Advanced Electrochemical Oxidation of Ultrafiltration Permeates from Cellulose Bleaching Effluents


Environmental Sciences Centre – EULA
Chemical Engineering Department
University of Concepcion. Chile
Presentation Outline

Introduction: Why cellulose effluent? Why UF and AEOP?

Experimental system

Results

Conclusions
2.5 million ha. Pine and Eucalyptus plantations
5.1 million ton/year bleached kraft cellulose
The Water Issue in Cellulose Production

Process Water

Waste Water

Water Availability

Water Quality
ECF Bleached Kraft pulp from pine and eucalyptus

35-60 m$^3$ water/ ton cellulose

70,000 – 120,000 m$^3$/day per mill

Total usage: 600,000 m$^3$/day

Discharges: 400 ton COD/day and 1.2 ton AOX/day
Rainfall Trends 1900 - 2000

Impact of climate change on global and local water cycle
Rainfall Changes (Dec-Jan-Feb)

1980/90 - 2080/99

Expected Impact of climate change in South America
Mid-term Rainfall Scenario (2030)

Rainfall Reduction above 20%

Rainfall Increase above 20%

95% Cellulose production
Bleached Kraft Cellulose Production Process

WOODY RAW MATERIALS → Cooking and O₂ Predelignification → UNBLEACHED PULP → ECF Bleaching Sequence → BLEACHED PULP

Chemical and Energy Recovery System

BLACK LIQUOR → WHITE LIQUOR

WASTE WATER → Waste Water Treatment plant

ELECTRICITY
UF Treatment of Acid (D₀) Bleaching Effluent

\begin{table}
\begin{tabular}{|c|c|c|}
\hline
 & \textbf{g / m}^3 & \textbf{kg / ton} \\
\hline
AOX & 3 & 0.05 \\
COD & 1,400 & 21 \\
BOD₅ & 400 & 6 \\
Chloride & 400 & 6 \\
Phenols & 8 & 0.12 \\
Volume & m³/ton & 15 \\
\hline
\end{tabular}
\end{table}

\begin{table}
\begin{tabular}{|c|c|c|}
\hline
 & \textbf{g / m}^3 & \textbf{kg / ton} \\
\hline
AOX & 2 & 0.02 \\
COD & 590 & 7 \\
BOD₅ & 300 & 4 \\
Chloride & 410 & 5 \\
Phenols & 4 & 0.05 \\
Volume & m³/ton & 12 \\
\hline
\end{tabular}
\end{table}

≈ 60-70% COD, AOX and phenols are retained in the concentrate
UF Treatment of Alkaline (E<sub>OP</sub>) Bleaching Effluents

≈ 70-80% COD, AOX and phenols are retained in the concentrate
Electricity Generation Potential at Mill

Total Electricity Consumption

Electricity Demand from National Grid, Exported by the Mill

In-Plant Electricity Consumption

Surplus

TIME, h

TIME, h

MWh
ELECTRO-OXIDATION MECHANISM

Direct Electron Transfer to the Anode

Chemical Reaction with Electrogenerated Species
ELECTRO-OXIDATION MECHANISM

Chemical Reaction with Electro-generated Species

Non-Active Anodes:
Generate Physisorbed •OH (eg. BDD)

Active Anodes:
Generate Chemisorbed “active oxygen” (eg. DSA-RuO₂)
Non-Active anodes

\[ M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \]

\[ 2M(\cdot OH) + R \rightarrow ROO + 2M + 2H^+ + 2e^- \]

\[ M(\cdot OH) \rightarrow \frac{1}{2} O_2 + M + H^+ + e^- \]

Unwanted Reaction eg. BDD
Active anodes

\[ M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \]

\[ M(\cdot OH) \rightarrow MO + H^+ + e^- \]

\[ MO + R \rightarrow RO + M \]

\[ M(\cdot OH) \rightarrow \frac{1}{2} O_2 + M + H^+ + e^- \]  
Unwanted Reaction

\[ 2 MO \rightarrow O_2 + 2 M \]
In the presence of Chloride:

\[
\text{M}^{(*)\text{OH}} + \text{Cl}^- \rightarrow \text{M}^{(*)\text{OCl}} + \text{H}^+ + 2\text{e}^-
\]

\[
\text{M}^{(*)\text{OCl}} + \text{Cl}^- \rightarrow \text{MO} + \text{Cl}_2 + \text{e}^-
\]

\[
\text{M}^{(*)\text{OCl}} + \text{Cl}^- \rightarrow \text{M} + \text{Cl}_2 + \frac{1}{2}\text{O}_2 + \text{e}^-
\]
In the presence of Chloride

\[
\begin{align*}
\text{Cl}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HOCl} \\
\text{HOCl} & \rightleftharpoons \text{H}^+ + \text{OCl}^- \\
\text{Cl}^- & \rightleftharpoons \frac{1}{2} \text{Cl}_2 + e^- \\
\end{align*}
\]

Reaction near the anode surface or at the bulk solution:

\[
\text{OCl}^- + R \rightleftharpoons \text{RO} + \text{Cl}^-
\]

Hypochlorite could be lost at the cathode:

\[
\text{OCl}^- + 2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\text{O} + \text{Cl}^-
\]
Dual Cell Electrochemical Reactor System

Cathode: Stainless Steel AISI-316

Anodes: DSA-Ti/RuO₂, DSA-Pt, Pt, Graphite

Saline Bridge

CH 1100 Potentiostat

Ag/AgCl Reference Electrode

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
<table>
<thead>
<tr>
<th>Molecular weight cut-off (kDa)</th>
<th>Membrane Material</th>
<th>Hydraulic permeability at 6 bar (dm3m-2bar-1h-1)</th>
<th>Volume Reduction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Fluoropolymer</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>Hydrophilic Polysulphone</td>
<td>125</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>Fluoropolymer</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Experimental

**Assayed Effluents:**

Raw Acid Bleaching (D₀) Effluents
Raw Alkaline Bleaching (E₀/P) Effluents
Acid and Alkaline UF permeates < 20 kDa
Acid and Alkaline UF permeates < 10 kDa
Acid and Alkaline UF permeates < 1 kDa

**Also Model Compounds:**

Dihydroxibenzene
4-Chlorophenol
Maleic, Fumaric, and Oxalic acids
Experimental System

**Conditions**

pH 3 – 10, 20°C  
Current density 0.1 – 5.5 mA/cm²  
Voltage 0 – 4 volts

**Electrochemical Techniques**

Voltammetric experiments (Linear Sweep; Cyclic)  
Bulk electrolysis in Dual Cell electrochemical system

**Main Assays:**

COD, BOD₅, Phenols, Active Chlorine, TOC  
Genotoxicity (*Bacillus subtilis*)  
Mutagenesis (*Salmonella typhimurium. Ames*)
Experimental Calculation of Electrodes Area

\[ i = n F A c_0 \sqrt{\frac{D}{\pi t}} \]

\[ J_{z=0} = \sqrt{\frac{D}{\pi t}} \times c_0 \]

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \]

IC: \( t = 0 \) \( c = c_0 \) \( \forall z \)

BC: \( z = 0 \) \( c = 0 \)

\( z = -\infty \) \( c = c_0 \)

Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}
Experimental Calculation of Electrode Area

\[ I = nFAC_0 \sqrt{\frac{D}{\pi t}} \]


\[ \text{Area} = |\text{slope}| \times (n^{-1} F^{-1} C_0^{-1} D^{-1/2} \pi^{1/2}) \]

\[ \text{Fe(CN)}_6^{-3} + e^- \rightarrow \text{Fe(CN)}_6^{-4} \]

\[ D = 6.5 \times 10^{-5} \]

\[ 7.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]
Average Current Efficiency  \(=\) ACE  \(=\) \(\frac{\Delta\text{COD} \times V \times F}{8 \times i_{AV} \times t}\)

Energy Consumption  \(=\) \(\frac{P \times i_{AV} \times t}{\Delta\text{COD} \times \text{volume}}\)

where

\[i_{AV} = \frac{[\sum (i_k)] \times \Delta t}{\text{total time}}\]
Linear Sweep Voltammetry. Scan rate 0.05 V/s
0.5M Na$_2$SO$_4$ solution, 100 mS/cm

- Grafito
- DSA-Pt
- DSA-RuO$_2$
Cyclic Voltammetry. Dihydroxybenzene. 0.01V. pH 5.3, 6 mS/cm

Ep, V | 0.53 | 0.27
Ip, A | 1.04E-4 | -8.06E-5

Potential, V
Current Intensity, A
Cyclic Voltammetry. Graphite Anode. 0.10 V/s. Acid Effluent. pH 3, 7.7 mS/cm. 5 g/L Na₂SO₄

Ep = 0.44 V
ip = 9.1E-8 A
Dihydroxybenzene Electrooxidation. Effect of Support Electrolyte.
0-60 mM Sodium Sulphate. DSA RuO\(_2\) anode.
Dihydroxybenzene. By-products formation. DSA-Pt anode. 10 A/m²

![Graph showing concentration of dihydroxybenzene, oxalic acid, maleic acid, and fumaric acid over time.](image-url)
Electrooxidation of Low Molecular Weight Organic acids
DSA-Pt anode. 10 A/m². 6 mS/cm

Concentration (mM)

Time (min)

Concentration (mM)

Fumaric Acid
Maleic Acid
Oxalic Acid
Dihydrobenzene
Dihydroxybenzene electrooxidation

1,2 DIHYDROXYBENZENE

-2H⁺ -2e⁻

O-BENZOQUINONE

+2OH⁻ -2e⁻

MUCONIC ACID
OXALIC ACID

+2H⁺ + 2e⁻ → H-C=O

SLOW REACTION

-2H⁺ - 2e⁻ → O=C

SLOW REACTION
DSA-Pt anode. 2V, 10-12 A/m²

Concentration (mM) vs. Time (min) for 1-Chlorobutane, 4-Chlorophenol, and Dihydroxibenzene.
DSA-Pt anode. 2V, 10-12 A/m²

Concentration (mM)

- 4-Chlorophenol pH 6
- 4-Chlorophenol pH 10
- Dihydroxibenzene pH 6
- Dihydroxibenzene pH 10

Time (min)

Concentration (mM)
4-Chlorophenol. DSA-Pt Anode. 70 A/m². 2V

- **Concentration (mM)**
  - 4-Chlorophenol
  - Chloride
  - Active Chlorine

- **pH**

- **Time (min)**
4-Chlorophenol electrooxidation

(Brillas E. et al., 2006).
4-Chlorophenol electrooxidation
COD Removal Untreated Alkaline Effluent. 2V. 1.8A/m²

- Graphite: kWh/kg COD = 0.4
- DSA-RuO₂: kWh/kg COD = 0.3
- DSA-Pt: kWh/kg COD = 0.2

ACE:
- Graphite: 22
- DSA-RuO₂: 26
- DSA-Pt: 37
COD Removal. Untreated Alkaline Effluent.

Effect of Supporting Electrolyte

The graph shows the COD removal over time for different electrolyte solutions. The x-axis represents time in minutes, ranging from 0 to 60, and the y-axis represents the COD concentration ratio, ranging from 0 to 1. The legend indicates different electrolyte solutions:

- DSA-Pt
- DSA-RuO2
- DSA-Pt + 1M Na2SO4
- DSA-RuO2 + 1M Na2SO4
COD Removal. Untreated Alkaline Effluent. 2V, 1.8 A/m²

Graphite
DSA-RuO₂
DSA-Pt
average pH

<table>
<thead>
<tr>
<th>Material</th>
<th>kWh/kg COD</th>
<th>ACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.4</td>
<td>22</td>
</tr>
<tr>
<td>DSA RuO₂</td>
<td>0.3</td>
<td>26</td>
</tr>
<tr>
<td>DSA-Pt</td>
<td>0.2</td>
<td>37</td>
</tr>
</tbody>
</table>
COD Removal 20kDa Alkaline Permeate. 2V. 1-2 A/m². 1.1mS/cm

<table>
<thead>
<tr>
<th>Material</th>
<th>kWh/kg COD</th>
<th>ACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.3</td>
<td>17</td>
</tr>
<tr>
<td>DSA RuO₂</td>
<td>0.4</td>
<td>18</td>
</tr>
<tr>
<td>DSA-Pt</td>
<td>0.5</td>
<td>18</td>
</tr>
</tbody>
</table>
COD Removal 20kDa Alkaline Permeate. 2V.

Graph showing the relationship between COD removal and electrical charge for different materials:
- DSA-RuO2
- DSA-Pt
- GRAPHITE
- Average pH

The graph displays the COD removal ratio ([COD] / [COD]₀) against electrical charge (Ah/m³) and average pH over a range of values.
COD Removal 10kDa Alkaline Permeate. 2V. 0.5-1.6A/m2

Graphite
DSA-RuO2
DSA-Pt

<table>
<thead>
<tr>
<th></th>
<th>kWh/kg COD</th>
<th>ACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.2</td>
<td>15</td>
</tr>
<tr>
<td>DSA RuO2</td>
<td>0.2</td>
<td>33</td>
</tr>
<tr>
<td>DSA-Pt</td>
<td>0.2</td>
<td>27</td>
</tr>
</tbody>
</table>
COD Removal 10kDa Alkaline Permeate. 2V, 1.1 mS/cm

DSA-Pt

DSA-RuO2

Average pH

Electrical Charge, A h m⁻³

[COD] / [COD]₀

0 5 10 15 20 25 30

0 0,2 0,4 0,6 0,8 0,9 1,0

7 7,5 8 8,5 9
COD Removal 1kDa Alkaline Permeate. 2V. 1.2A/m²

Graphite
DSA-RuO₂
DSA-Pt

<table>
<thead>
<tr>
<th></th>
<th>kWh/kg COD</th>
<th>ACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.4</td>
<td>25</td>
</tr>
<tr>
<td>DSA RuO₂</td>
<td>0.3</td>
<td>27</td>
</tr>
<tr>
<td>DSA-Pt</td>
<td>0.2</td>
<td>30</td>
</tr>
</tbody>
</table>
COD Removal 1kDa Alkaline Permeate. 2V. 1 mS/cm

Graphite

DSA-Pt

DSA-RuO2

Average pH

Electrical Charge, A h m⁻³

[COD] / [COD]₀

0,0 0,2 0,4 0,6 0,8 1,0

0,0 0,2 0,4 0,6 0,8 1,0

7 7,5 8 8,5 9

0 5 10 15 20 25 30
COD Removal. Untreated Acid Bleaching Effluent. 2V, 2.3 mS/cm

- Graphite
- DSA-RuO2
- DSA-Pt
- average pH

Graph showing COD concentration (OD/ODo) vs. Electrical Charge (Ah/m3) with average pH on the right axis.
COD Electro-oxidation. Effect of pH.

pH 3-6, 22°C, 4-5 V, 50-150 mA
COD Electro-oxidation. Raw Do and Permeate.

- DSA Permeate
- Graphite Permeate
- DSA
- Graphite

COD Electro-oxidation. Raw Do and Permeate.

- 0.2 - 0.4 kWh/kg COD
- 0.1 - 0.2 kWh/kg COD

pH 3, 22°C, 4-5 V, 50-150 mA
Active Chlorine Generation. Raw Do Effluent

**Chloride**

- Chloride - Graphite
- Chloride - DSA
- Active Chlorine - DSA
- Active Chlorine - Graphite

**Active Chlorine**

- pH 6.8, 22°C, 4-5 V, 50-150 mA
COD Removal 10kDa Acid Permeate. 2V. 10-20 A/m². 1.7 mS/cm

Graphite 0.5
DSA-RuO₂ 0.4
DSA-Pt 0.4

<table>
<thead>
<tr>
<th>Material</th>
<th>kWh/kg COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.5</td>
</tr>
<tr>
<td>DSA RuO₂</td>
<td>0.4</td>
</tr>
<tr>
<td>DSA-Pt</td>
<td>0.4</td>
</tr>
</tbody>
</table>
COD Removal 10kDa Acid Permeate, 2V, 1.7 mS/cm

![Graph showing COD removal efficiency for different materials: Graphite, DSA-RuO2, DSA-Pt. The x-axis represents electrical charge (Ah/m³) and the y-axis represents the ratio of COD concentration ([COD] / [COD]₀). The graph illustrates the efficiency of each material in removing COD over a range of electrical charges.]
COD Removal 1kDa Acid Permeate. 2V. 10 A/m². 1.7 mS/cm

- GRAPHITE
- DSA-RuO₂
- DSA-Pt

<table>
<thead>
<tr>
<th>Material</th>
<th>kWh/kg COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.3</td>
</tr>
<tr>
<td>DSA RuO₂</td>
<td>0.2</td>
</tr>
<tr>
<td>DSA-Pt</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Time (min) vs. $[\text{COD}] / [\text{COD}]_0$
COD Removal 1kDa Acid Permeate. 2V, 1.4 mS/cm.

- Graphite
- DSA-RuO2
- DSA-Pt

Electrical Charge, A h / m3

$\frac{[\text{COD}]}{[\text{COD}]_0}$
AOX Removal Raw Do and Permeate Effluents

![Graph showing AOX removal over time for DSA, Graphite, DSA-permeate, and Graphite-permeate.](image)

- **DSA**: 8 - 9 kWh/kg AOX
- **Graphite**: 11 - 12 kWh/kg COD

**Conditions:**
- pH 3
- 22°C
- 4-5 V
- 50-150 mA
OH• Electro-generation. pCBA Degradation

$pH\ 3, 22°C, 4-5\ V, 50-150\ mA$
Effect of Radical Scavengers on Electrooxidation of Do effluent

\[ \frac{[\text{COD}]}{[\text{COD}]_0} \]

Time (min)

\( pH 3, 22^\circ C, 4-5 \text{ V}, 50-150 \text{ mA} \)
## Toxicity Results

<table>
<thead>
<tr>
<th></th>
<th>COD (g/m³)</th>
<th>BOD&lt;sub&gt;5&lt;/sub&gt; (g/m³)</th>
<th>BOD&lt;sub&gt;5&lt;/sub&gt;: COD Ratio</th>
<th>TOC (g/m³)</th>
<th>AOX (g/m³)</th>
<th>Genotoxic Activity Rec+/Rec–</th>
<th>Mutagenicity Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T98</td>
</tr>
<tr>
<td>Raw Effluent</td>
<td>1,370</td>
<td>290</td>
<td>0.21</td>
<td>1,720</td>
<td>10</td>
<td>1.51</td>
<td>1.9</td>
</tr>
<tr>
<td>2 min treat.</td>
<td>1,300</td>
<td>275</td>
<td>0.21</td>
<td>1,718</td>
<td>8</td>
<td>1.42</td>
<td>1.9</td>
</tr>
<tr>
<td>5 min treat.</td>
<td>930</td>
<td>303</td>
<td>0.33</td>
<td>1,514</td>
<td>6</td>
<td>1.13</td>
<td>1.4</td>
</tr>
<tr>
<td>10 min treat.</td>
<td>890</td>
<td>318</td>
<td>0.36</td>
<td>1,480</td>
<td>4</td>
<td>1.11</td>
<td>0.9</td>
</tr>
<tr>
<td>15 min treat.</td>
<td>850</td>
<td>322</td>
<td>0.38</td>
<td>1,330</td>
<td>3</td>
<td>1.05</td>
<td>0.7</td>
</tr>
<tr>
<td>20 min treat.</td>
<td>790</td>
<td>327</td>
<td>0.41</td>
<td>1,320</td>
<td>2</td>
<td>1.03</td>
<td>0.7</td>
</tr>
</tbody>
</table>
• Genotoxic activity detected in all untreated samples.

• No frame-shift mutation mechanism (T98).

• No pro-mutagenic chemicals (S9).

• Untreated samples:
  Mutagenic activity by base pair substitution (T100)
  Presence of a direct-acting mutagen (T100)

• Electrochemical oxidation removed those mutagenic activity after 2 min treatment
Conclusions

1) Permeates from bleaching could be electrooxidised using DSA and/or graphite anodes, without addition of supporting electrolytes.

2) Alkaline conditions promote greater COD removal.

3) Genotoxic and mutagenic activities disappear rapidly with electrooxidation.

4) AOX is significantly removed by anodic oxidation.

5) Electrogendrenerated active chlorine enhances the rate of COD removal in acid bleaching effluents.