Wet Air Oxidation
Process and Catalyst Developments

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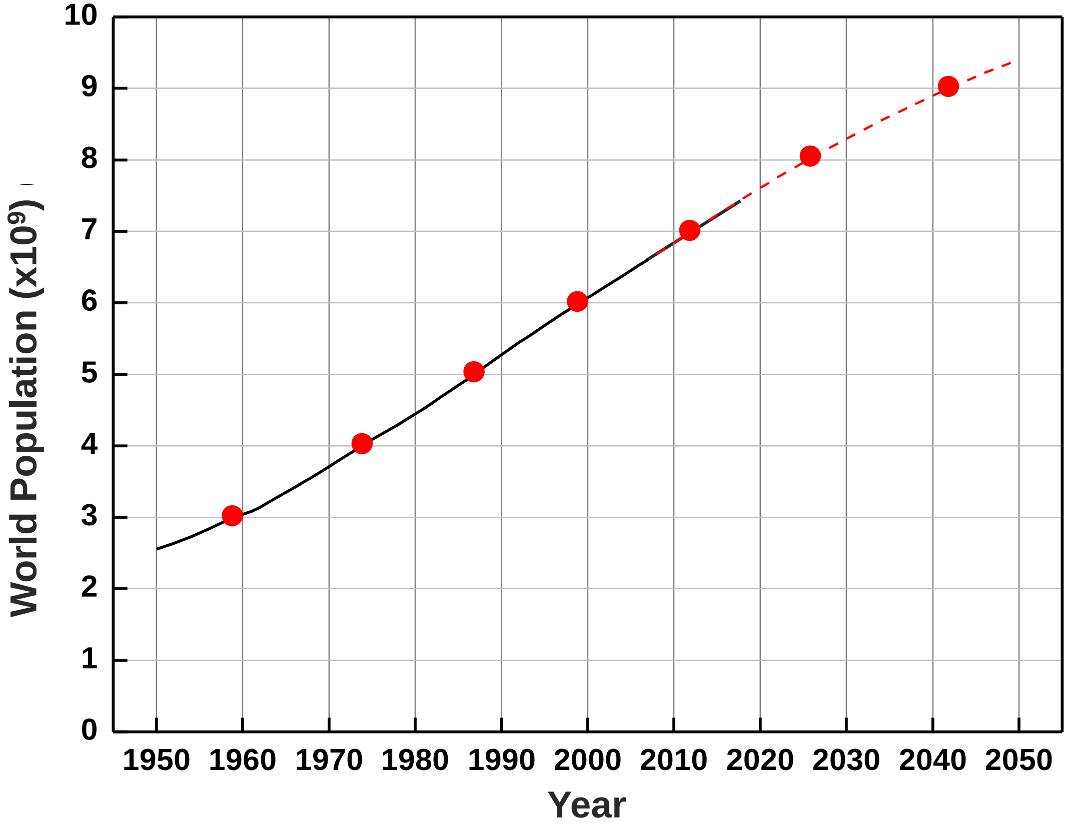
Introduction
World Population



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

World Population

Increase in World Population

Desire to Increase Life Quality

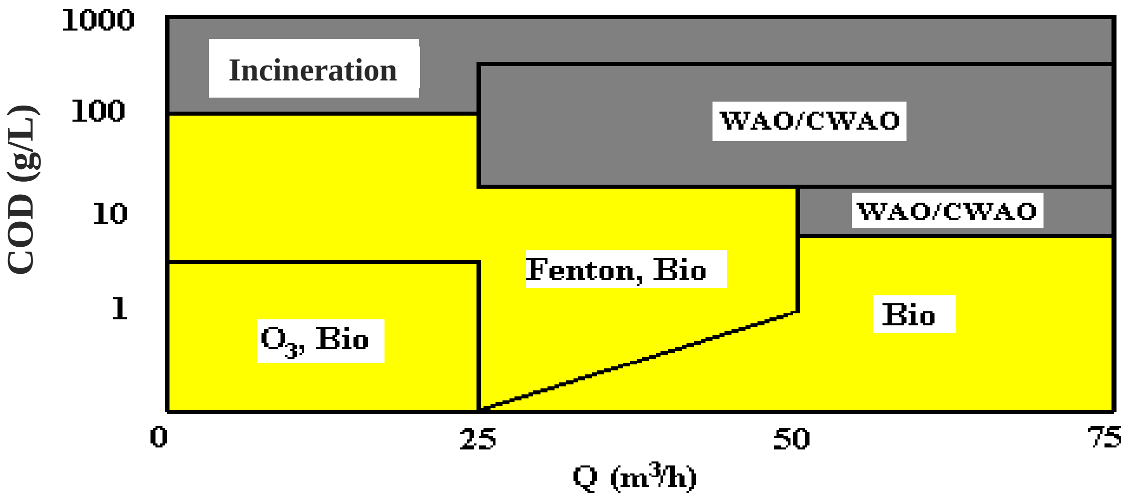
Intensification of Agricultural and Industrial Development

WATER POLLUTION

TREATMENT TECHNOLOGIES

Biological Treatment

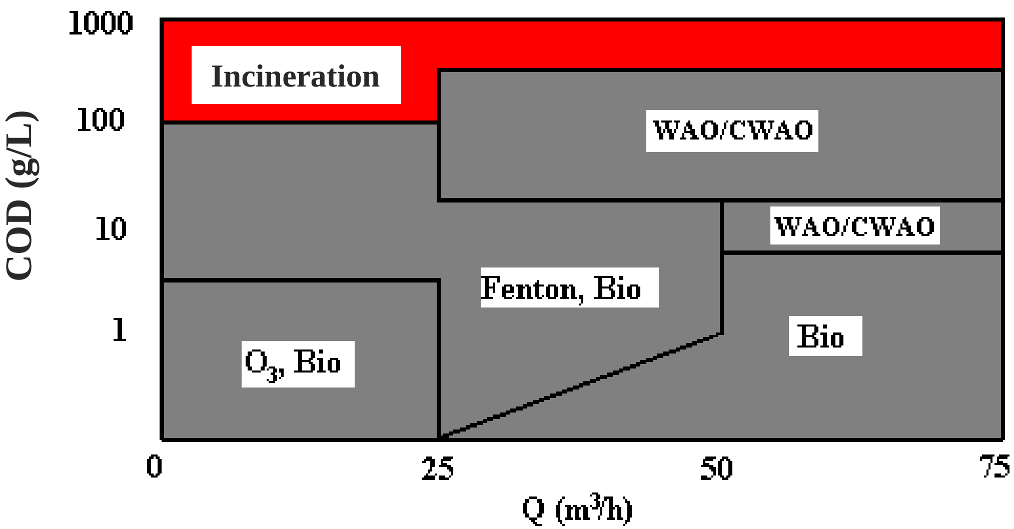
Pollutants Degradation Through the Action of Microorganisms



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

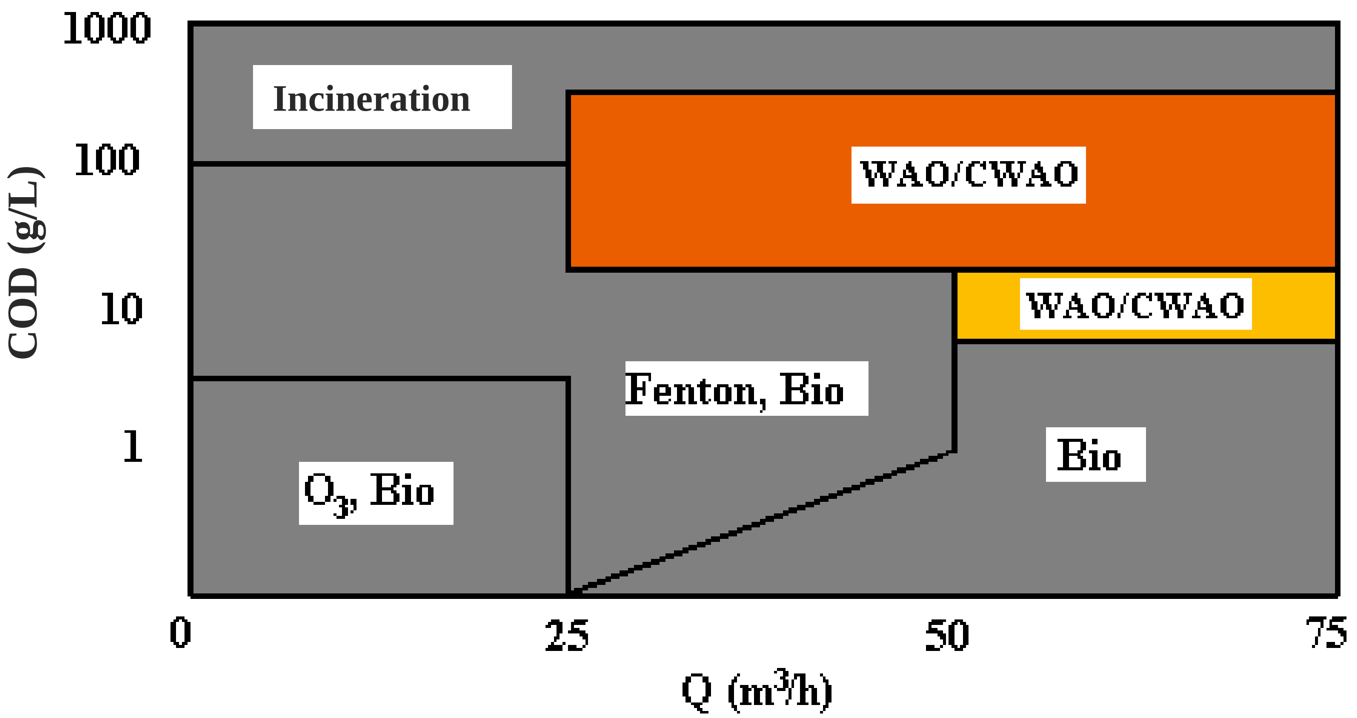
Incineration

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

WAO

- **Wet Air Oxidation (WAO)**

$$RH + O_2 \xrightarrow{T,\ P} CO_2 + H_2O + N_2 + R'COOH^* \qquad \Delta H << 0$$

Low Biodegradability
Toxic Contaminants
High Concentration

- **R'COOH* : Residual Oxidation Intermediates**
  Low Molecular Weight Carboxylic Acids

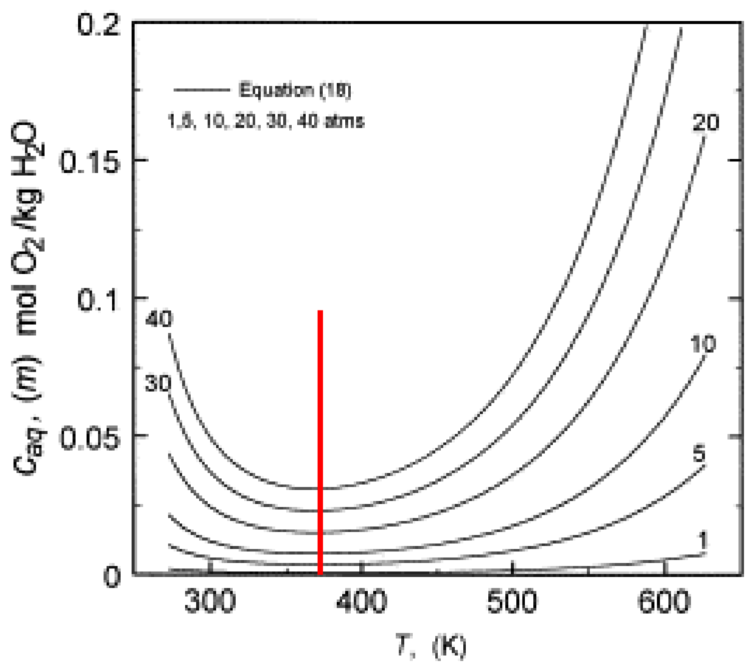
Oxidizing Agent: Oxidizing Potential

- **Oxidizing Agent: O_2**
- **Oxidizing Potential: low when compared with other oxidizing agents**

Oxidant	E^0 (V)
Fluor (F_2)	3.03
Hydroxyl Radical ($HO^\bullet$)	2.80
Atomic Oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen Peroxide (H_2O_2)	1.77
Hydroperoxyl Radical ($HOO^\bullet$)	1.70
Chlorine dioxide (ClO_2)	1.50
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Oxygen (O_2)	**1.23**

Oxidizing Agent: Solubility

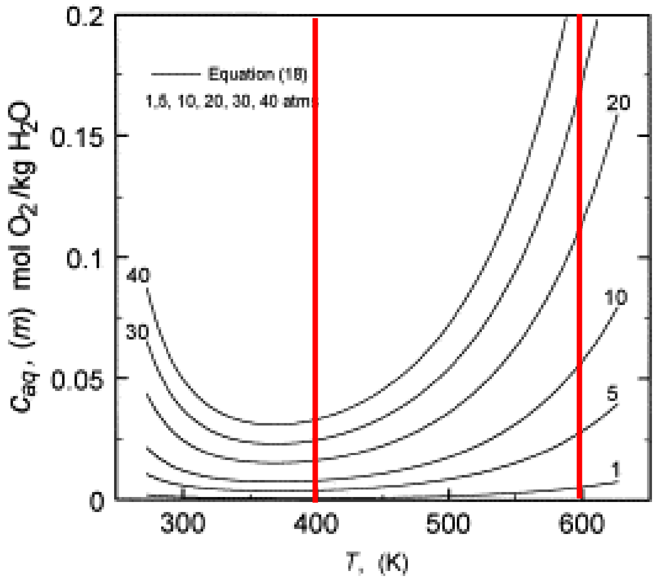
- Up to 100ºC the solubility of O_2 in aqueous media decreases with T
- Above 100ºC the solubility of O_2 in aqueous media increases with T
- The solubility of O_2 in aqueous media increases with P



Hydrometallurgy, 48 (1998), 327-342

WAO: Typical Conditions

- **Temperature: 125-320°C**



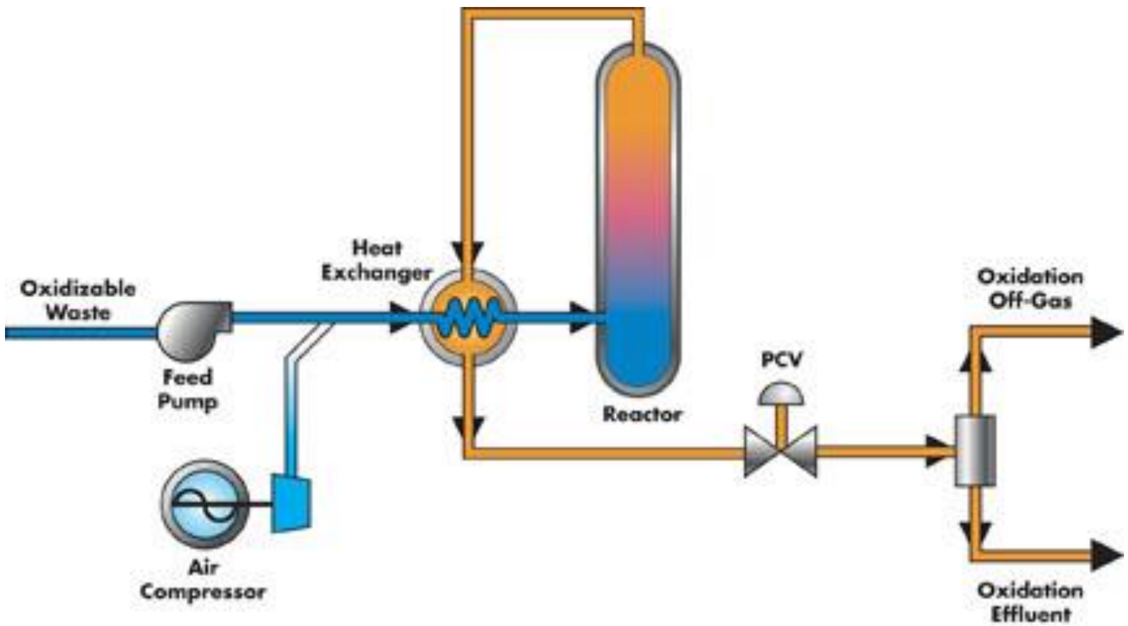
Increased O_2 solubility and reaction rate

- **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)

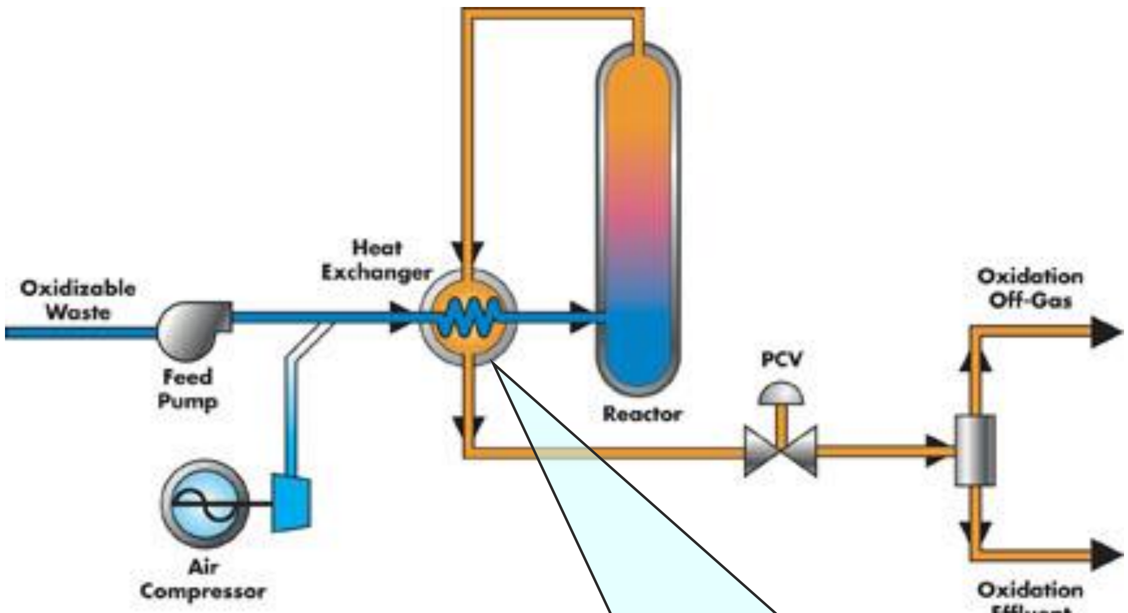
WAO: Process



Zimpro® Wet Oxidation: www.usfilter.com

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

WAO: Process



Zimpro® Wet Oxidation: www.usfilter.com

Energy Recovery
COD > 20 g/L

WAO Reactions

$RH + O_2 \rightarrow RO\text{-}OH$

$RO\text{-}OH \rightarrow RO^\bullet + HO^\bullet$

$RO\text{-}OH + RH \rightarrow RO^\bullet + R^\bullet + H_2O$

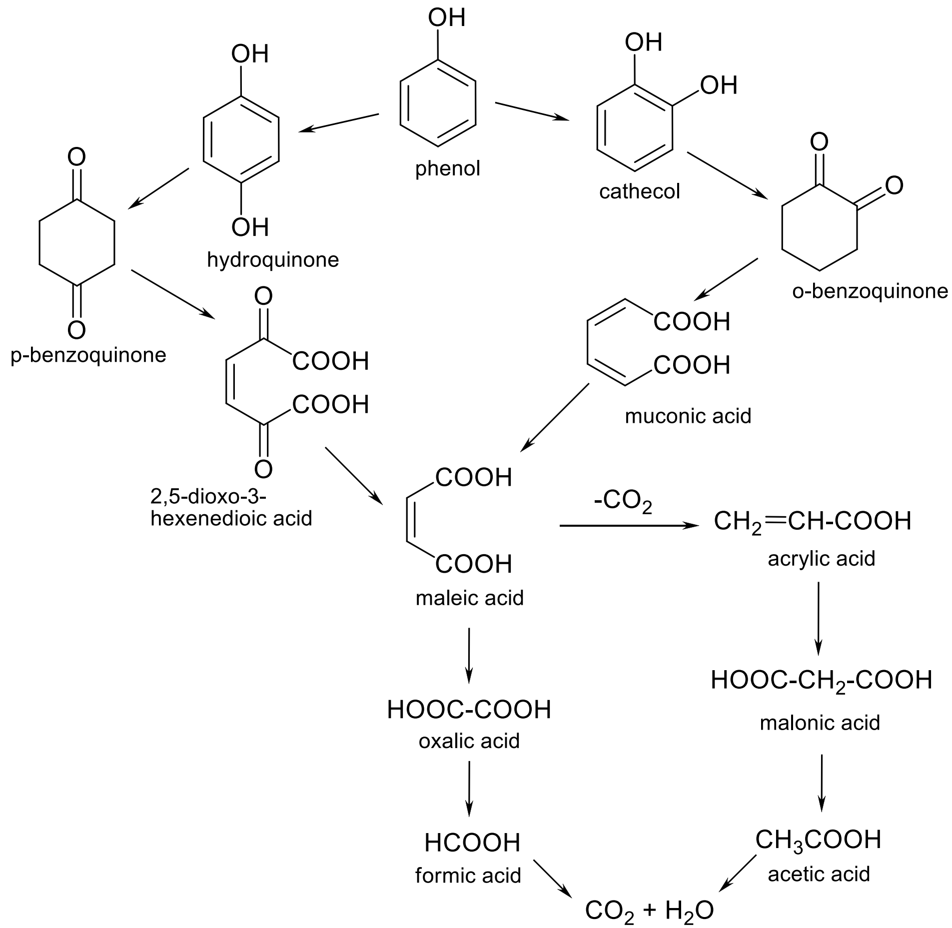
$R^\bullet + O_2 \rightarrow RO\text{-}O^\bullet$

$RO\text{-}O^\bullet \rightarrow R'^\bullet + CO_2$

$R^\bullet + HO^\bullet \rightarrow ROH$

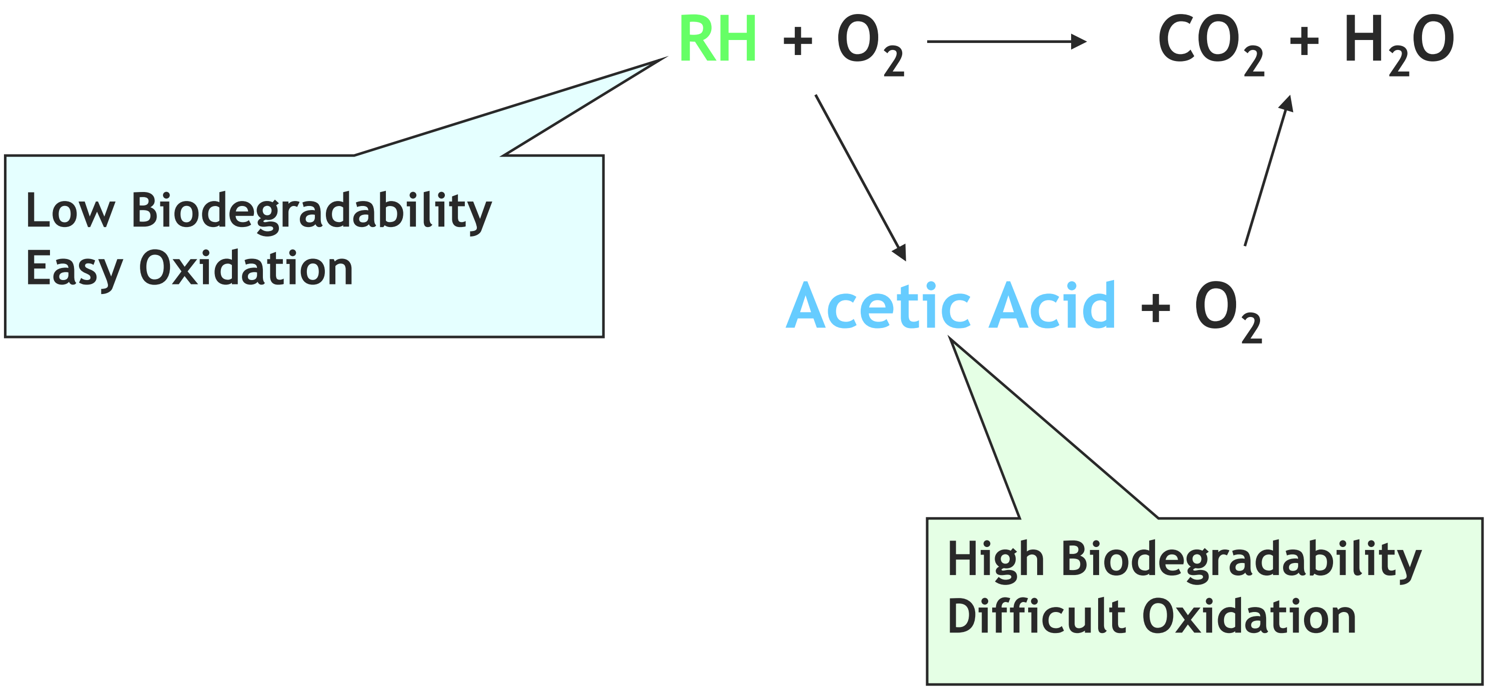
$R^\bullet + 2HO^\bullet \rightarrow R'COOH$

Phenol Oxidation



Duprez et al., Catal. Today 1996, 29, 317-322

Combined Process



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

- **Kenox® (1980's)**

  Kenox Technology Corporation Canada

  → Merichem Company (since 2015)

- **VerTech® (1970's)**

  Providentia Environment Solutions Holland (since 2008)

Treatment of Highly Polluted Industrial Wastewaters (Chemical, Pharmaceutical …), Spent Caustics (Petrochemical) and Sludges

WAO vs CWAO

non catalytic	catalytic
125 to 320 ºC	100 to 220 ºC
50 to 200 bar P_T	5 to 50 bar P_T

WAO vs CWAO

non catalytic	catalytic
125 to 320 ºC	100 to 220 ºC
50 to 200 bar P_T	5 to 50 bar P_T

Lower Energetic and Investment Costs
Higher Oxidation Efficiency

DEVELOPMENT OF SUITABLE CATALYSTS

Homogeneous Catalysts

- **Catalysts**
  - $Cu(SO_4)$, $FeCl_2$, …

Loprox® at Bayer HealthCare, La Felguera Spain (1993) www.bayertechnology.com

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

Homogeneous Catalysts

- **Catalysts**
  - $Cu(SO_4)$, $FeCl_2$, …

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_2O_3, Fe/SiO_2, …

↓

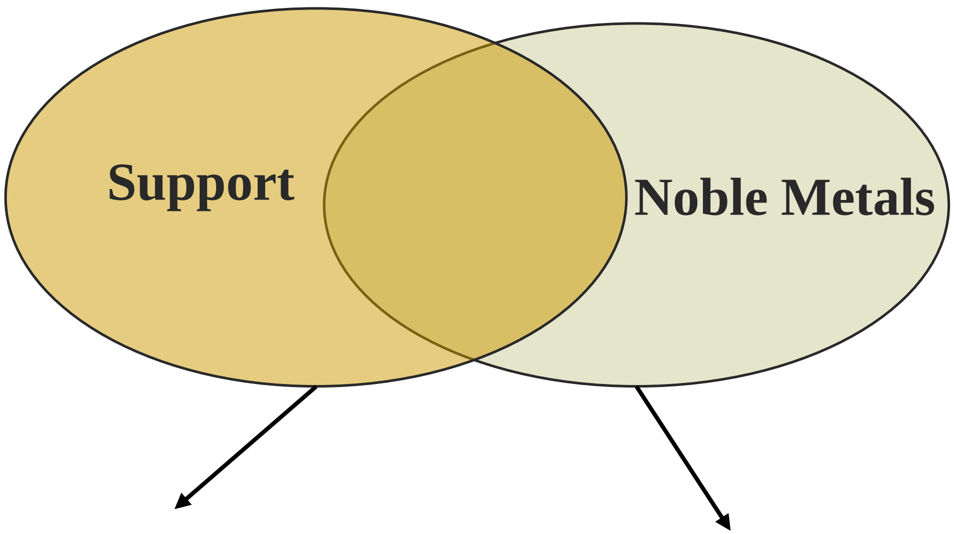
Fast Deactivation (condensation products)
Metal leaching into the solution

↳ **Additional Separation Step**

Heterogeneous Catalysts: Noble Metal Supported Catalysts

Objectives

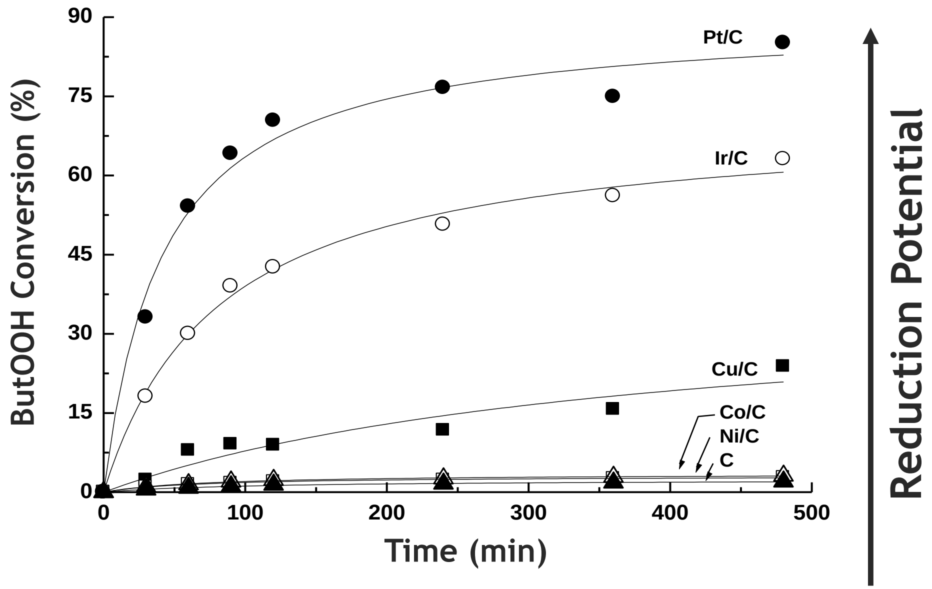
- High Activity → Total Oxidation of Pollutants
- High Stability → Leaching Absent

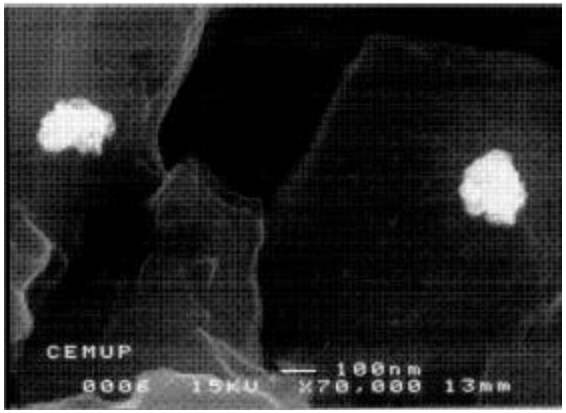


Al_2O_3, SiO_2, TiO_2, ZrO_2, AC, …

Pt, Ru, Pd, Ir, …

Nobel Metal Supported Catalysts





Ir/AC (5% Ir)

- **Experimental Conditions :**
  - **T = 200 °C**
  - **p_{O2} = 6.9 bar**
  - **w_{cat} = 0.8 g**
  - **M/AC (5% M)**
  - **C_{ButOOH} = 5 g/L**

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

Adsorption Mechanism

Metal with Higher Reduction Potential

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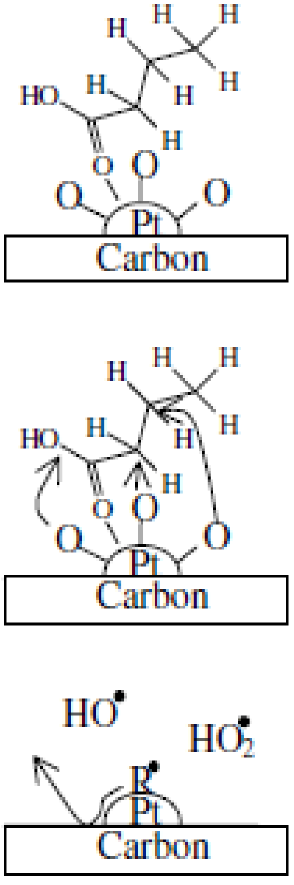
Lower Oxygen Adsorption at the Metal Surface

↓

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



More Available Active Sites for Pollutant Adsorption

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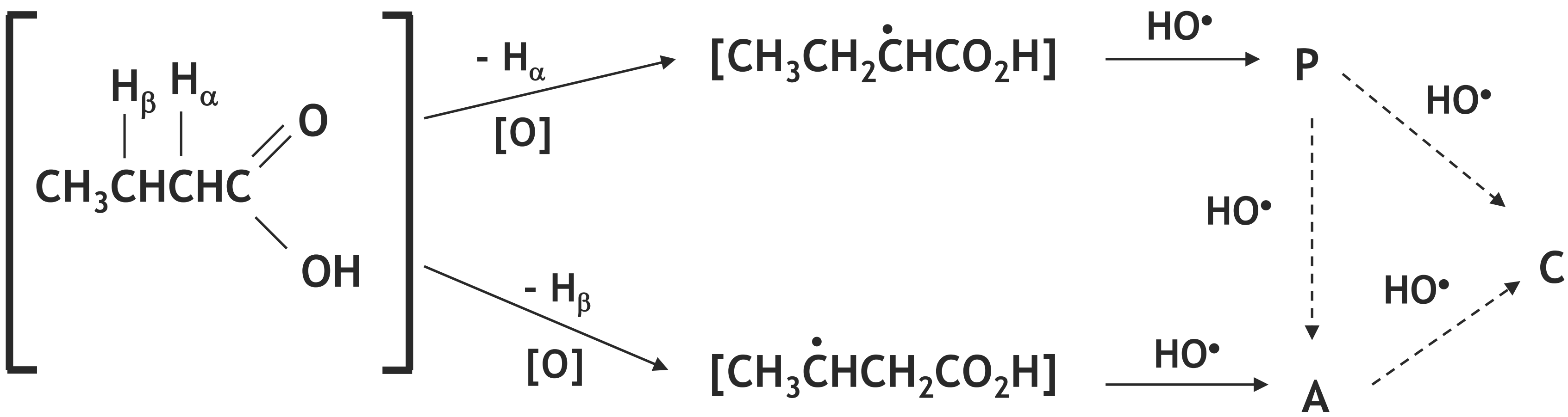
Higher Activity

Reaction Mechanism

$$ButO_2H \rightleftharpoons [ButO_2H]_{Ads}$$

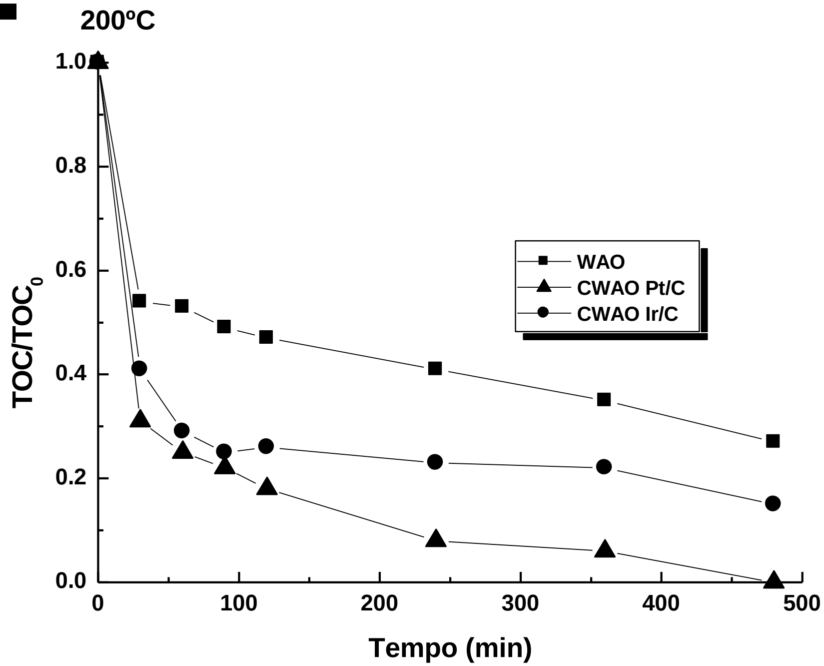


P: Propionic acid

A: Acetic acid

C: Final oxidation products (CO_2 and H_2O)

Olive Mill Wastewaters CWAO



Gomes et al., Catalysis Today 124 (2007) 254-259

→ 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 200ºC after 8 h

Heterogeneous CWAO: Commercialization

- Process NS-LC® (Nippon Shokubai, Japan)
  - 10 Units in Operation
  - Operating costs: 1.5-3x lower than WAO
  - **Catalyst: Pt-Pd/TiO_2-ZrO_2**
  - Temperature: 220ºC; Pressure: 40 bar
  - Pollutants: Phenol, Formaldehyde, Acetic Acid, Glucose …

- Process Osaka Gas® (Osaka Gas, Japan)
  - **Catalyst: Precious metals/TiO_2-ZrO_2**
  - Temperature: 250ºC; Pressure: 68.6 bar
  - Pollutants: effluents from coal furnaces, concentrated in cyanides, municipal wastewaters …

NS-LC® wet air oxidation
http://www.shokubai.co.jp

Non-supported Carbon Catalysts in CWAO

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

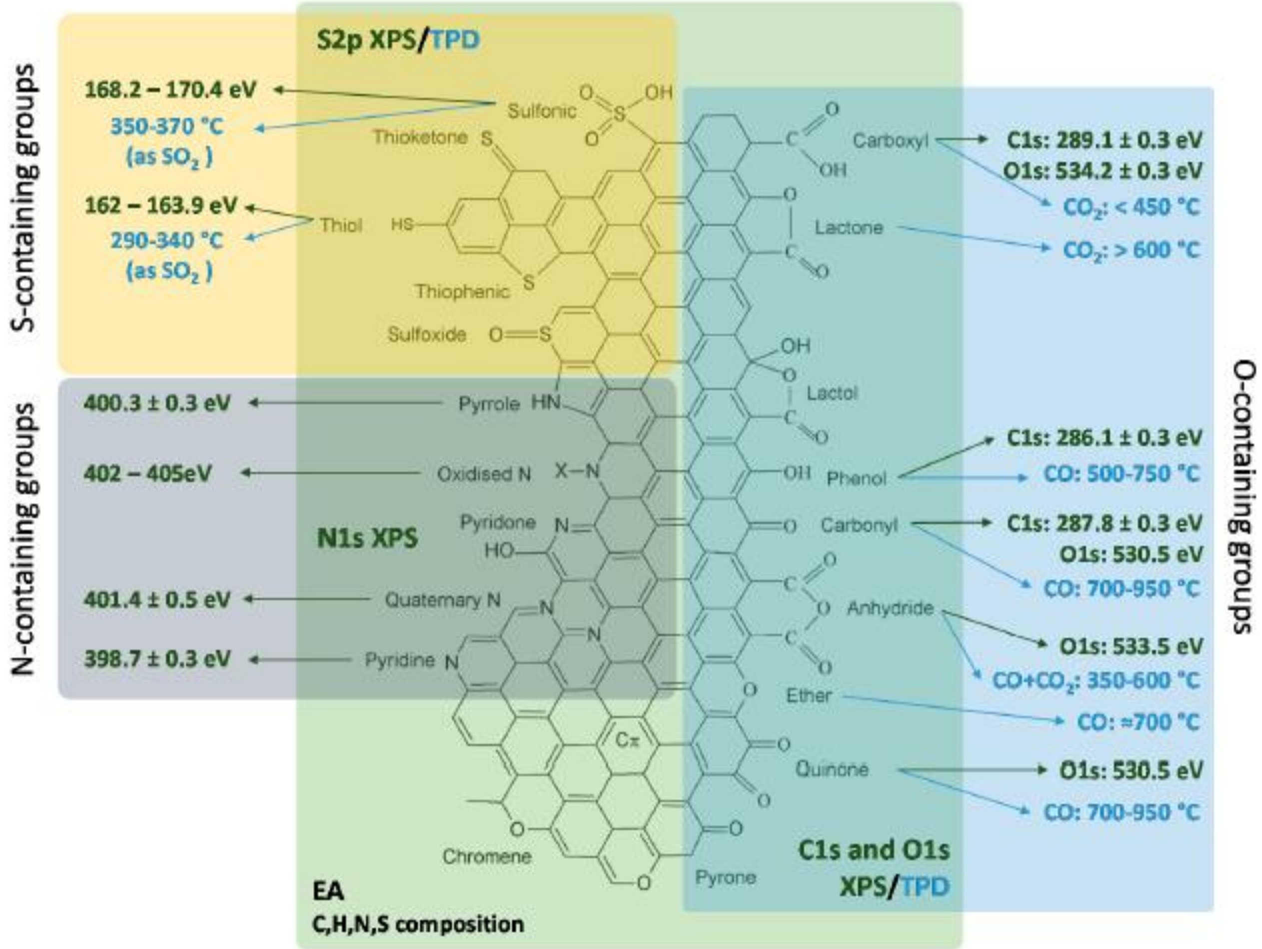
- Important Features: Texture and Surface Chemistry

- 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

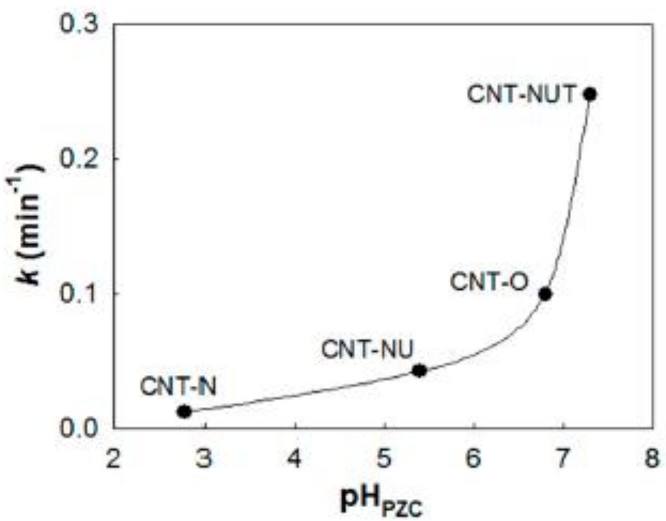


Rocha et al., C Journal of Carbon Research 2 (2016) 17

Non-supported carbon materials: CWAO studies

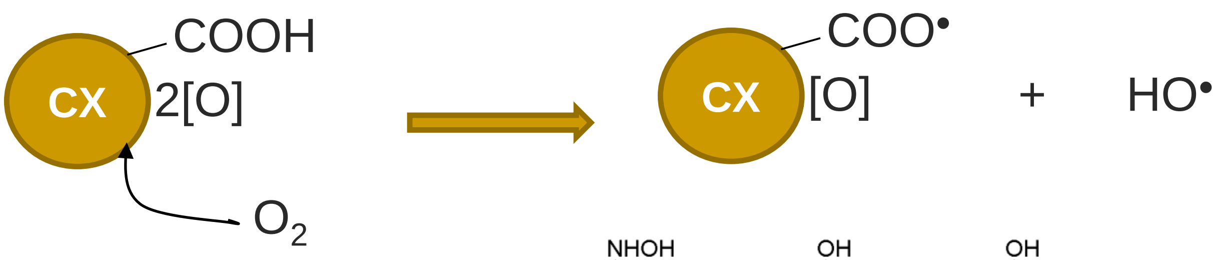
- The catalytic activity of carbon materials in CWAO was subject of many studies considering O-, N- and S-containing groups

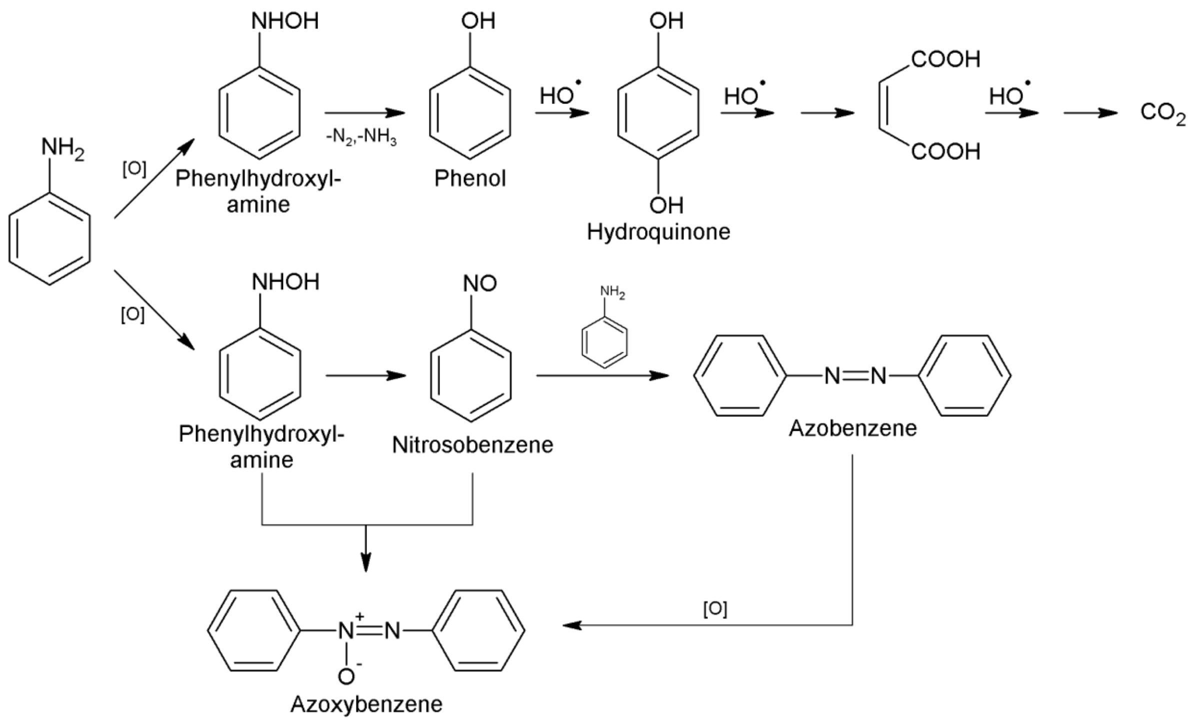
- Although it is generally accepted that basic carbon materials present higher performance, in some works catalysts with acidic nature present high pollutant removals



Oxalic Acid
Rocha et al., Appl. Catal. B Environ. 2011, 104, 330-336

Acidic Carbon Xerogels: Aniline Removal Mechanism





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