:1) and Mn:Ce (1:1) composite oxides
  - Cu, Zn, Cr, V and Ti oxides
  - Cu/Al$_2$O$_3$, Fe/SiO$_2$, ...

  Fast Deactivation (condensation products)
  Metal leaching into the solution

  Additional Separation Step
Heterogeneous Catalysts: Noble Metal Supported Catalysts

Objectives

High Activity ⇔ Total Oxidation of Pollutants
High Stability ⇔ Leaching Absent

Support

Al₂O₃, SiO₂, TiO₂, ZrO₂, AC, ...

Noble Metals

Pt, Ru, Pd, Ir, ...
Nobel Metal Supported Catalysts

Experimental Conditions:

- **T** = 200 °C
- **pO₂** = 6.9 bar
- **w_{\text{cat}}** = 0.8 g
- **M/AC (5% M)**
- **C_{\text{ButOOH}}** = 5 g/L

Gomes et al., Catalysis Today 75 (2002) 23-28
Adsorption Mechanism

Metal with Higher Reduction Potential

Lower Oxygen Adsorption at the Metal Surface

Less Competition between Oxygen and the Organic Substrate at the Active Sites

More Available Active Sites for Pollutant Adsorption

Higher Activity
Reaction Mechanism

ButO$_2$H $\rightleftharpoons$ [ButO$_2$H]$_{Ads}$

$\text{CH}_3\text{CHCHC}$

P: Propionic acid
A: Acetic acid
C: Final oxidation products (CO$_2$ and H$_2$O)
Olive Mill Wastewaters CWAO

→ OMW are characterized by high COD (>40 g/L) and strong brown colour

→ OMW contain a large diversity of organic compounds (including phenols, polyphenols and polyalcohols) with low biodegradability and high toxicity

- Pt/AC and Ir/AC increase considerably effluent’s TOC removal
- Complete TOC removal is obtained with Pt/AC at 200°C after 8 h

Gomes et al., Catalysis Today 124 (2007) 254-259
Heterogeneous CWAO: Commercialization

- **Process NS-LC® (Nippon Shokubai, Japan)**
  - 10 Units in Operation
  - Operating costs: 1.5-3x lower than WAO
  - **Catalyst: Pt-Pd/TiO₂-ZrO₂**
  - Temperature: 220°C; Pressure: 40 bar
  - Pollutants: Phenol, Formaldehyde, Acetic Acid, Glucose ... 

- **Process Osaka Gas® (Osaka Gas, Japan)**
  - **Catalyst: Precious metals/TiO₂-ZrO₂**
  - Temperature: 250°C; Pressure: 68.6 bar
  - Pollutants: effluents from coal furnaces, concentrated in cyanides, municipal wastewaters ... 

16/07/2017
In the last decade, metal-free carbon materials were investigated as catalysts in CWAO

Important Features: Texture and Surface Chemistry

Textural properties easily tuned during synthesis procedure

  e.g. Mesoporous Carbon Xerogels: more advantageous for liquid phase reactions → minimization of diffusion limitations and catalyst deactivation

Surface chemistry properties are easily tuned by proper liquid phase and gas phase treatments
Carbon Materials: Surface Chemistry

[Schematic diagram showing the analysis of S-containing and O-containing groups using XPS/TPD techniques.

- S-containing groups:
  - 168.2 – 170.4 eV, 350-370 °C (as SO₂)
  - 162 – 163.9 eV, 290-340 °C (as SO₂)

- O-containing groups:
  - 400.3 ± 0.3 eV
  - 402 – 405 eV
  - 401.4 ± 0.5 eV
  - 398.7 ± 0.3 eV

N-containing groups:
- 400.3 ± 0.3 eV
- 402 – 405 eV
- 401.4 ± 0.5 eV
- 398.7 ± 0.3 eV

EA C,H,N,S composition

C₁s and O₁s XPS/TPD

CO₂ < 450 °C
CO₂ > 600 °C
CO₂ < 500 °C
CO₂ > 750 °C
CO₂ < 1000 °C
CO₂ > 950 °C

Rocha et al., C Journal of Carbon Research 2 (2016) 17
Non-supported carbon materials: CWAO studies

- The catalytic activity of carbon materials in CWAO was subject of many studies considering O-, N- and S-containing groups.

- Although it is generally accepted that basic carbon materials present higher performance, in some works catalysts with acidic nature present high pollutant removals.

Oxalic Acid
Acidic Carbon Xerogels: Aniline Removal Mechanism

\[
\text{CX} \quad \text{COOH} \quad 2[O] \quad \text{O}_2
\]

\[
\text{CX} \quad \text{COO}^* \quad [O] \quad + \quad \text{HO}^*
\]

Gomes et al., J. Haz. Mat. 159 (2008) 420
Conclusions

• Wet Air Oxidation (WAO)
  → Suitable process to treat wastewaters with high organic load
  → Final Solution or pre-treatment technology
  → Economic alternative to incineration

• Catalytic Wet Air Oxidation (CWAO): Introduction of Catalysts
  → Lower operating conditions and investment costs
  → Higher oxidation efficiency

• Catalysts in CWAO
  → Homogeneous catalysts
  → Supported transition metals
  → Supported noble metals
  → Carbon materials with proper texture and surface chemistry