Electrochemical Advanced Oxidation Processes

Prof. Manuel A. Rodrigo
Department of Chemical Engineering
University of Castilla La Mancha. SPAIN

Manuel.Rodrigo@uclm.es
Electrochemical Advanced Oxidation Processes

- Environmental Engineering & Electrochemical Technology
- Electrochemical Treatment of Water & Wastewater
- Anodic oxidation
- Enhanced mediated electrolysis
- Remarks on the application of electrolysis to water & wastewater treatment
- Conclusions and remarks
- To learn more...
- Annex I: pre-sizing of electrochemical processes
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Perhaps, you are thinking that I’m going to tell you that electrochemical technology is the best set of environmental remediation technologies...

... but be sure, this is not want I want to tell you. I just want to show some cases in which electrochemical engineering could be of a great help for the remediation of environmental problems and to describe briefly the fundamentals of these technologies.
Do not forget that electrochemical technology is...

...Not very appreciated in the conventional chemical industry:

- Low efficiency
- Too expensive
- Rarely tested at the full plant scale
- Not conventional
- ...

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But... there are many industrial processes that are electrochemical processes.
And... why not? There is a very important question in the air: Could it be used in Environmental Engineering?
Electrolysis: organic and metals
Electrodialysis: desalination and purification of streams
Electrocoagulation: colloids and emulsions
Industry

**Recover materials or energy**

**Reuse**

**Recycle**

- **Electrodeposition** (Electrowinning of metals and metal recovery)
- **Electrodialysis** (Membranes as material engineering in the construction of electrochemical cells)

**Coagulation-Flocculation-Sedimentation-Filtration**

**Electrocoagulation**

**Municipal sewer or environment**

**Electrochemical oxidation**

**Remove non biodegradable organics**

**Remove biodegradable organics**

**Remove particles**

**Biological treatment**

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- Electrocoagulation: removal of NOM
- Electrodialysis: desalination
- Electrodisinfection
- Gaseous streams treatment
- Soil electroremediation: ionic pollutants, organics, etc
Which are the expected advantages of electrochemical technologies in environmental remediation?

- **Environmental compatibility**: “the main reagent used is the electron” No residues are formed.
- **Versatility**:
  - Many processes occur simultaneously in any electrochemical cell. Plethora of reactors, electrode materials, shapes, configuration can be utilized and allow to promote different kinds of treatment technologies.
  - Point-of-use production of chemicals is facilitated by electrochemical technology
  - Volumes of fluid from microliters to thousand of cubic meters can be treated
- **Processes work at room temperature and atmospheric pressure**
- **Selectivity**: in some cases the applied potentials can be controlled to selectively attack specific compounds.
- **Easy operation. Amenability to automation.**
- **Cost effectiveness when properly used**
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ELECTROCHEMICAL TREATMENT OF WATER AND WASTEWATER

1. Electrooxidation
2. Electroreduction
3. Electrodissolution
4. Electrodeposition
5. Migration of anions
5. Migration of cations

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What are the main parameters used to assess these processes?

Rate of electrochemical processes vs intensity

\[ R \pm ne^- \rightarrow \ldots \]

\[ r \left( \frac{\text{mol} R}{s} \right) = \frac{I(A)}{n \left( \frac{\text{mol} e^-}{\text{mol} R} \right) F \left( \frac{96500 \text{C}}{\text{mol} R} \right)} \]

Take care: just one Intensity in the whole cell!!!

Current density

\[ j \left( \frac{kA}{m^2} \right) = \frac{I(kA)}{A_{electrode} \left( m^2 \right)} \]
Cell voltage

\[ E(V) = -I \cdot R_{\text{circ}}^c - (E_e^c + |\eta_c|) - I \cdot R_{\text{cat}} - I \cdot R_{\text{sep}} - I \cdot R_{\text{anod}} - (E_e^a + |\eta_a|) - I \cdot R_{\text{circ}}^d \]
Specific applied current charge

- Batch processes:
  \[ q \left( \frac{kAh}{m^3} \right) = \frac{I(kA) \cdot t(h)}{V_r(m^3)} \]

- Continuous processes:
  \[ q \left( \frac{kAh}{m^3} \right) = \frac{I(kA)}{Q\left( \frac{m^3}{h} \right)} \]

Specific Power consumption

\[ W\left( \frac{kWh}{m^3} \right) = q\left( \frac{kAh}{m^3} \right) \cdot E(V) \]
Electrocoagulation

An alternative to the direct use of a solution containing the coagulant salts, is the in situ generation of coagulants by electrolytic oxidation of an appropriate anode material (e.g. iron or aluminium). This process is called **electrocoagulation** or electrochemically assisted coagulation.
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Hydraulic circuits
- at least three circuits concentrated, diluted and electrode rinse.
- Concentrations up to 20%
- Ratios concentrated/diluted up to 100

Advantages
- No chemicals are required
- Selectivity
- Ions separation without phase change
- Easy scale-up

Drawbacks
- Membrane fouling.
- Polarization
- extreme pHs

Applications
- Desalination of brackish water
- Purification of acids and bases
- Recovery of chromates

Electrodes
- Typically plates
- Anodes with a high chemical resistance such as platinized titanium or DSA.
- Cathodes of stainless steel or with the same material than anodes (for reversible electrodialysis).

Membranes
- Alternate anionic and cathionic membranes.
- Membranes separated by path spacers and/or flow distributor.
- Bipolar membranes for purification
- Long lifetime of membranes.

Electrodialysis
- Typically plates
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Changes in the chemical composition of a wastewater using electricity

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineralization of organics (full treatment)</td>
<td>Electrodeposition of metal ions</td>
</tr>
<tr>
<td>Partial oxidation of organics (complementary treatment)</td>
<td>Dehalogenation of halogenated organics</td>
</tr>
<tr>
<td>Oxidation of inorganic pollutants</td>
<td>Reduction of inorganic pollutants</td>
</tr>
<tr>
<td>Production of chemical oxidant agents</td>
<td>Production of chemical reduction agents</td>
</tr>
</tbody>
</table>

Electrolysis

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- Annex I: pre-sizing of electrochemical processes
Most significant parameters

- Electrochemical Advanced Oxidation Processes
- Prof. M.A. Rodrigo
- 2nd Summer School on Environmental applications of AOPs
- Porto, July 10-14, 2017

**ANODIC OXIDATION**

1. **Electrochemical properties**
   - Electrode Material choice
   - Promotion of mediated processes
   - Irradiation of US/UV

2. **Mass transfer**
   - Cell design

3. **Enhanced mediated electrolysis**
DESIRABLE PROPERTIES

MECHANICAL STABILITY.
CHEMICAL STABILITY
MORPHOLOGY.
ELECTRICAL CONDUCTIVITY
CATALYTIC PROPERTIES
RATIO PRICE/ LIFETIME.

anodes
- Production of oxygen
- Oxidation of organic matter
- Oxidation of chloride
- Production of oxidants
- Disinfection
- Other specific purposes

cathodes
- Production of hydrogen
- Production of hydrogen peroxide
- Dehalogenation of pollutants
- Electrodeposition of metals
- Other specific purposes
1. Direct electrolysis
Oxidation of the pollutant on the electrode surface

2. Advanced oxidation processes
With some anode materials it is possible the generation of OH·

3. Chemical oxidation
On the electrode surface several oxidants can be formed from the salts contained in the electrolyte
### ANODES FOR THE OXIDATION OF ORGANIC MATTER

**Electrode material**

<table>
<thead>
<tr>
<th>Metals</th>
<th>Platinum</th>
<th>Stainless steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>Grafite</td>
<td><strong>Conductive-Diamond</strong></td>
</tr>
<tr>
<td>Oxides</td>
<td>DSA-O₂</td>
<td>DSA-Cl₂</td>
</tr>
<tr>
<td></td>
<td>Ti/SnO₂</td>
<td>Ti/PbO₂</td>
</tr>
</tbody>
</table>

**Lowly efficient anodes**

**Highly efficient anodes**

![Graph showing COD vs. Q for different electrode materials](image)

**Graphite**

**DSA-O₂**

**Ti/PbO₂**

**p-Si DDB**

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Lowly efficient anodes

SOFT OXIDATION CONDITIONS

- Many intermediates
- Small conversion to carbon dioxide
- Slow oxidation rates
- Small current efficiencies
- Formation of polymers from aromatic pollutants is favoured

Quinones, polymers, carboxylic acids

Fouling by polymers

Pt
Ti/Pt
Ti/RuO₂
Ti/IrO₂

Ti/IrO₂ Promotes water oxidation (DSA-O₂)

Ti/RuO₂ Promotes chlorine production (DSA-Cl₂)
Highly efficient anodes

HARD OXIDATION CONDITIONS

- Few intermediates
- Large conversion to carbon dioxide (mineralization)
- Large current efficiencies only limited by mass transfer

Drawbacks of highly efficient electrodes:
- Conductive diamond: large price
- PbO$_2$/SnO$_2$: Dissolution of toxic species

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COD\_0

ICE=100%

COD\_lim

Discharge to sewer

\( ICE(t) = \frac{COD(t)}{COD\_lim} \times 100\% \)

Discharge to environment

Full treatment

0 ppm

125 ppm

1500 ppm

Instantaneous Current Efficiency / %

COD / g m\(^{-3}\)

\( ICE = \frac{COD(t)}{COD\_lim} \)

\( ICE = 1 \)
2. CATHODE

1. Production of hydrogen
   Main side reaction
   \[ e^- + H_2O \rightarrow \ H_2 + OH^- \]

2. Reduction of pollutant or intermediates
   - Normally not useful for the treatment of organics except for dechlorinations
   - Very important in the recovery of metals
CATHODIC MATERIALS

Main reactions

- deposition of metallic ions
- dehalogenation of halogenated organics
- hydrogen peroxide production
- hydrogen production

The organic-oxidation processes that occur in an electrochemical cell are usually irreversible.
- Hydrogen evolution is the main cathodic reaction.

- Glassy carbon
- Carbon felts, fibers of cloths
- Graphite
- Metals (Ni, stainless steel, Pt, Ti/Pt etc.)
Cathodes for metal deposition

**Glassy carbon.** High Surface/volumen ratio (>66 cm²/cm³). Inert with most chemical. Low cost and easy to be adapted to any reactor geometry. Applied successfully in the removal from wastes of Cu, Cd, Cr, Pb, U, Hg, Ag, Zn

**Graphite / carbon fibers.** Good area/volumen ratio, (1000 m²/g), low cost, high chemical resistance. Applied successfully in the treatment of wastes with Au, Ir, Pt, Ag, Pd, Cd, Pb, Ni y Hg

**Porous graphite.** Interesting for the removal of Eu³⁺ from lantanides mixtures

**Metals.** Used as grids or fibers. Commonly used for the removal of Ni, Al, Cu, Au, Ag, mixtures

**Advantages of metal deposition**

- Metal is recovered in its most valuable form. Highly valued products
- Low sludge production
- Low operating cost
- Widely used. Very easy to be applied
- Not easy to control the quality of the product. Many parameters influenced on results (gas formation, mass transfer, fluid dynamic conditions, etc.)
FORMATION OF CARBONATES DURING ELECTROLYSES

Deposit of carbonates
\[ \text{OH}^- + \text{HCO}_3^- \]

Increase in the cell potential

Increase in the energy consumption

Polarity reversal

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Electrochemical cell

DESIRABLE CHARACTERISTICS FOR A ELECTROCHEMICAL CELL

- SIMPLE MECHANICAL DESIGN. SMALL PRICE. EASY TO USE. LOW MAINTENANCE COST.
- ENHANCED MASS TRANSFER.
- HOMOGENEOUS CURRENT DISTRIBUTION ON THE ELECTRODES.
- LARGE DURABILITY
- SAFETY
ELECTROLYTIC CELLS

Room temperature and pressure
Cell voltage: 3-6 V
Current densities: 500 - 2000 A/m²

Design parameter: amount of COD to be removed

\[
2H_2O + 2e^- = H_2(g) + 2OH^- \quad \text{(catódica)}
\]

\[
\text{COD} - 4e^- = ... \quad \text{(anódica)}
\]
USE OF DIVIDED CELLS IN WASTEWATER TREATMENT PROCESSES?

1. The membrane increases the cell potential and consequently the operating cost.
2. Most organic-oxidation processes are irreversible.
3. Most inorganic redox reactions are reversible.
Electrolyte flow

- Electrodes connection

monopolar

bipolar
Most applied cells

TANK CELLS

ADVANTAGE: Simplest cell

DRAWBACK: Low mass transfer coefficients

Take care! This is also a tank cell!
**FILTER PRESS CELL**

- Large electrode surfaces / volume ratios
- Small interelectrode gap
- Plane electrodes

---

**SINGLE FLOW CELL**

- Single – Compartment Electrochemical Cell
- Double compartment Electrochemical Cell

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**ANODE**

**CATHODE**

**DIAPHRAGM**

**Anodic Compartment**

**Cathodic Compartment**

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Fluidized bed cell

Other electrolytic cells

Rotatory electrode cell

Packed bed cell

large particles

small particles

anolyte

catholyte

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Advantages of the direct electrolysis

- Environmental compatibility: “the main reagent used is the electron” No residues are formed.
- Can be a complementary treatment or a final treatment
- Operation at room temperature and atmospheric pressure
- High efficiency if proper anode material is used.
- The efficiency can be easily increased by promoting indirect processes
- Easy operation. Amenability to automation.
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Aims to improve the efficiency of oxidative electrolytic processes by promoting the production of reagents which acts on the bulk.
The oxidation is carried out in the whole reaction volume (not limited to the electrode surface)

- OPTIMIZATION OF PERFORMANCE WITH THE USE OF OXIDANTS
- NO MASS TRANSFER LIMITATIONS

- SURFACE TO VOLUMETRIC PROCESS
- CATHODE CAN BE USED TO PRODUCE AN OXIDANT

No mass transfer control

**higher efficiency**

Both direct and indirect electro-oxidation develop simultaneously in the cell

- Particularly good for low concentrations
- Specially important processes based on cathodically produced hydrogen peroxide
- For oxidation of organic free wastewaters, very interesting the production of chlorine

- Production of reagents and treatment of the waste in the same cell (in situ)
- Production of reagents and treatment of the waste in different cells (ex-situ)
In situ

- Raw wastewater
- Reagent to produce oxidant
- Production of oxidants and wastewater oxidation
- Treated wastewater
- Reduced form of the oxidant reagent
- Separation of the oxidant or of its reduction product

Ex-situ

- Raw wastewater
- Reagent to produce oxidant
- Production of oxidants
- Wastewater oxidation
- Treated wastewater
- Reduced form of the oxidant reagent
- Separation of the oxidant or of its reduction product
To take in mind...

- The potential at which the electrogenerated oxidants are produced must not be near the potential for water oxidation, since then a large portion of the current will be employed in the side reaction.

- The rate of generation of the electrogenerated oxidant should be large.

- The rate of oxidation of pollutant by the electrogenerated oxidant must be higher than the rates of any competing reactions.

- The electrogenerated oxidant must not be a harmful product.

- Reduced form of reagents should be easily eliminated or environmentally friendly.
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<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reversible oxidant</strong></td>
<td></td>
</tr>
</tbody>
</table>
Ag(I) / Ag(II)  
Co(II) / Co(III)  
Ce(III) / Ce (IV)  
Fe(II) / Fe (III)  
SO$_4^{2-}$ / S$_2$O$_8^{2-}$  
PO$_4^{3-}$ / S$_2$O$_8^{4-}$ |
| The oxidant can be reduced in the cathode. A divided cell may be considered | |

| **Irreversible (killers)** |  
Cl$_2$  
O$_3$  
H$_2$O$_2$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>The oxidant is not reduced on the cathode. Non-divided cells are used for their production</td>
<td></td>
</tr>
</tbody>
</table>

These oxidants are generated from anions typically present in a wastewater

It can be formed by a cathodic process. Extra oxidation efficiency!
Electro-fenton: a way to optimize the cathode

1. Production of hydrogen
   Main side reaction
2. Production of hydrogen peroxide
3. Reduction of Iron (III)

Combination of electrooxidation with cathodic generation of hydrogen peroxide allows to obtain current efficiencies over 100%. It is the best way of obtaining a valuable compound from the cathodic reaction in wastewater treatment processes.
\[ \text{H}_2\text{O}_2/\text{Fe}^{2+} \]

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \\
\text{rate} \sim 76 \text{ M}^{-1} \text{ s}^{-1}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2\text{H}^- \\
\text{rate} \sim 0.01 \text{ M}^{-1} \text{ s}^{-1}
\]

Fenton oxidation only happens with iron (II). Then, main reaction is Fenton like reaction, with a much more lower rate.

Alternative catalyst: cupper instead of iron
Electrochemical reactions

It can be formed on the cathode by reduction of oxygen

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^- \quad E^0=-0.065 \text{ V} \]

However, the main drawback is the decomposition of the hydroperoxide anion that it is favoured at alkaline conditions.

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

Cathodic reduction of iron (III) is required because iron(II) is a catalyst

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

Special attention should be paid to the low solubility of iron (III) species
To promote the efficiencies it is required:

- A cathode material with a high overpotential for the reduction of the hydroperoxide anion to water (carbon-base).
- Good oxygen transfer rates to the cathode surface.

Anodic oxidation processes:

- Best pH: around 3.0.
- Cathode material: carbon felt, graphite, porous carbon...
- Not necessary iron anodes. With iron anodes no Electro-Fenton but peroxicoagulation occurs.
- Very good results in the combination with Conductive Diamond anodes (complementary electrochemical technologies).
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What do we know about full scale wastewater electrolytic processes?

- Easier temperature regulation (heat disipation)
- Enhanced mixing conditions by pumping
- Increased hydraulic residence time for mediated processes
☑️ **Commercial cells**

- Designed for electrosynthesis, not for wastewater treatment

- Designed specifically for diamond. Applied commercially for disinfection

- ELECTROCELL (ElectroCell A/S, Denmark)
  - FC01-LC (former ICI Chemicals and Polymers Ltd., now INEOS Chlor-chemicals, UK)

- DIACELL (former ADAMANT TECH, Switzerland, now WaterDiam)
  - CONDIAS’ Cells for target applications

☑️ **Flow pattern**

Mixed tank vs Filter press flow
Mechanical design

- Inlet & outlet
- Flow distributors
- Current feeders
- Increase electrode size
- stacking

Uniform current distribution
Non-uniform current distribution

30 x 30 cm²

Stack of ELECTROCELL
Stack of DIACELL
Auxiliary equipments

- Recirculation tank
- Stack of cells
- Filter
- Pumps
- Electrical connections
- Piping

Power supply
SCADA

Electrical connections
Heat exchanger
Stacks of electrolytic cells

Regulation devices
Measurement devices (temperature, flowrate, concentration, level, pressure)

SCADA, fieldbus

Electrovalves
Regulation valves
Resistances

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Does the cell really influence?

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Electrochemical technologies are not cheap. Try to combine them with cheaper technologies.

Sizing requires experimental data always!. Look for:
- Feasibility
- Getting data for design (optimum current density, cell voltage, etc.)
- Efficiency for a given degree of treatment
- Operation problems
**Case study: wooden-door manufacturing factories**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effluent 1</th>
<th>Effluent 2</th>
<th>Effluent 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD₃ (mg dm⁻³)</td>
<td>13.068</td>
<td>15.310</td>
<td>7.110</td>
</tr>
<tr>
<td>pH</td>
<td>7.2</td>
<td>6.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Conductivity (mS cm⁻¹)</td>
<td>7.5</td>
<td>4.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Total nitrogen (mg N dm⁻³)</td>
<td>347</td>
<td>410</td>
<td>184</td>
</tr>
<tr>
<td>Suspended solids (mg dm⁻³)</td>
<td>13.574</td>
<td>3.766</td>
<td>2.040</td>
</tr>
</tbody>
</table>

Main pollutants:
- Formaldehyde / urea
- Formaldehyde / resorcinol
- Polyvinyl acetate

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**Diagram:**

- **molding**
- **glueing**
- **Press and finishing**

**Wood pieces**

**Water to clean equipments**

**Effluent of the factory**

**Doors to market**

**Water to clean machinery**

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Parameter | Effluent 1 | Effluent 2 | Effluent 3
--- | --- | --- | ---
COD$_0$ (mg dm$^{-3}$) | 13.068 | 15.310 | 7.110
Coagulant Concentration (mmol dm$^{-3}$) | aluminium | iron | aluminium
COD$_f$ (mg dm$^{-3}$) | 8.120 | 9.640 | 4.770
COD removal (%) | 38 | 37 | 33

Limit of discharge to municipal sewers
**BIOLOGICAL TREATMENT + CDEO**

- **Biological Treatment**
  - Influent
  - Biological Treatment
  - Effluent
  - Air

- **CDEO**
  - Electrochemical Treatment or Alternative
  - Biological Treatment

**Graph**
- **COD / g m⁻³**
  - Time / days
  - Limit of discharge to municipal sewers
  - Fast biodegradation
  - Slow biodegradation

- **Removal of COD / %**
  - COO / Kg O₂ m⁻³

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Applications of Electrolysis

Industrial wastewater

- Pharmaceutical industries
- Ink manufacturing
- Hospital
- Food processing
- Metalworking fluids
- Petrochemical
- Melanoidins

Range (COD)

<table>
<thead>
<tr>
<th>Method</th>
<th>COD Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct electrolysis</td>
<td>1500-20000 mg dm⁻³</td>
</tr>
<tr>
<td>Enhanced Mediated Electrolysis</td>
<td>&lt;1500 mg dm⁻³</td>
</tr>
</tbody>
</table>
Simultaneous deposition of metal ions and oxidation of CN⁻ in exhausted baths

It is also used for disinfection of swimming pools, reclaimed wastewater and drinking water

Electrochemical Advanced Oxidation Processes. Prof. M.A. Rodrigo.
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Electrochemical Advanced Oxidation Processes

- Environmental Engineering & Electrochemical Technology
- Electrochemical Treatment of Water & Wastewater
- Anodic oxidation
- Enhanced mediated electrolysis
- Remarks on the application of electrolysis to water&wastewater treatment
- Conclusions and remarks
- To learn more...
- Annex I: pre-sizing of electrochemical processes
CONCLUSIONS AND REMARKS

People from academia

it works!, needs to be promoted

People from industry

too expensive?, low efficiency?, not promising?
Remarks on electrochemical treatment of liquid wastes

Robustness of electrochemical technologies
Electrochemical technologies provide good results in the treatment of many industrial effluents but they have to be used properly. Lab and bench scale assessments have to be carried out to confirm the feasibility of a particular treatment and to get data for sizing.

Efficiency of electrochemical technologies
For the removal of soluble organics, conductive-diamond electrochemical oxidation is a very good technology for the range 1500-20000 mg dm$^{-3}$ (lower limit correspond to the discharge of effluents to municipal sewers), because it can achieve the complete mineralization of the organics with a 100% current efficiency. Below this concentration, enhanced mediated electrolysis processes, and particularly electro-Fenton are promising alternatives to the treatment of industrial wastewater.

Integration of electrochemical technologies
Electrochemical technologies should not be the only treatment proposed for a given industrial waste but integrated with other technologies looking for an efficient solution of the environmental problem.
Assessment of applications!
Treatment of industrial waste.

Most interesting applications are:

- Treatment of wastes polluted with metal ions by electrodeposition.
- Removal of highly refractory or toxic anthropogenic pollutants contained in industrial wastes (1,000-20,000 mg dm$^{-3}$ COD) by electrolysis.
- Breakup of emulsions and removal of colloids from industrial wastes can be obtained by electrocoagulation. This technology has also been proposed for the removal of some other more specific pollutants like dyes or metallic ions from waste, becoming a very interesting alternative to coagulation.
- Removal of gaseous pollutants, based on the absorption on aqueous solutions and in the later treatment of the liquid waste produced.

And for the next future...

- the coupling of electrolysis with other oxidation technologies in the removal of anthropogenic pollutants from wastewater at low concentrations.
- Purification of industrial flow streams for waste valorization using electrodialysis.
Water treatment and reclaiming of treated wastewater

Most interesting application is:
- desalination of brackish waters using electrodialysis.

And for the next future...

- Removal of colloids or phosphate anions from urban wastewater (reclaiming of wastewater) or in the conditioning of surface water for supply.
- Disinfection of water, either for supply or for treated wastewater reclaiming by electrolysis.
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This section contains two very simple examples to show students how can they use equations explained in section 1 to do a pre-sizing of an electrochemical process for water or wastewater treatment.

\[
R \pm ne^- \rightarrow ... \\
\]

\[
r \left( \frac{\text{mol R}}{s} \right) = \frac{I(\text{A})}{n \left( \frac{\text{mol e}^-}{\text{mol R}} \right) F \left( \frac{96500 \text{C}}{\text{mol R}} \right)}
\]

Current density

\[
j \left( \frac{kA}{m^2} \right) = \frac{I(kA)}{A_{\text{electrode}}(m^2)}
\]

Specific applied current charge

\[
q \left( \frac{kAh}{m^3} \right) = \frac{I(kA)}{Q \left( \frac{m^3}{h} \right)}
\]

Specific Power consumption

\[
W \left( \frac{kWh}{m^3} \right) = q \left( \frac{kAh}{m^3} \right) \cdot E(V)
\]
Case 1. A waste stream (10 m³/d) in a pharmaceutical company is going to be treated by electrolysis with conductive–diamond anodes. Chemical Oxygen Demand (COD₀) of the effluent is 5000 mg/l and concentration at the discharge of the treatment process (CODₖ) should be =1000 mg/l, because of municipal discharge regulations. Calculate operation cost and electrode area requirements.

Notes.
Consider the following data obtained after a lab scale evaluation of the technology:
Current efficiency = 80%; Cell voltage= 5V; Current density= 1000 A/m².
COD removal rate

\[ [G] = [I] - [O] \]

**COD removal rate**

\[ q^* (\text{COD}_0 - \text{COD}_f) = 10 \ (\text{m}^3/\text{d})^* (5000-1000) \ \text{g/m}^3 = 40000 \ \text{g/d} = 0.463 \ \text{g/s} \]

**Estimation of intensity**

For a 100% current efficiency

\[ r = \frac{I}{(nF)} = \text{mol DQO/s} \]

\[ F=96500 \ \text{C/mol e}^- \]

Then:

\[ r = 0.463 \ \text{g/s} \] of COD to be removed

\[ r = \frac{(I \cdot m_{\text{DQO}})}{(nF)} = 0.463 \ \text{g/s} \]

\[ (I \cdot 32) / (4 \cdot 96400) = 0.463 \ \text{g/s} \]

**For COD oxidation**

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

\[ m_{\text{DQO}} = 32 \ \text{g/mol} \]

\[ n = 4 \ \text{mol e}^- / \text{mol COD} \]

From Experimental data

Efficiency = 80%

\[ \eta = \frac{I_{\text{stoichiometric}}}{I_{\text{actual}}} \]

efficiency = 80%

\[ I_{\text{actual}} = \frac{5585}{0.8} = 6980 \ \text{A} \]

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Estimation of electrode area

From Experimental data
\( j = 1000 \text{ A/m}^2 \)

\[ l = j \cdot S \quad S = \frac{6980}{1000} \text{ m}^2 = 7 \text{ m}^2 \]

...And a very rough economic estimation

Price\( = 20000 \cdot A^{0.78} = 91200 \text{ euros} \)
Investment\( = 4.2 \times 91200 = 384000 \text{ euros} \)
Amortization \( = 384000 / 10 \times 365 = 105 \text{ euros/d} \)
Estimation of energy consumption

From experimental data: V= 5 Volts

\[ W = I \cdot V = 6980 \cdot 5 = 34900 \text{ watts} = 35 \text{ kW} \]

Specific Power: \( W/q = 83 \text{ kwh/ m}^3 \)

...And a very rough economic estimation

Energy cost: \( 35 \text{ kWd/d} = 840 \text{ kWh/d} = 92.4 \text{ euros/d} (0.11 \text{ €/kWh}) \)
Case 2. Size a Water Treatment Plant for a small village with a population of 3000 p.e. Plant should remove turbidity by electrocoagulation and disinfect water with electrochemically produced hypochlorite.

Notes.
Consider that specific water demand for this population is 250 l/p.e./d
The dose of aluminium and hypochlorite were determined experimentally in a bech scale plant study being 30 mg Al$^{3+}$/l and 2 mg Cl-ClO$^-$ of hypochlorite. Ti/RuO$_2$ anodes for chlorine production and aluminium plates were used in that study. Calculate operation cost and electrode area requirements
Consider the following data for electrocoagulation: Current efficiency = 100%; J= 5 mA cm$^{-2}$; V= 2.5 V
Consider the following data for chlorine production: Current efficiency = 55%; j= 100 mA cm$^{-2}$; V= 5 V
Estimation of the amount of aluminium that should be dosed daily:

\[ r \text{ (g/d)} = 3000 \text{ (h.e.)} \times 250 \text{ (l/h.e./d)} \times 30 \text{ mg Al/l} = 22500 \text{ g/d} = 22.5 \text{ kg/d Al} \]

\[ r \text{ (mol/d)} = 22500 \text{ g/d} \times 1 \text{ mol Al}^{3+}/26.9 \text{ g Al}^{3+} = 836.4 \text{ mol Al}^{3+}/d \]
Estimation of the intensity that should be applied

\[ r = \frac{l}{nF} \]

\[ l = r \cdot n \cdot F = 836.4 \text{ mol Al}^{3+}/\text{d} \cdot 3 \text{ mol e}^-/\text{mol} \]
\[ \text{Al}^{3+} 96500 \text{ C/mol e}^- \cdot 1 \text{d}/86400 \text{s} = 2802.6 \text{ A} \]

Estimation of energy consumption

From experimental data
\[ V = 2.5 \text{ V} \]

\[ \text{Power} = l \cdot V = 2802.6 \cdot 2.5 = 7 \text{ kW} \]

\[ \text{Energy consumption} = 7 \text{kW} \cdot 24 \text{ h/d} = 168 \text{kWh/d} \]
Estimation of the anode area required

From experimental data
\[ j = 5 \text{ mA cm}^{-2} \]

\[ I = 2802.6 \text{ A} \]

\[ j = 5 \text{ mA cm}^{-2} = 50 \text{ A m}^{-2} \]

Electrode area = \( \frac{I}{j} = \frac{2802.6}{50} = 56.05 \text{ m}^2 \)

10 anodes de 2.4·2.4 m

Replacement of the sacrifice electrode

Width: 1 mm
Weight: 2.7 kg/m²/mm

Density of aluminium: 2700 kg/m³

Weight per electrode (2.4·2.4 m²) = 155.5 kg

Total aluminium in the reactor = 10·155.5 = 1555 kg

Maximum period to replace Al = 1555 kg/22.5 (kg/d) = 69 days

Do not forget it is a sacrifice electrode: it is consumed during time and electrode area will diminish during the operation of the process. This means that current density will increase with time! The effects should be assessed at the lab or bench scale.

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Estimation of the amount of hypochlorite to be dosed to water

\[ r (g/d) = 3000 \text{ (h.e.)} \times 250 \text{ (l/h.e./d)} \times 2 \text{ mg Cl-ClO}^-/l = 1500 \text{ g/d} = 1.5 \text{ kg/d Cl-ClO}^- \]

\[ r(\text{mol/d}) = (1500 \text{ g/d}) \times (1 \text{ mol Cl-ClO}^-/35.5 \text{ g Cl-ClO}^-) = 42.25 \text{ mol Cl-ClO}^-/d \]
Estimation of intensity

From experimental data
\( j = 100 \text{ mA cm}^{-2} = 1000 \text{ A m}^{-2} \)
\( V = 5 \text{ V} \)
efficiency = 55%

\( r = 42.25 \text{ mol Cl-ClO}^-/d \)

\( I = r \cdot n \cdot F = 42.25 \text{ mol Cl-ClO}^-/d \cdot 2 \text{ mol e}^-/\text{mol Cl-ClO}^- \cdot 96500 \text{ C/mol e}^- \cdot 1d/86400s = 94.4 \text{ A} \)

\( I_{\text{real}} = I / \text{efficiency} = 94.4/0.55 = 171.6 \text{ A} \)

Estimation of electrode area

Anode area = \( I/j = 171.6/1000 = 0.17 \text{ m}^2 \)

Estimation of energy requirements

\( W = I \cdot V = 171.6 \cdot 5 \text{ W} = 858 \text{ W} \)

Energy requirements = \( 858\text{W} \cdot (24 \text{ h}/\text{d})/(1000\text{ w/kW}) = 20.6 \text{ kWh/d} \)