Electrochemical Technologies in Wastewater Treatment

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Water Pollution Impacts
Wastewater Treatment Techniques

Coagulation
Sedimentation
Flotation
Filtration

⇒ to remove particles

Biological processes
Advanced oxidation
Adsorption
Membrane processes

⇒ to remove organic compounds
Electricity Is Not a Stranger
Electrochemical methods

- Electrodeposition
- Electrocoagulation
- Electroflotation
- Electrooxidation
- Electrodisinfection
- Electroreduction

⇒ High efficiency
⇒ Easy operation
⇒ Compact facilities
Electrodeposition for heavy metal recovery

\[ Mn^{n+} + ne \rightarrow M \]
Electrocoagulation

- Generating coagulant electrically

  \[
  \text{Al} - 3e \rightarrow \text{Al}^{3+} \\
  \text{Fe} - 2e \rightarrow \text{Fe}^{2+}
  \]

- Sludge floated by hydrogen gas

  \[
  2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^-
  \]
Applications of Electrocoagulation

- Suspended solids
- Oil & grease

Facilities Required

- Al or Fe plates as electrodes
- DC power supply
- Pumping facility
Electrocoagulation units

(a) Horizontal flow

(b) Vertical flow
### The aluminum demand and power consumption for removing pollutants from water

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Unit quantity</th>
<th>Preliminary purification</th>
<th>Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al(^{3+}), mg</td>
<td>E, W·h/m(^3)</td>
</tr>
<tr>
<td>Turbidity</td>
<td>1 mg</td>
<td>0.04 – 0.06</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Colour</td>
<td>1 unit</td>
<td>0.04 – 0.1</td>
<td>10 - 40</td>
</tr>
<tr>
<td>Silicates</td>
<td>1 mg/SiO(_2)</td>
<td>0.2 – 0.3</td>
<td>20 - 60</td>
</tr>
<tr>
<td>Irons</td>
<td>1 mg Fe</td>
<td>0.3 – 0.4</td>
<td>30 - 80</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1 mg O(_2)</td>
<td>0.5 - 1</td>
<td>40 - 200</td>
</tr>
<tr>
<td>Algae</td>
<td>1000</td>
<td>0.006 – 0.025</td>
<td>5 -10</td>
</tr>
<tr>
<td>Bacteria</td>
<td>1000</td>
<td>0.01 – 0.04</td>
<td>5 -20</td>
</tr>
</tbody>
</table>
Electroflotation

• Generating gas bubbles electrically

\[ 2\text{H}_2\text{O} - 4e \rightarrow \text{O}_2 + 4\text{H}^+ \]

\[ 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \]

• Gas bubbles attaching to flocs

• Floating to top of water surface
## Economic parameters in treating oily effluents

<table>
<thead>
<tr>
<th></th>
<th>EF</th>
<th>DAF</th>
<th>IF</th>
<th>Settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble size, µm</td>
<td>1 - 30</td>
<td>50 - 100</td>
<td>0.5 – 2</td>
<td></td>
</tr>
<tr>
<td>Specific electricity consumption, W/m³</td>
<td>30 - 50</td>
<td>50 - 60</td>
<td>100 - 150</td>
<td>50 – 100</td>
</tr>
<tr>
<td>Air consumption, m³/m³ water</td>
<td></td>
<td>0.02 – 0.06</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Chemical conditioning</td>
<td>IC</td>
<td>OC + F</td>
<td>OC</td>
<td>IC + F</td>
</tr>
<tr>
<td>Treatment time, minutes</td>
<td>10 - 20</td>
<td>30 - 40</td>
<td>30 - 40</td>
<td>100 - 120</td>
</tr>
<tr>
<td>Sludge volume as % of treated water</td>
<td>0.05 – 0.1</td>
<td>0.3 – 0.4</td>
<td>3 - 5</td>
<td>7 - 10</td>
</tr>
<tr>
<td>Oil removal efficiency, %</td>
<td>99 – 99.5</td>
<td>85 - 95</td>
<td>60 - 80</td>
<td>50 – 70</td>
</tr>
<tr>
<td>SS removal efficiency, %</td>
<td>99 – 99.5</td>
<td>90 - 95</td>
<td>85 - 90</td>
<td>90 - 95</td>
</tr>
</tbody>
</table>
Challenges in $O_2$ Evolution Anodes

Economical
Stable
Active

$O_2$ Evolution Anodes

Pt (wire, mesh, plates)
PbO$_2$
Graphite
DSA (TiO$_2$-RuO$_2$; IrO$_2$ with Ta$_2$O$_5$, ZrO$_2$ or CeO$_2$)
DSA (Ti/IrO$_2$-Sb$_2$O$_5$-SnO$_2$)
Electrooxidation

Indirect electrooxidation

- Cl\textsubscript{2} formation
- H\textsubscript{2}O\textsubscript{2} generation
- O\textsubscript{3} generation
- Mediator, Ag\textsuperscript{2+}

Direct oxidation

- OH radicals for complete mineralization
Formation Potential of Typical Chemical Reactants

<table>
<thead>
<tr>
<th>Oxidants</th>
<th>Formation potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}/\cdot\text{OH}$ (hydroxyl radical)</td>
<td>2.80</td>
</tr>
<tr>
<td>$\text{O}_2/\text{O}_3$ (ozone)</td>
<td>2.07</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}/\text{S}_2\text{O}_8^{2-}$ (peroxodisulfate)</td>
<td>2.01</td>
</tr>
<tr>
<td>$\text{MnO}_2/\text{MnO}_4^{2-}$ (permanganate ion)</td>
<td>1.77</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}/\text{H}_2\text{O}_2$ (hydrogen peroxide)</td>
<td>1.77</td>
</tr>
<tr>
<td>$\text{Cl}^-/\text{ClO}_2^-$ (chlorine dioxide)</td>
<td>1.57</td>
</tr>
<tr>
<td>$\text{Ag}^+/\text{Ag}^{2+}$ (silver (II) ion)</td>
<td>1.50</td>
</tr>
<tr>
<td>$\text{Cl}^-/\text{Cl}_2$ (chlorine)</td>
<td>1.36</td>
</tr>
<tr>
<td>$\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$ (dichromate)</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}/\text{O}_2$ (oxygen)</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Basic Requirements of Electrodes

• Good activity
• High stability
• Low cost
## Potential of Oxygen Evolution of Anodes

<table>
<thead>
<tr>
<th>Anode</th>
<th>Value, V</th>
<th>Over-potential, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1.3 – 1.6</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>IrO₂</td>
<td>1.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Graphite</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>PbO₂</td>
<td>1.9</td>
<td>0.7</td>
</tr>
<tr>
<td>SnO₂</td>
<td>1.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Pb-Sn</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Ebonex (Ti₄O₇)</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Si/BDD</td>
<td>2.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Ti/BDD</td>
<td>2.7 – 2.8</td>
<td>1.5 – 1.6</td>
</tr>
</tbody>
</table>
Analysis of Available Electrodes

- Graphite: unstable, ineffective, cheap
- Pt, IrO$_2$: too expensive, ineffective
- PbO$_2$, SnO$_2$: unstable, easy to make
- B-diamond (BDD), effective, expensive
Oxidation of acetic acid
Oxidation of phenol

![Graph showing the oxidation of phenol with different charge loadings and residual COD values. The graph compares the performance of Ti/BDD and Ti/Sb$_2$O$_5$-SnO$_2$.](image-url)
Oxidation of orange II

COD, mg/L

Charge loading, Ah/L

Ti/Sb₂O₅-SnO₂

Ti/BDD
Reproducibility comparison, 500 mg/l phenol at 100 A/m², 30 °C.
Electrodisinfection

• Generating chlorine electrically

\[ 2\text{Cl}^- - 2e \rightarrow \text{Cl}_2 \quad \text{(anode)} \]

\[ 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(cathode)} \]

• Generating OH radicals electrically
  (similar to electrooxidation)
Log-kill of bacteriophage MS2 versus time at different currents at salt content 1% NaCl by mass

$N_0 = 10^7 - 10^8$ PFU/mL

$pH = 7.0$

$[\text{NaCl}] = 1\%$
Comparison between the log-kill of bacteriophage MS2 in the EC and PC systems at currents of 0.05 and 0.15 A
Electroreduction

• Direct reduction on the surface of cathode

\[ \text{M}^{n+} + n\text{e} \rightarrow \text{M} \quad \text{(cathode)} \]

• Mediated reduction by H\(_2\) generated

\[ 2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(cathode)} \]

• Mediated reduction by Fe\(^{2+}\) generated

\[ \text{Fe} - 2\text{e} \rightarrow \text{Fe}^{2+} \quad \text{(anode)} \]
Influent solution

Fe plate

Compressed air

draft tube

EC

EF1 effluent solution

EF2

effluent solution

Anode (oxidation): \[ \text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e^- \] (1)

Mediated reduction: \[ \text{Cr}^{6+} + 3\text{Fe}^{2+} \leftrightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} \] (2)

Cathode (reduction): \[ 2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \] (3)

Co-precipitation: \[
\begin{align*}
\text{Cr}^{3+} + 3\text{OH}^- & \leftrightarrow \text{Cr(OH)}_3 \\
\text{Fe}^{3+} + 3\text{OH}^- & \leftrightarrow \text{Fe(OH)}_3 \\
\text{Fe}^{2+} + 2\text{OH}^- & \leftrightarrow \text{Fe(OH)}_2
\end{align*}
\] (4-6)
CONCLUSIONS

• Electrodeposition established

• Electrocoagulation works

• Electrocoagulation & electroflotation works better

• BDD is an excellent anode for electrooxidation

• Electrodisinfection outperforms pump chlorine system

• Electroreduction is finding more application
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