AOPs PhD School

# Electrochemical Advanced Oxidation Processes

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**Environmental applications of AOPs**
Porto, July 10-14, 2017

# 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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# ENVIRONMENTAL ENGINEERING AND ELECTROCHEMICAL TECHNOLOGY

Perhaps, you are thinking that I'm going to tell you that electrochemical technology is the best set of environmental remediation technologies…

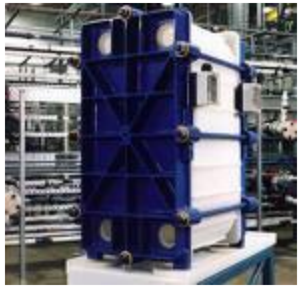
… but be sure, this is not want I want to tell you. I just want to show some cases in which electrochemical engineering could be of a great help for the remediation of environmental problems and to describe briefly the fundamentals of these technologies

Do not forget that electrochemical technology is…

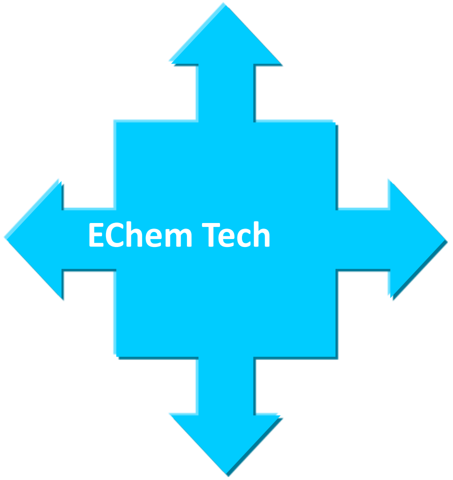
…Not very appreciated in the conventional chemical industry:

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

But… there are many industrial processes that are electrochemical processes



PRODUCTION OF ADIPONITRILE BY MEANS OF MONSANTO PROCESS

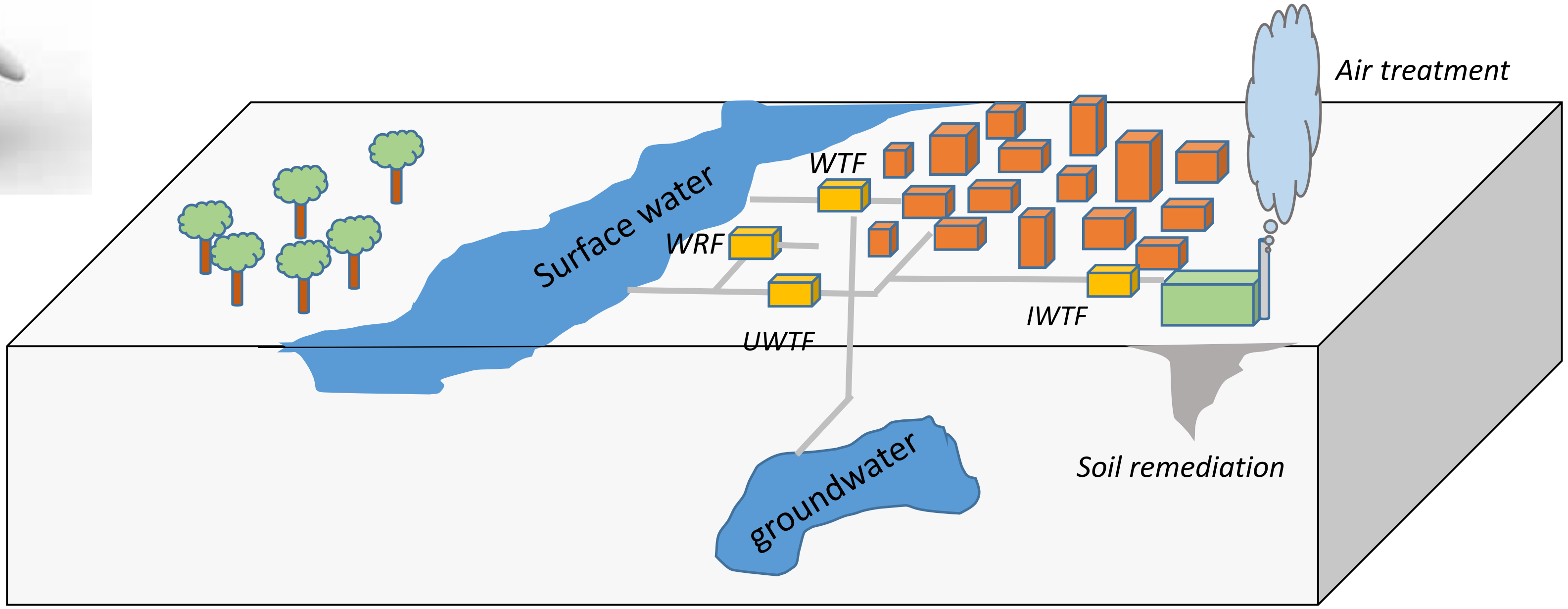



ALUMINIUM PRODUCTION FROM BAUXITE

CHLOR-ALKALI INDUSTRY

BRACKISH WATER DESALINATION

And… why not? There is a very important question in the air: Could it be used in Environmental Engineering?

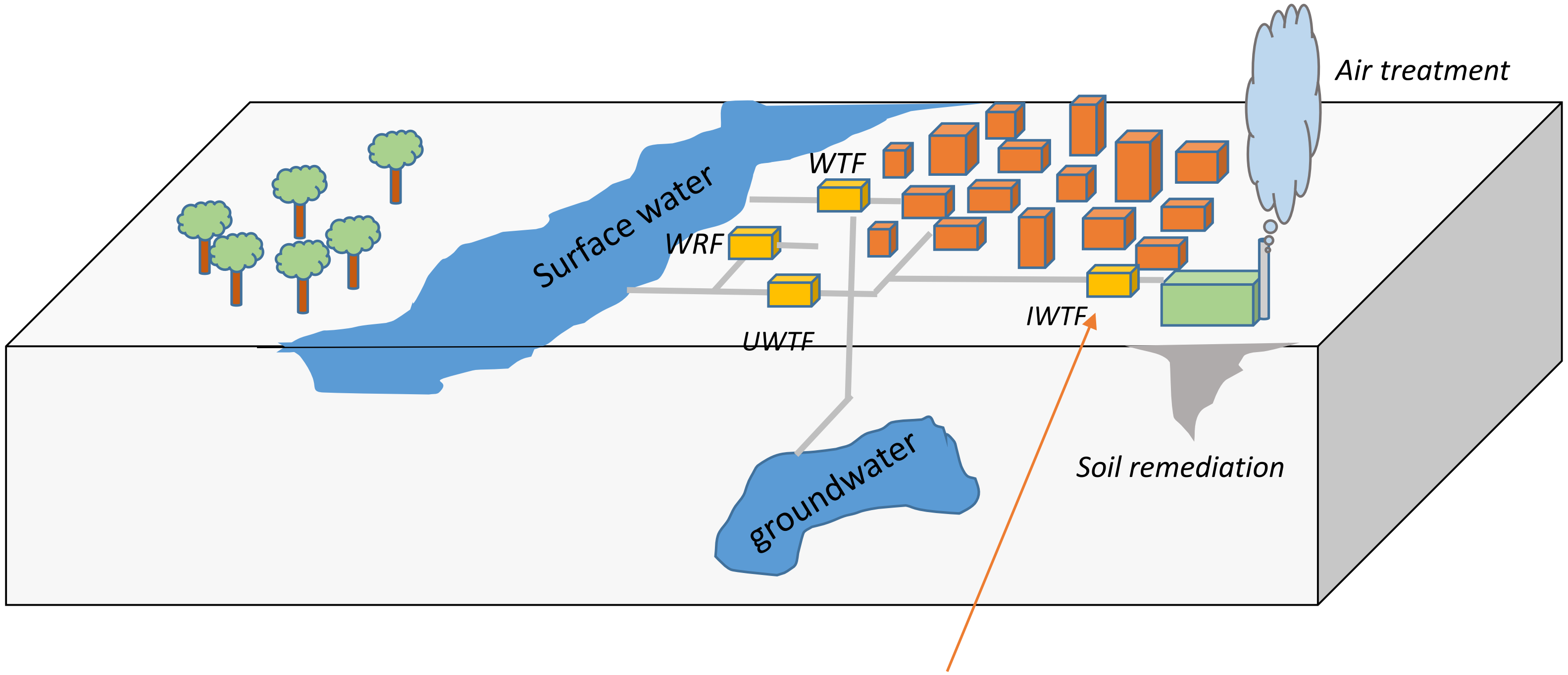



*Industrial wastewater treatment facility (IWTF)*

*Wastewater reclaiming facility (WRF)*

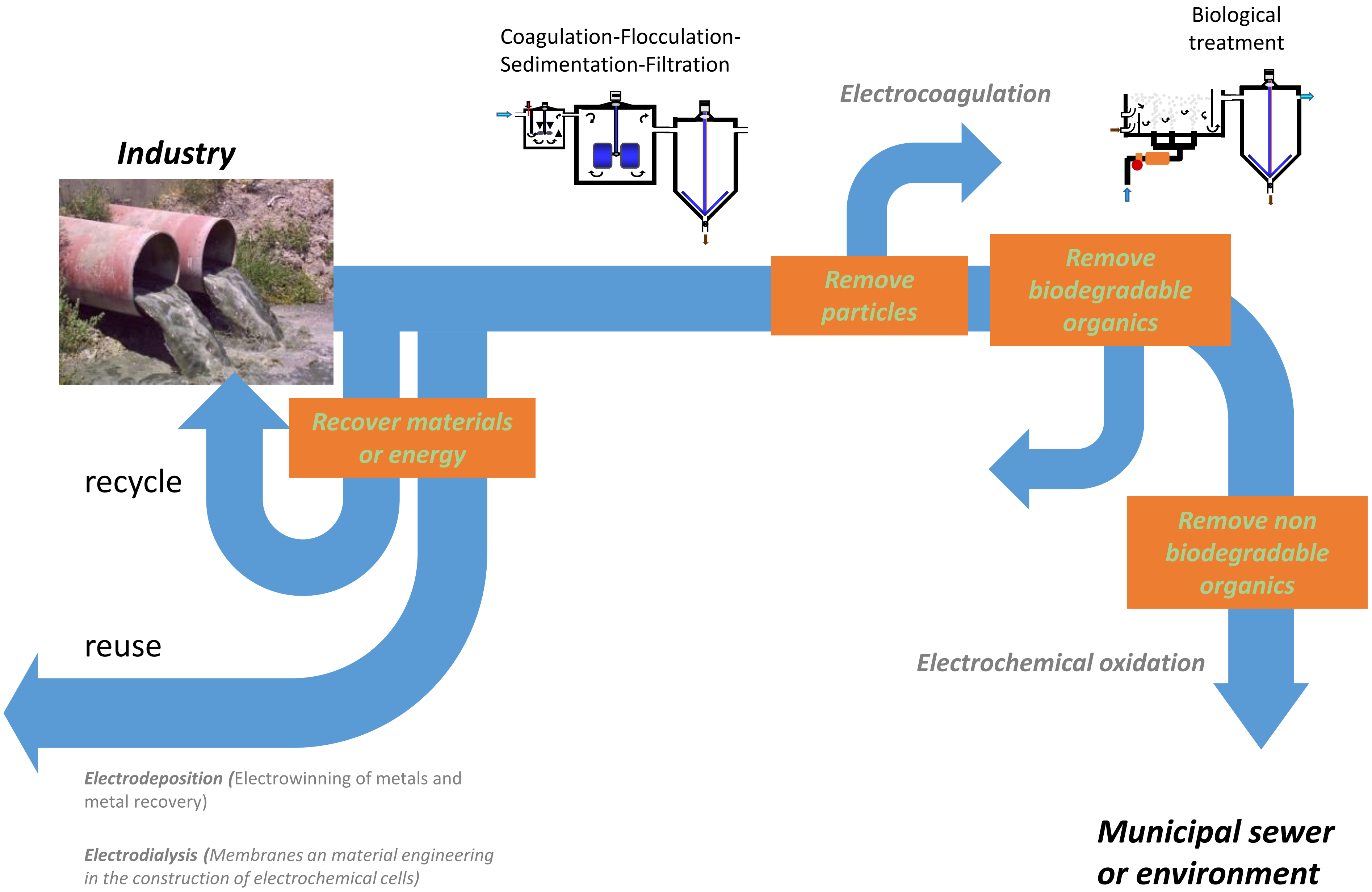
*Urban wastewater treatment facility (UWTF)*

*Water treatment Facility (WTF)*




*Industrial wastewater treatment facility (IWTF)*

- Electrolysis: organic and metals
- Electrodialysis: desalination and purification of streams
- Electrocoagulation: colloids and emulsions

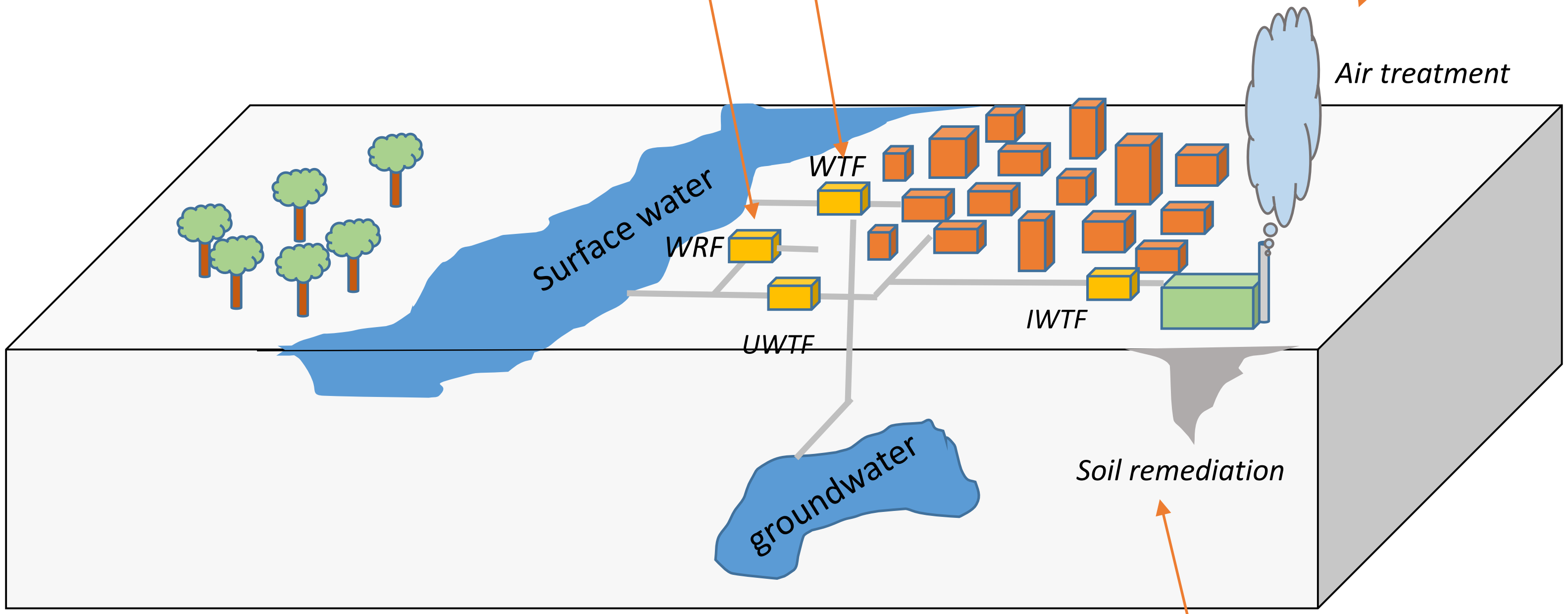

Coagulation-Flocculation-
Sedimentation-Filtration
Biological
treatment
Electrocoagulation
Industry
Remove
particles
Remove
biodegradable
organics
Recover materials
or energy
recycle
Remove non
biodegradable
organics
reuse
Electrochemical oxidation
Electrodeposition (Electrowinning of metals and
metal recovery)
Electrodialysis (Membranes an material engineering
in the construction of electrochemical cells)
Municipal sewer
or environment

❖ 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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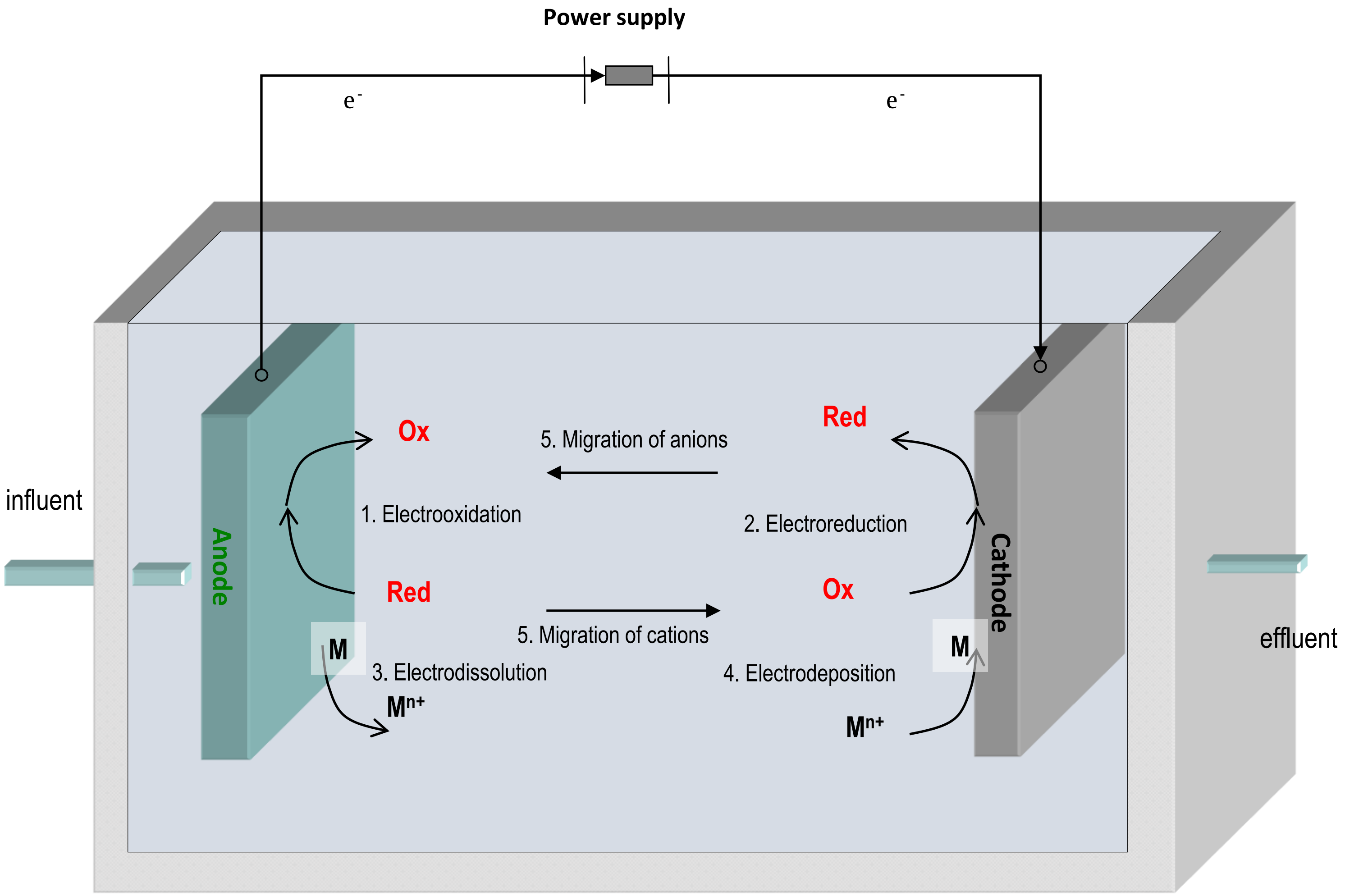
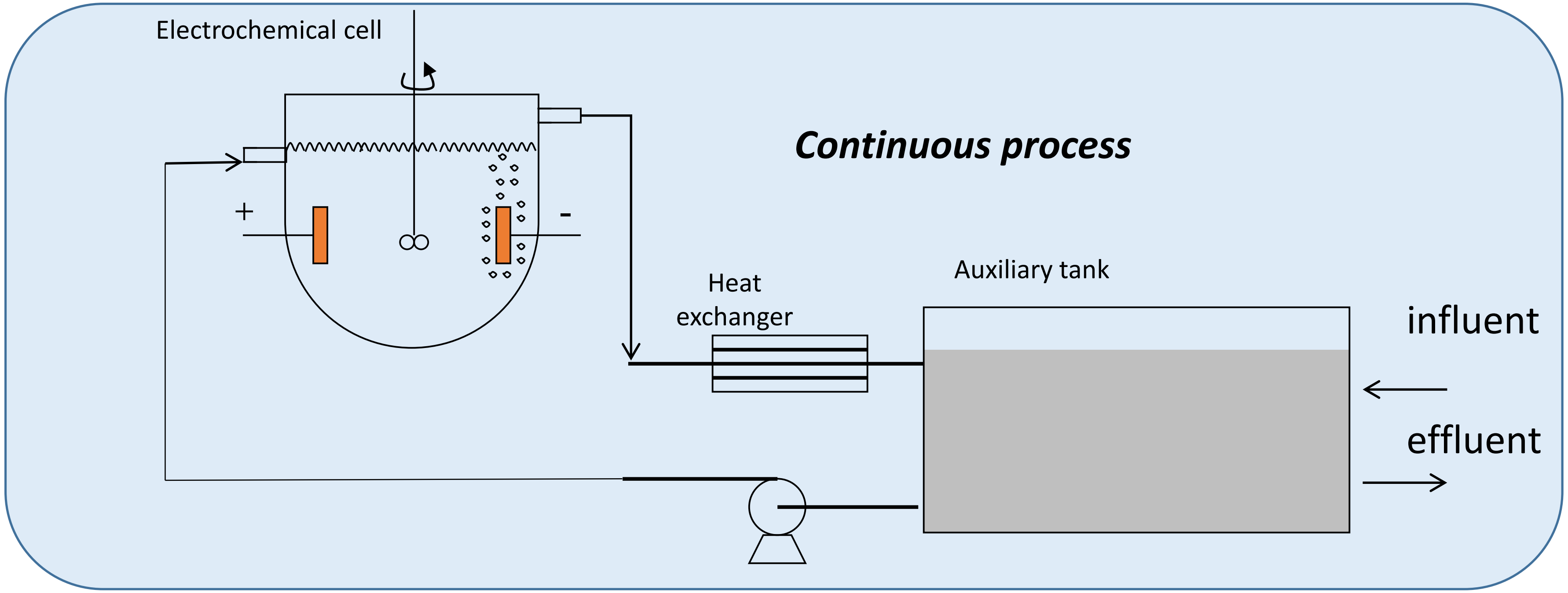
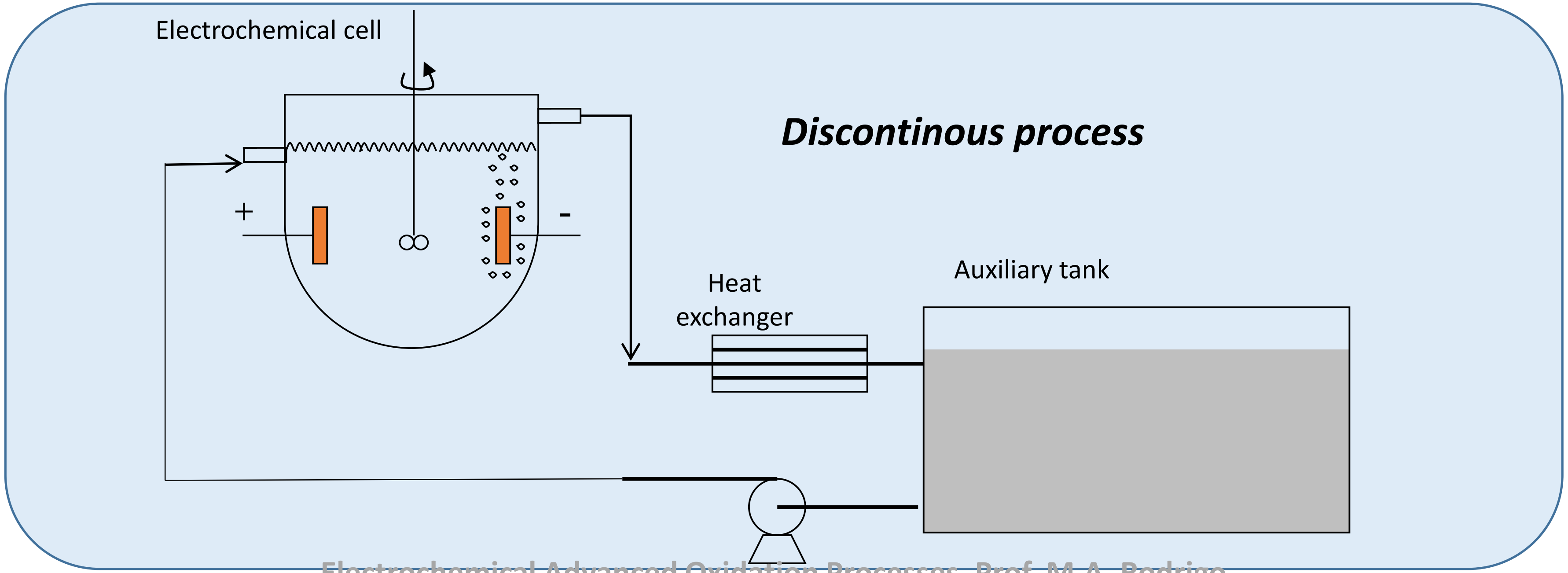
# ELECTROCHEMICAL TREATMENT OF WATER AND WASTEWATER




Electrochemical cell
+
-
Continuous process
Heat
exchanger
Auxiliary tank
influent
effluent

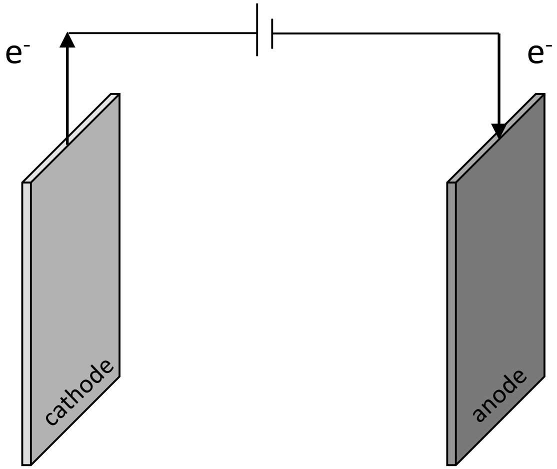

Electrochemical cell
+
-
Discontinous process
Heat
exchanger
Auxiliary tank

## ☑ What are the main parameters used to assess these processes?

Rate of electrochemical processes vs intensity

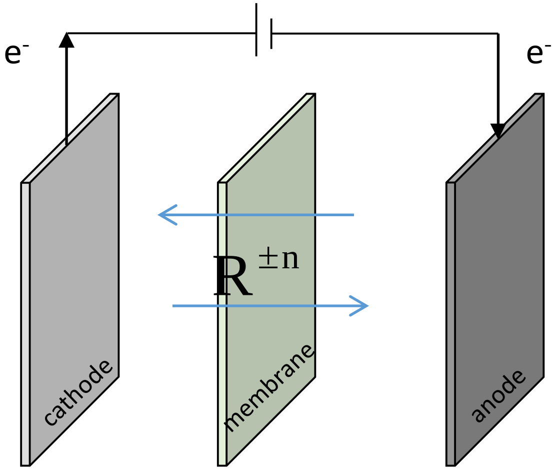
$$R \pm ne^- \rightarrow \ldots$$

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



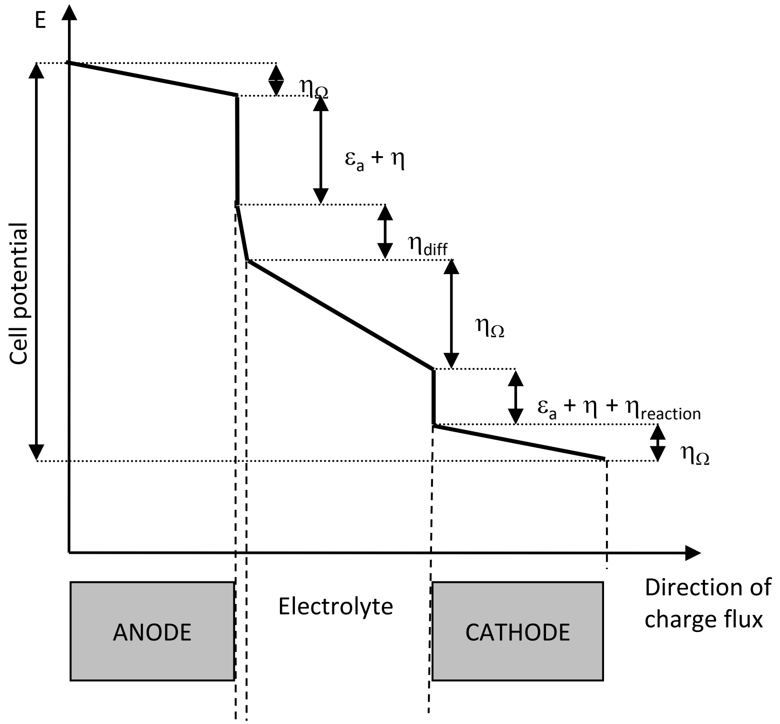

***Take care: just one Intensity in the whole cell!!!***

$$r\left(\frac{\text{mol charges}}{\text{s}}\right) = \frac{I(A)}{F\left(\frac{96500\text{C}}{\text{mol R}}\right)}$$




Current density

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




Cell voltage

$$E(V) = -I \cdot R_{circ}^{c} - (E_e^c + |\eta_c|) - I \cdot R_{cat} - I \cdot R_{sep} - I \cdot R_{anod} - (E_e^a + |\eta_a|) - I \cdot R_{circ}^{a}$$

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

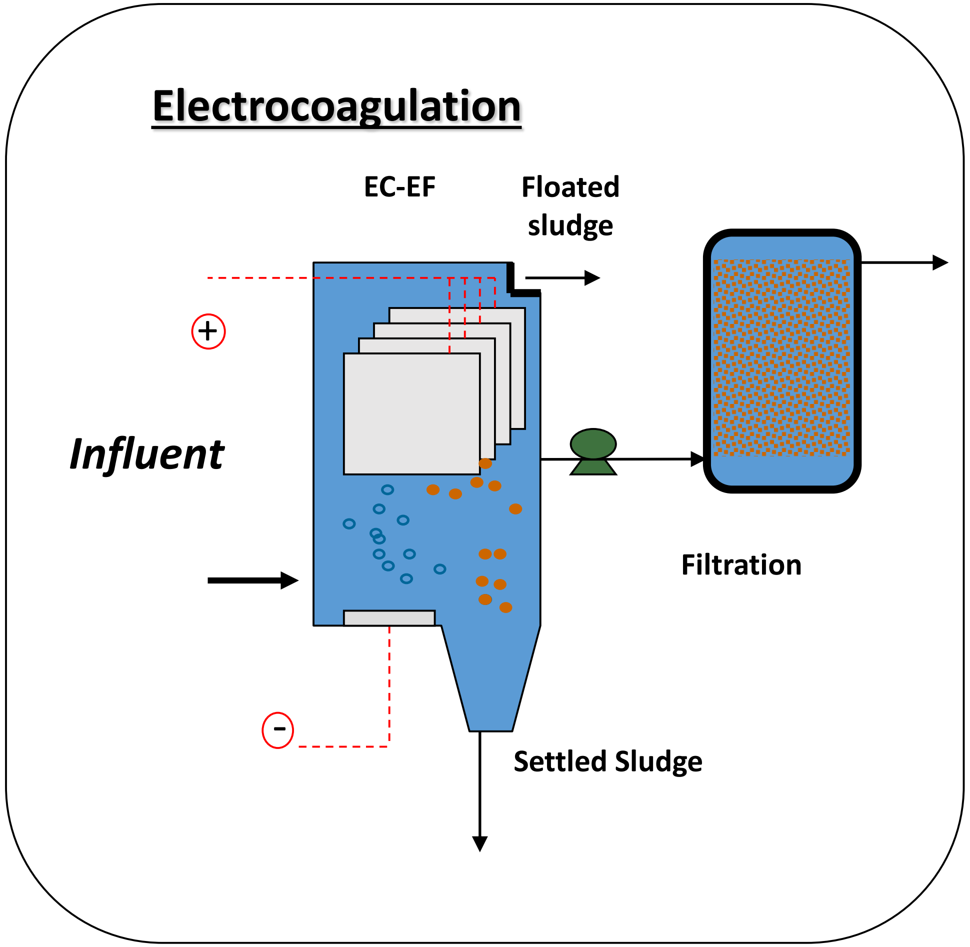
$$q\left(\frac{kAh}{m^3}\right)=\frac{I(kA)}{Q\left(\frac{m^3}{h}\right)}$$

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.



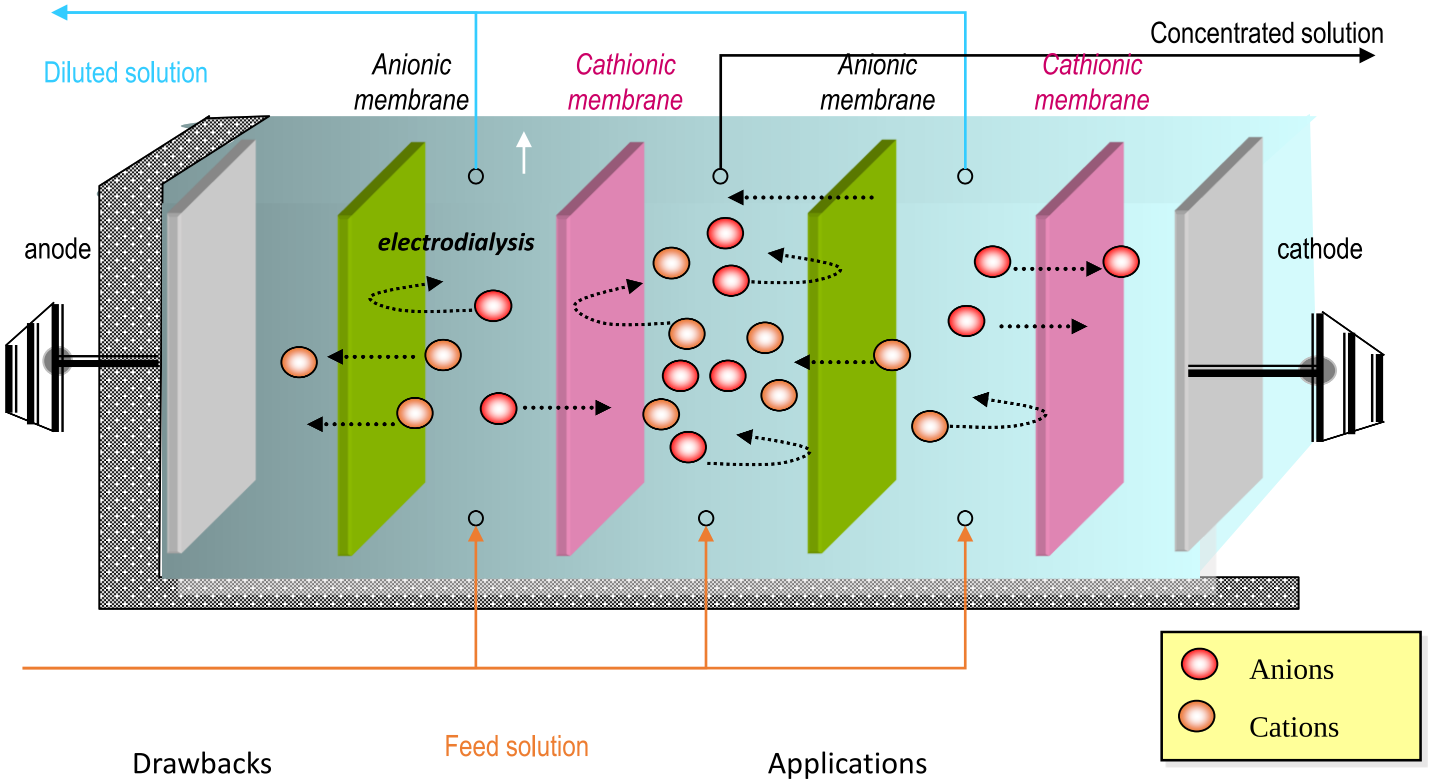
# ELECTRODIALYSIS

Hydraulic circuits

- ✓ at least three circuits concentrated, diluted and electrode rinse.
- ✓ Concentrations up to 20%
- ✓ Ratios concentrated/diluted up to 100

Membranes

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




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).

Advantages

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

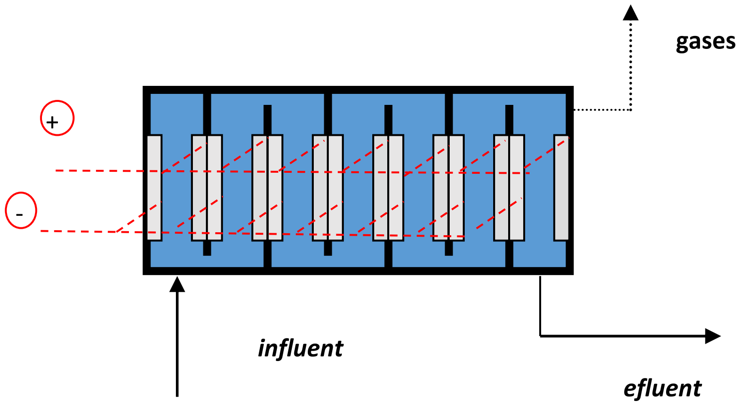
Drawbacks

- ✓ Membrane fouling.
- ✓ Polarization .
- ✓ extreme pHs

Applications

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

# ELECTROLYSIS




***Changes in the chemical composition of a wastewater using electricity***

| oxidation | reduction |
|---|---|
| Mineralization of organics (full treatment) | Electrodeposition of metal ions |
| Partial oxidation of organics (complementary treatment) | Dehalogenation of halogenated organics |
| Oxidation of inorganic pollutants | Reduction of inorganic pollutants |
| Production of chemical oxidant agents | Production of chemical reduction agents |

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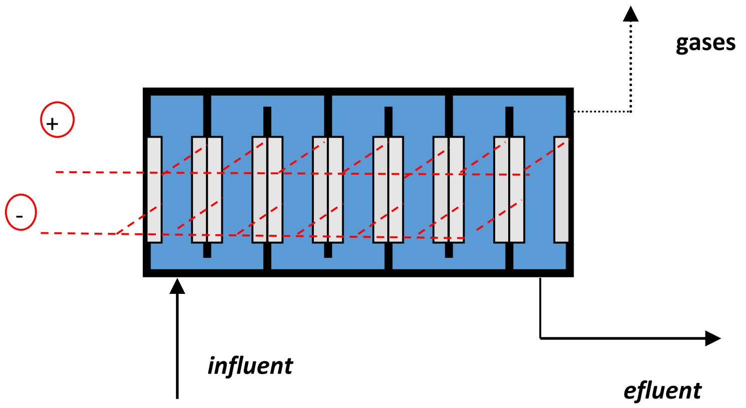
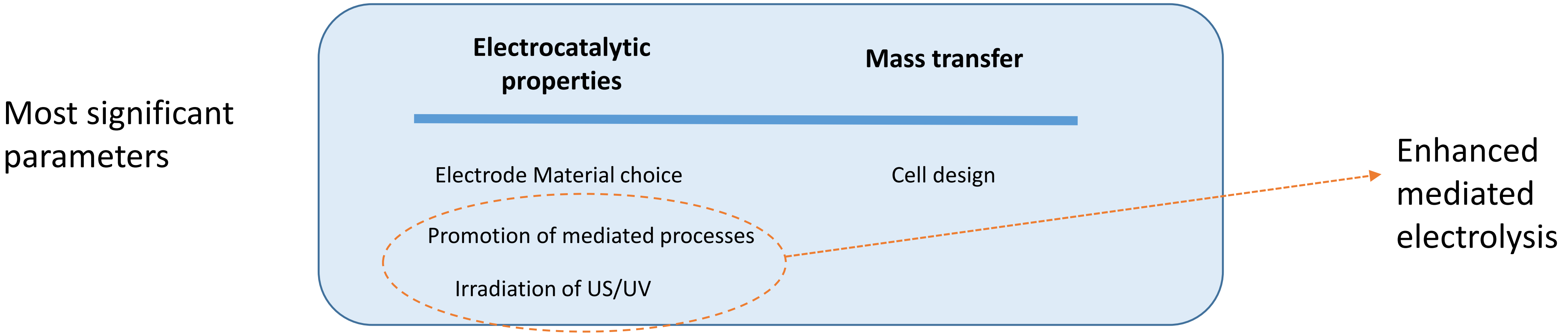
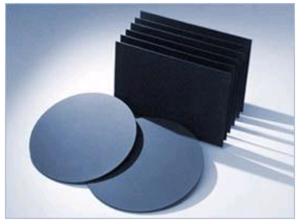
# 3 ANODIC OXIDATION



## ☑ Electrodes



DESIRABLE PROPERTIES

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

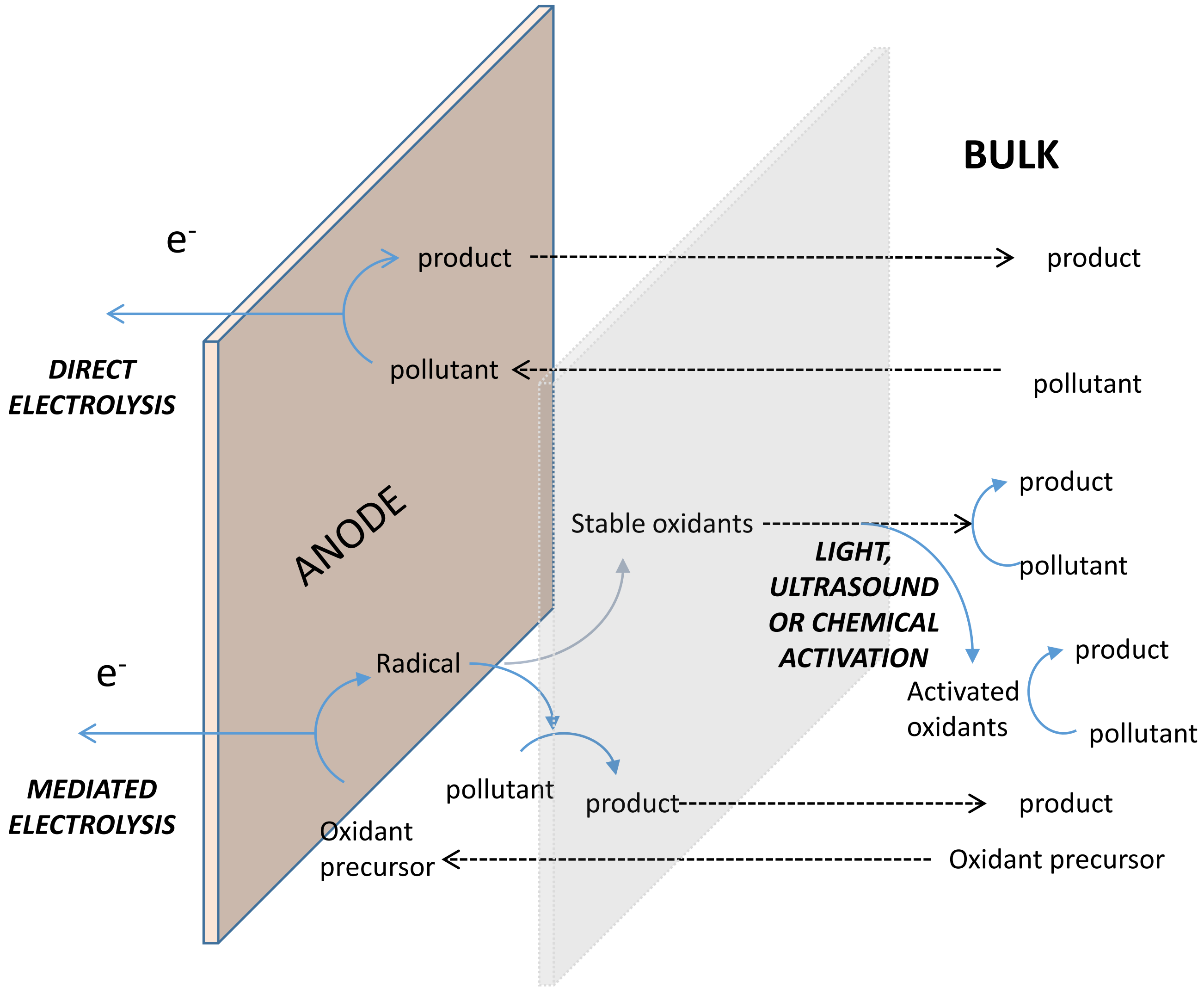
**anodes**

- 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. ANODE




**1. Direct electrolysis**

Oxidation of the pollutant on the electrode surface

**2. Advanced oxidation processes**

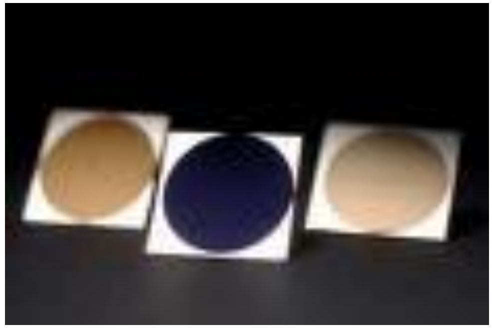
With some anode materials it is possible the generation of OH·

**3. Chemical oxidation**

On the electrode surface several oxidants can be formed from the salts contained in the electrolyte

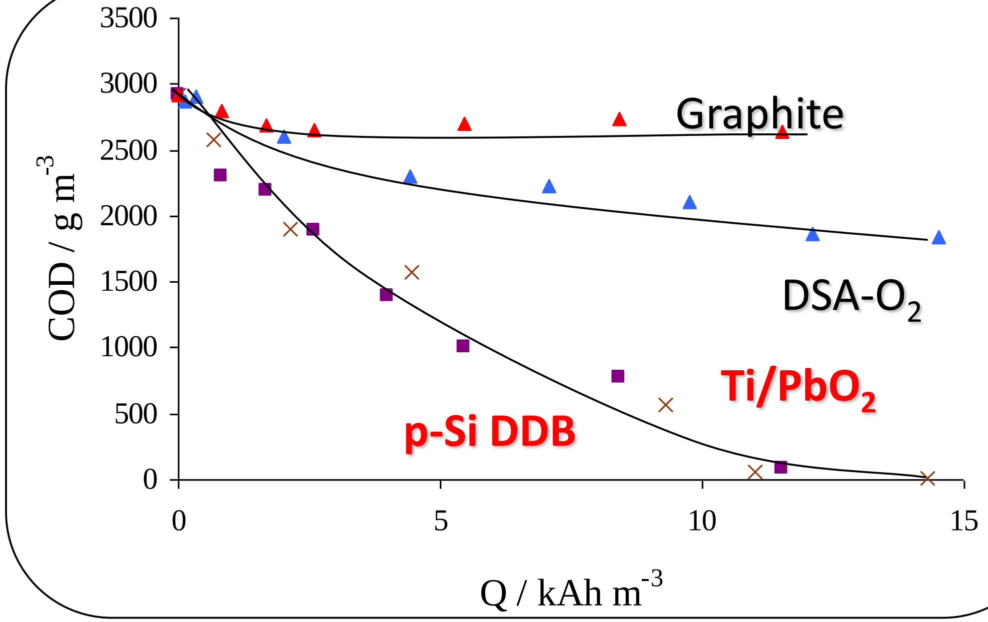
# ANODES FOR THE OXIDATION OF ORGANIC MATTER

| | | |
|---|---|---|
| **Electrodic material** | Metals | Platinum<br>Stainless stell |
| | Carbon | Grafite<br>**Conductive-Diamond** |
| | oxides | DSA-$O_2$<br>DSA-$Cl_2$<br>**Ti/$SnO_2$**<br>**Ti/$PbO_2$** |

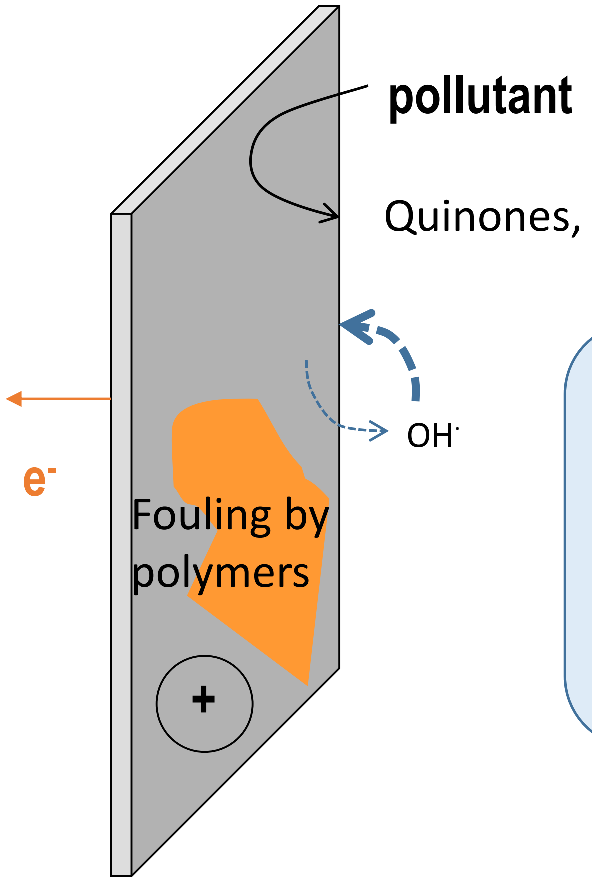


Lowly efficient anodes

**Highly efficient anodes**



## Lowly efficient anodes




### SOFT OXIDATION CONDITIONS

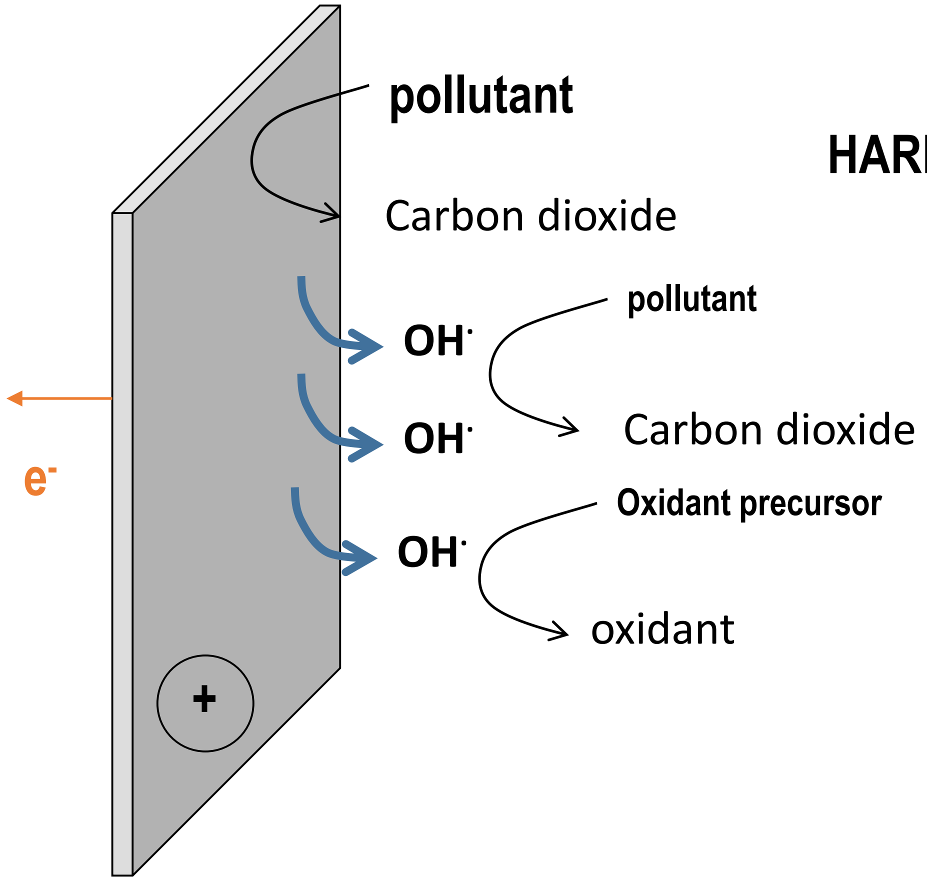
- ✓Many intermediates
- ✓Small conversion to carbon dioxide
- ✓Slow oxidation rates
- ✓Small current efficiencies
- ✓Formation of polymers from aromatic pollutants is favoured

Pt
Ti/Pt
$Ti/RuO_2$
$Ti/IrO_2$

$Ti/IrO_2$ Promotes water oxidation(DSA-$O_2$)

$Ti/RuO_2$ Promotes chlorine production (DSA-$Cl_2$)

# Highly efficient anodes



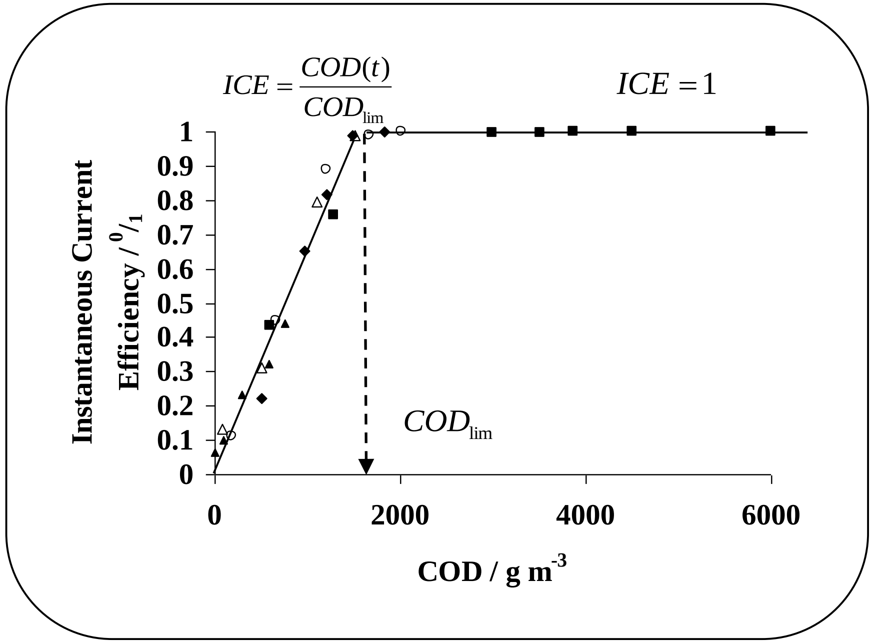

**HARD OXIDATION CONDITIONS**

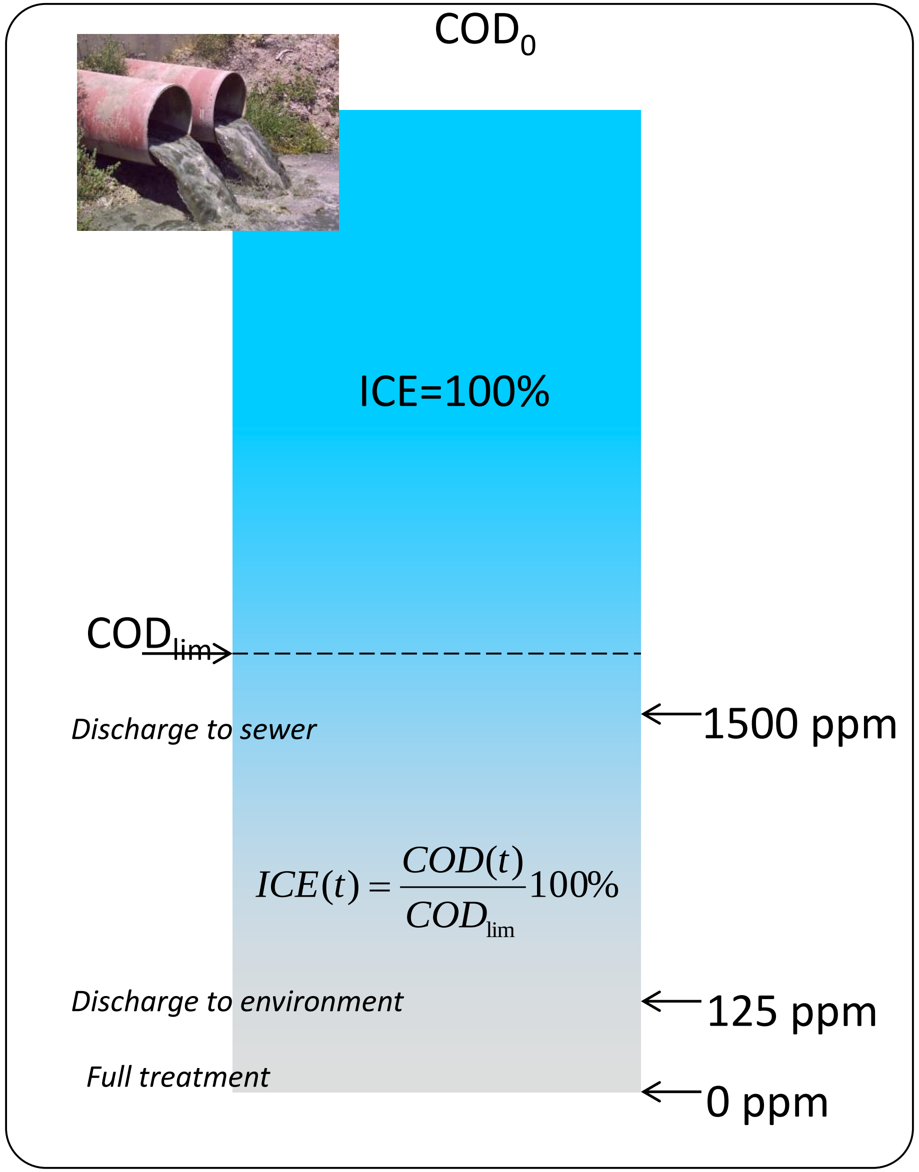
- ✓Few intermediates
- ✓Large conversion to carbon dioxide (mineralization)
- ✓Large current efficiencies only limited by mass transfer

Drawbacks of highly efficient electrodes:

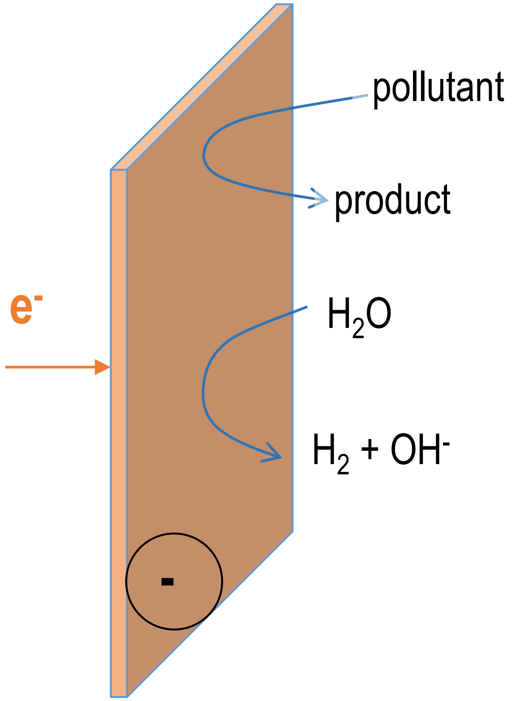
Conductive diamond: large price
$PbO_2/SnO_2$: Dissolution of toxic species

**BDD (Conductive Diamond)**
$Ti/PbO_2$


$ICE = \frac{COD(t)}{COD_{lim}}$
$ICE = 1$
Instantaneous Current Efficiency / $^0/_1$
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$COD_{lim}$
0
2000
4000
6000
COD / g m$^{-3}$


$COD_0$
ICE=100%
$COD_{lim}$
Discharge to sewer
1500 ppm
$ICE(t) = \frac{COD(t)}{COD_{lim}} 100\%$
Discharge to environment
125 ppm
Full treatment
0 ppm

## 2. CATHODE




1. Production of hydrogen
Main side reaction

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 $cm^2/cm^3$). Inert with most chemical. Low cost and easy to be adapted to any reactor geometry. Applied succesfully in the removal from wastes of Cu, Cd, Cr, Pb, U, Hg, Ag, Zn

**Graphite / carbon fibers.** Good area/volumen ratio, (1000 $m^2/g$), low cost, high chemical resistance. Applied succesfully in the treatment of wastes with Au, Ir, Pt, Ag, Pd, Cd. Pb, Ni y Hg

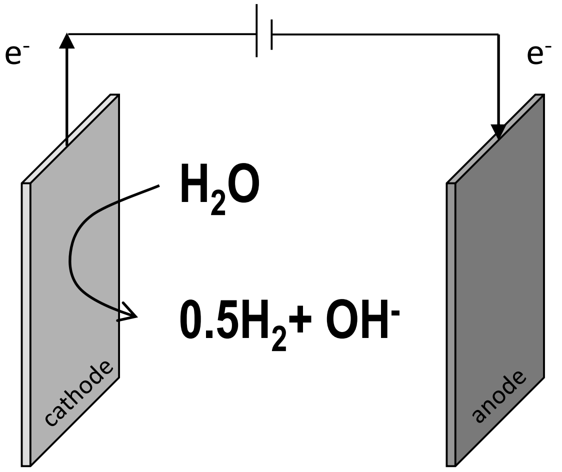
**Porous graphite.** Interesting for the removal of $Eu^{3+}$ from lantanides mixtures

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

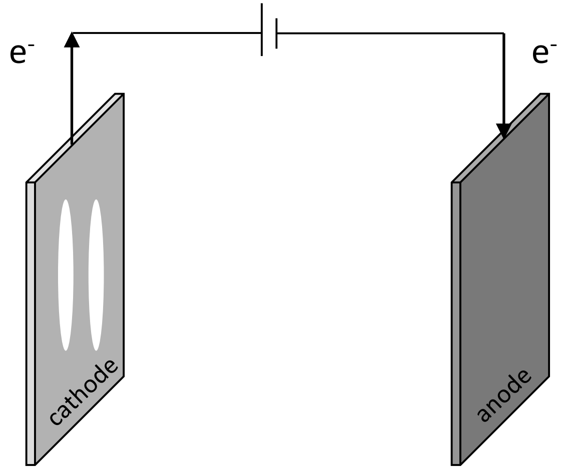
## Advantages of metal deposition

- ✓ 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

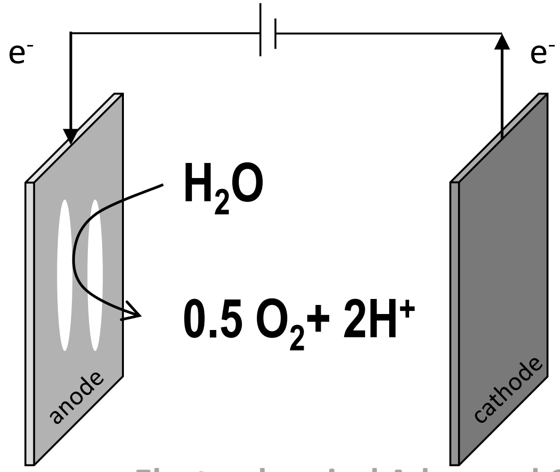



Deposit of carbonates
$OH^- + HCO_3^-$




Increase in the cell potential

Increase in the energy consumption




Polarity reversal

## ☑ Electrochemical cell

DESIRED 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

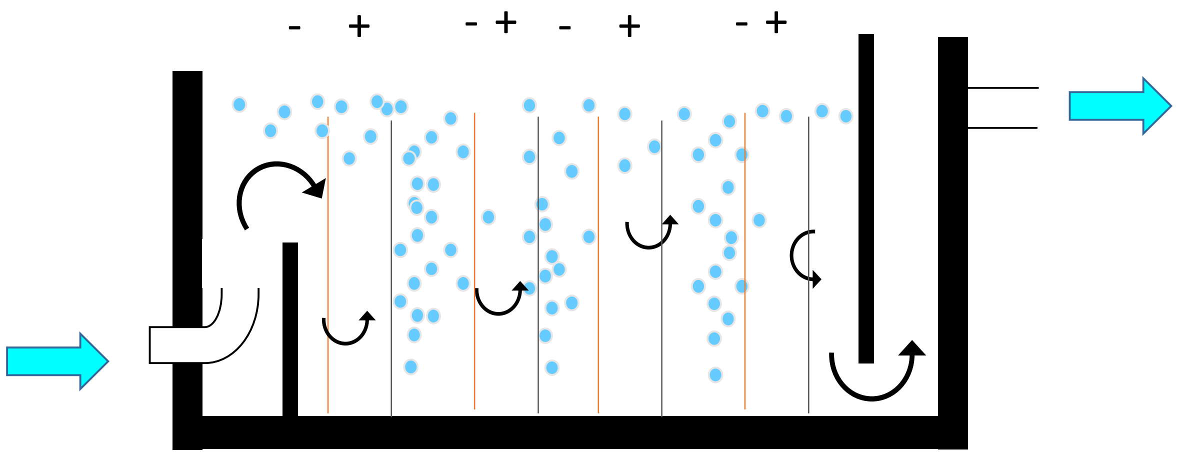
ELECTROLYTIC CELLS

Room temperature and pressure
Cell voltage: 3-6 V
Current densities: 500 -2000 $A/m^2$

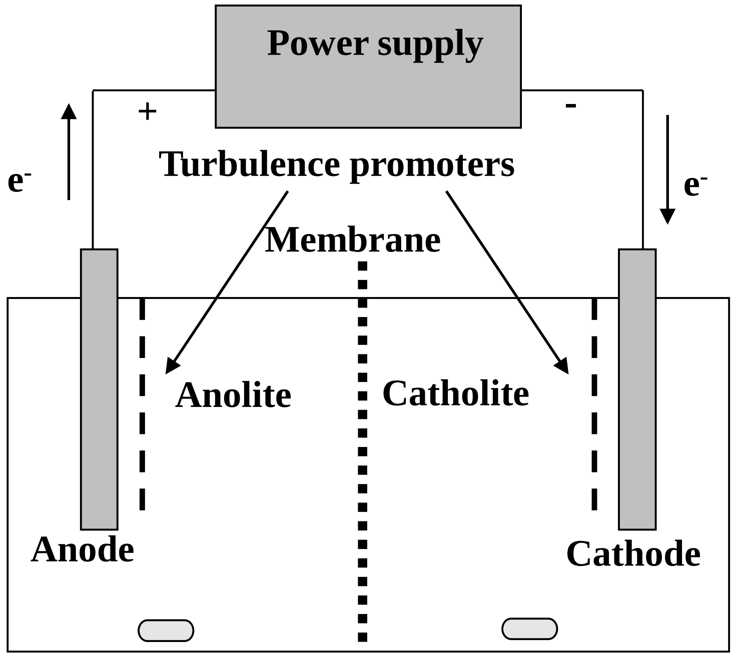
Design parameter: amount of COD to be removed

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

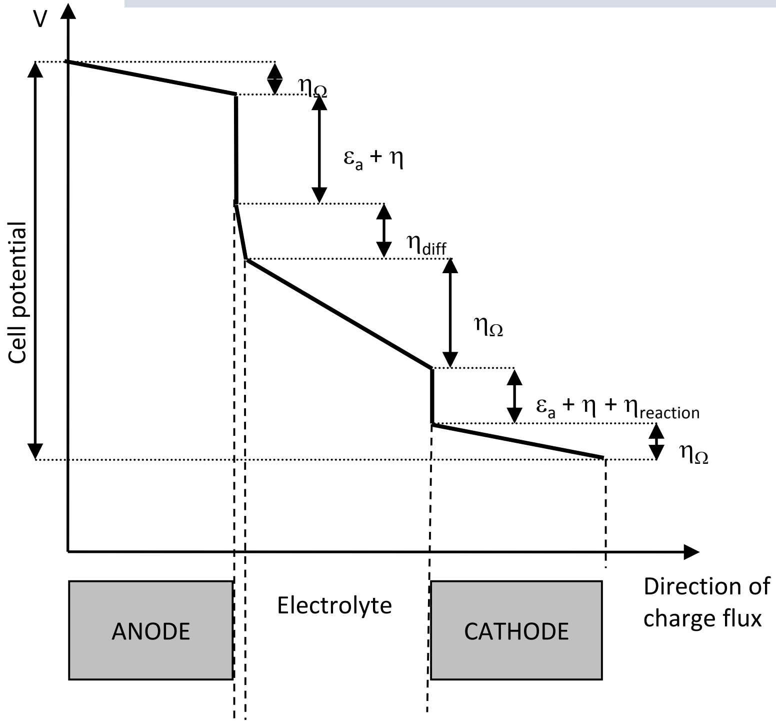
$$COD - 4e^- = \ldots \quad \text{(anódica)}$$



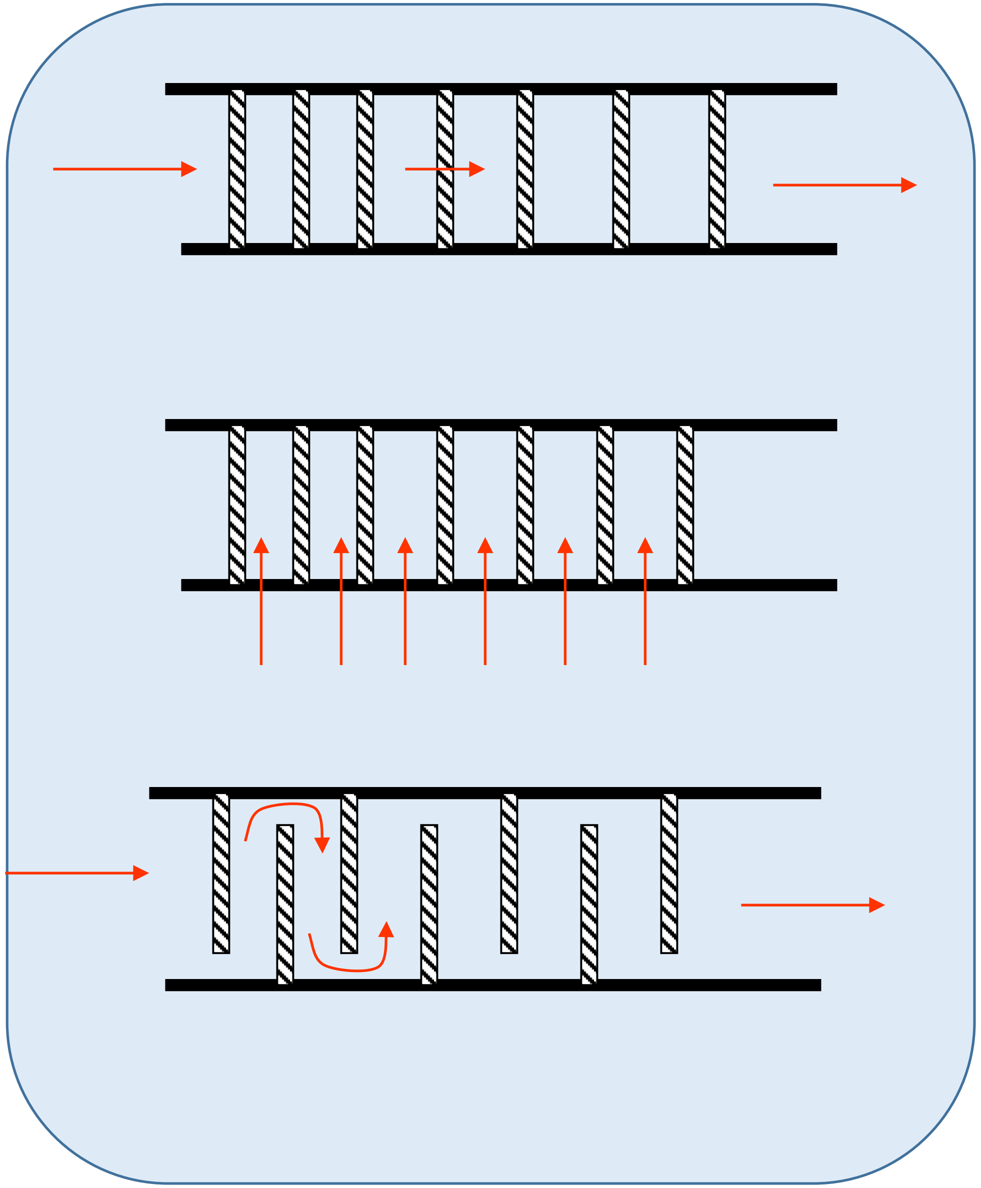
USE OF DIVIDED CELLS IN WASTEWATER TREATMENT PROCESSES?



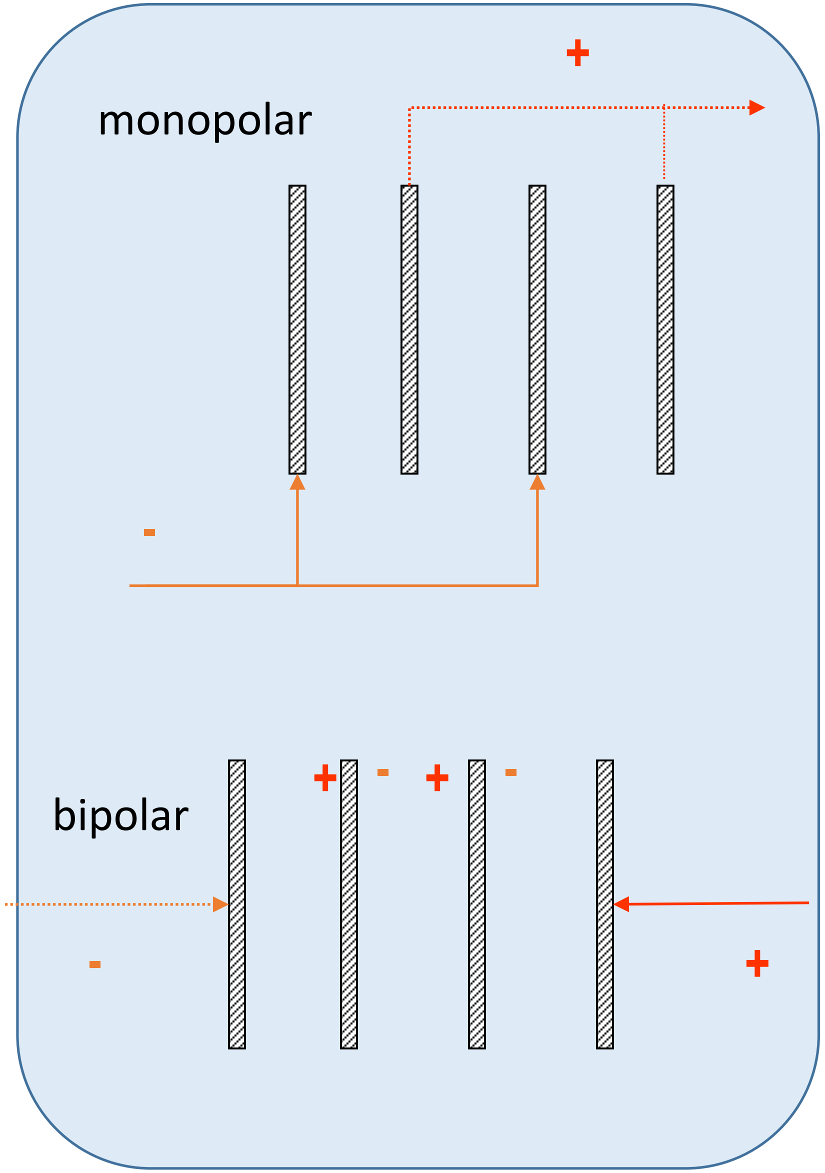

1. The membrane increases the cell potential and consequently the operating cost.
2. Most organic-oxidation processes are irreversible
3. Most inorganic redox reactions are reversible



**Electrolyte flow**

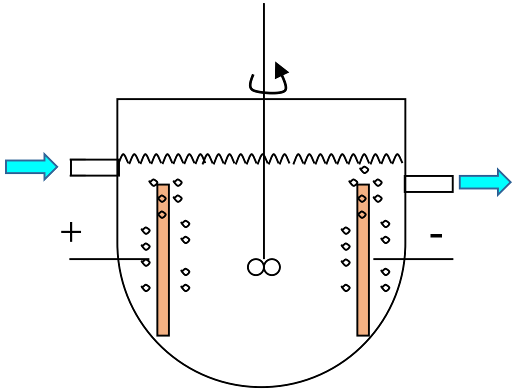


**Electrodes connection**



# Most applied cells

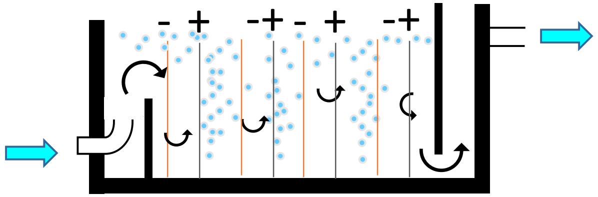
TANK CELLS



ADVANTAGE: Simplest cell

DRAWBACK: Low mass transfer coefficients

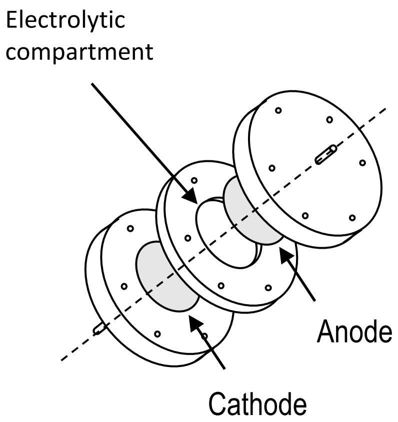
Take care! This is also a tank cell!



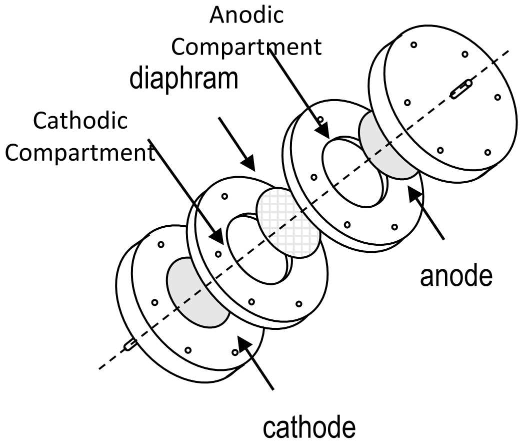
SINGLE FLOW CELL

FILTER PRESS CELL

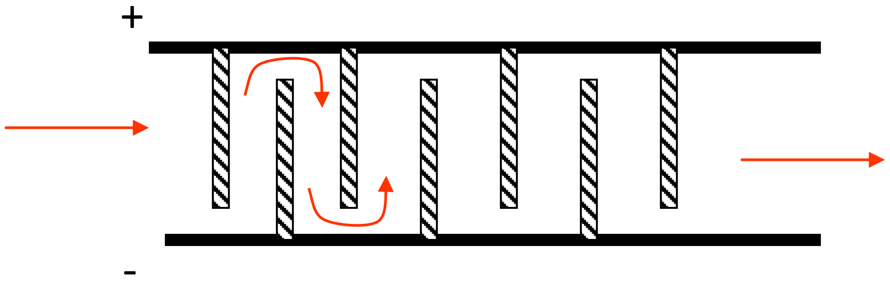
Large electrode surfaces / volume ratios
Small interelectrode gap
Plane electrodes



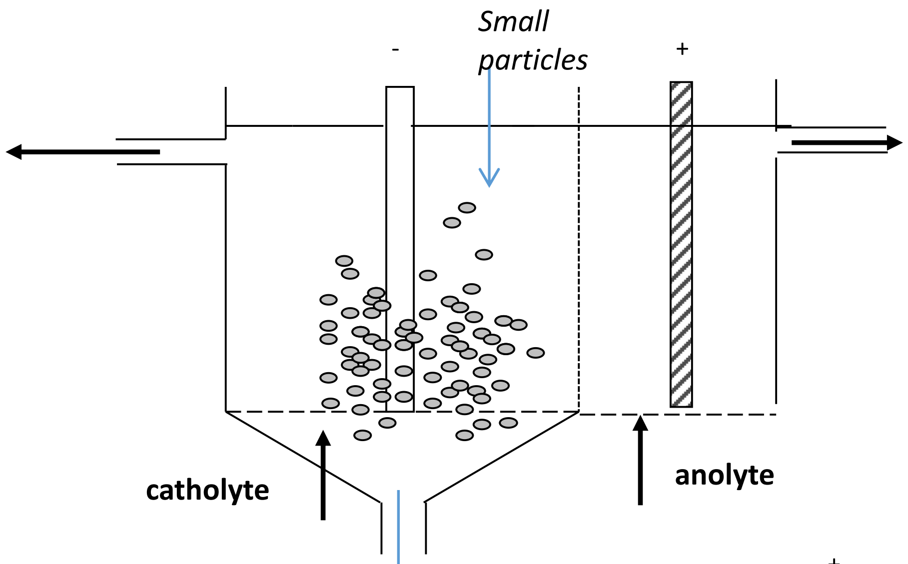

*Single – Compartment Electrochemical Cell*



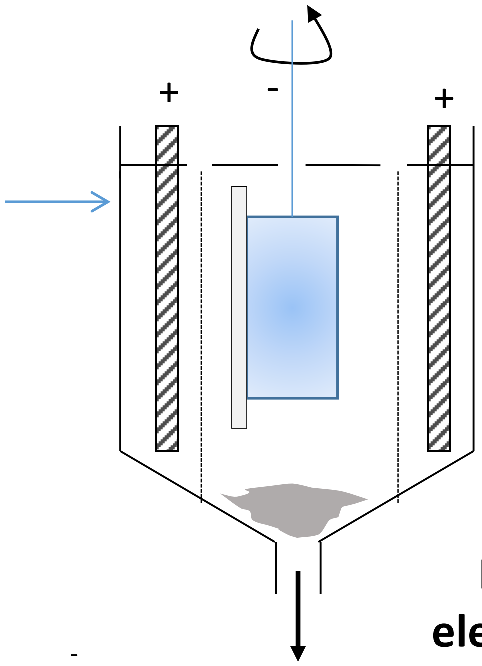

*Double compartment Electrochemical Cell*



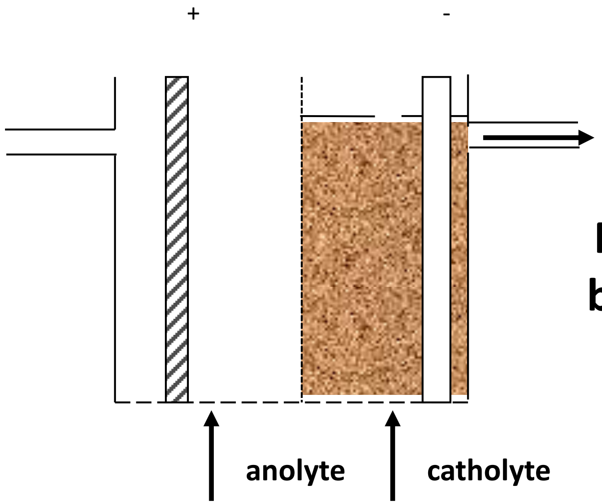

OTHER ELECTROLYTIC CELLS




***Fluidized bed cell***



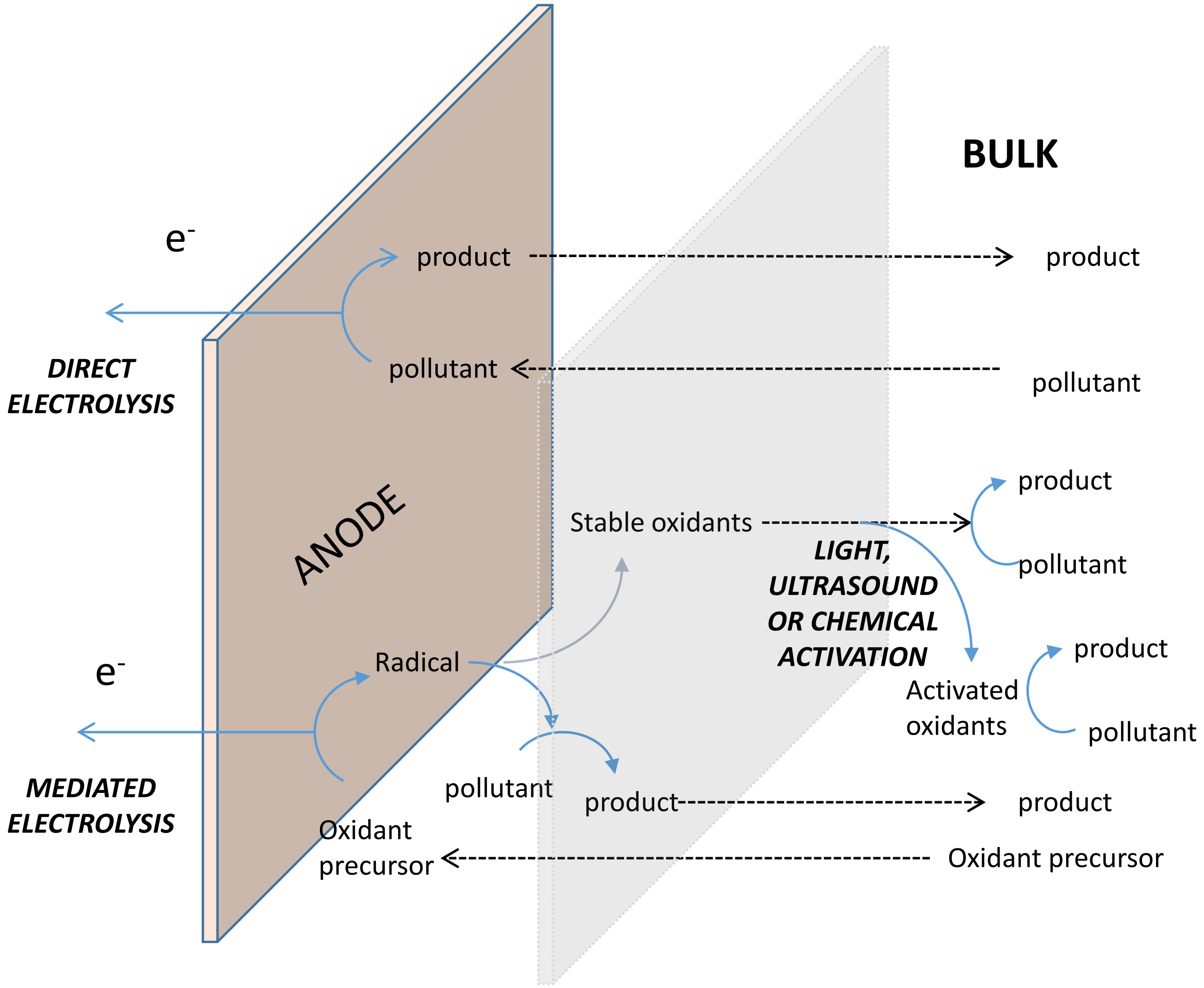

**Rotatory electrode cell**




**Packed bed cell**

Particularly aiming at optimizing the cathodic reduction processes

# ☑ 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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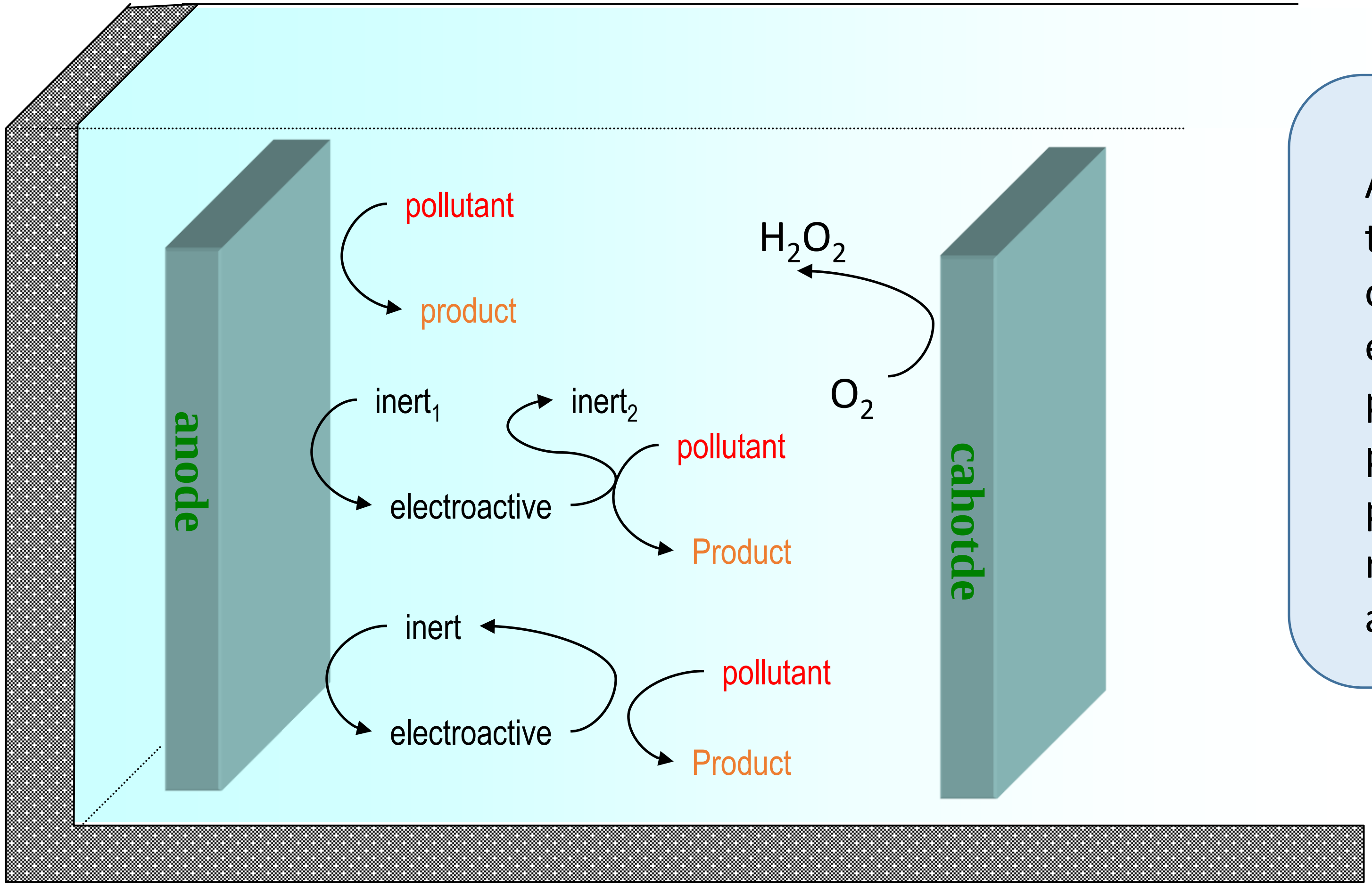
# ENHANCED MEDIATED ELECTROLYSIS




Aims to improve the efficiency of oxidative electrolytic processes by promoting the production of reagents which acts on the bulk

## ☑ Why?

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

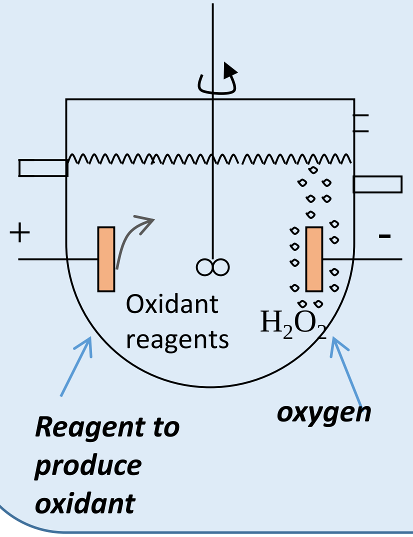
No mass transfer control

higher efficiency

✓SURFACE TO VOLUMETRIC PROCESS

✓CATHODE CAN BE USED TO PRODUCE AN OXIDANT

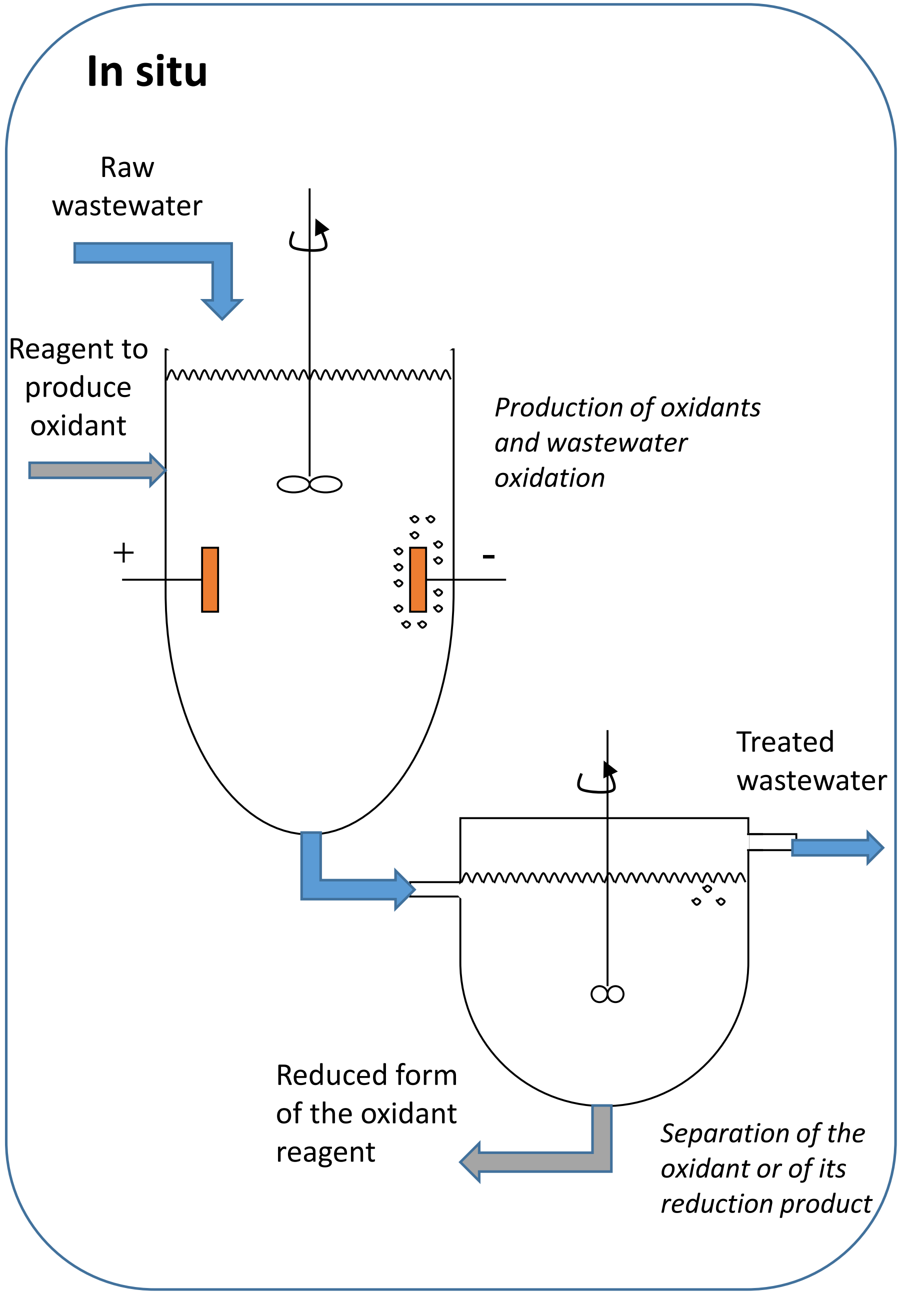
Both direct and indirect electro-oxidation develop simultaneously in the cell

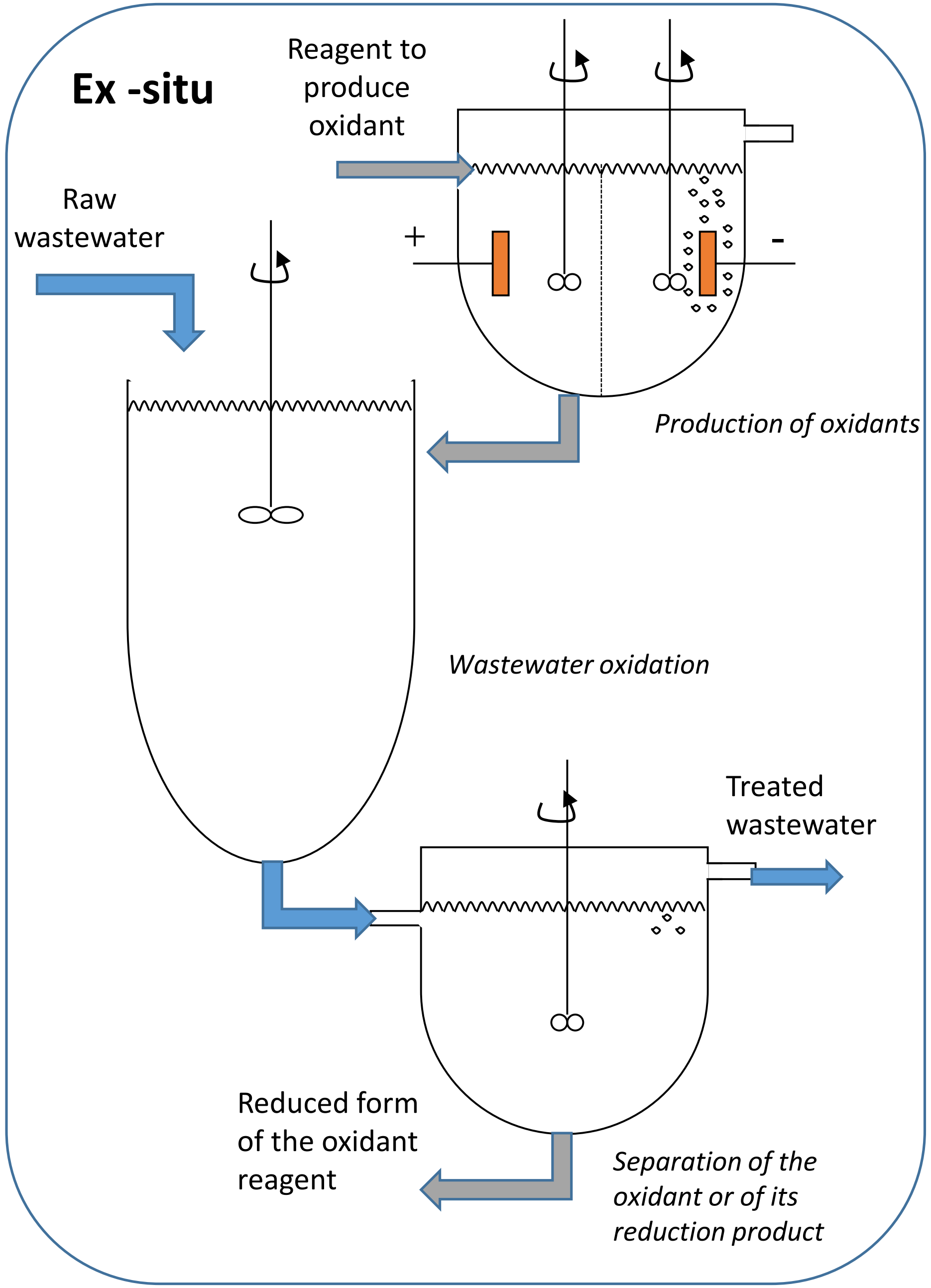



✓Particularly good for low concentrations
✓Specially important processes based on cathodically produced hydrogen peroxide
✓For oxidation of organic free wastewaters, very interesting the production of chlorine

✓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
Reagent to produce oxidant
Raw wastewater
+
-
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 environmental friendly

## ☑ Possibilities

Reversible oxidant

The oxidant can be reduced in the cathode. A divided cell may be considered

**Ag(I) / Ag(II)**

Co(II) / Co(III)

Ce(III) / Ce (IV)

Fe(II) / Fe (III)

$SO_4^{2-}$ / $S_2O_8^{2-}$

$PO_4^{3-}$ / $S_2O_8^{4-}$

These oxidants are generated from anions typically present in a wastewater

**$Cl_2$**

Irreversible (killers)

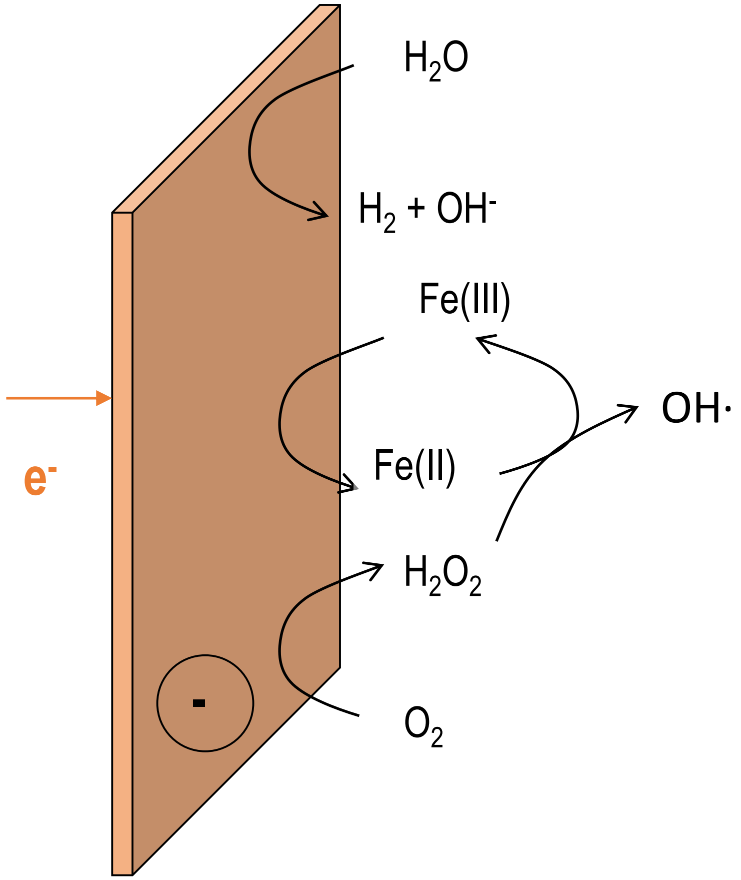
The oxidant is not reduced on the cathode. Non-divided cells are used for their production

$O_3$

**$H_2O_2$**

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

## $H_2O_2$/ $Fe^{2+}$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$$ → Fenton process

rate~ 76 $M^{-1}$ $s^{-1}$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + O_2H^{\cdot}$$ → Fenton like reaction

rate~ 0.01 $M^{-1}$ $s^{-1}$

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

$$O_2 + 2H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad E^0 = -0.065\ V$$

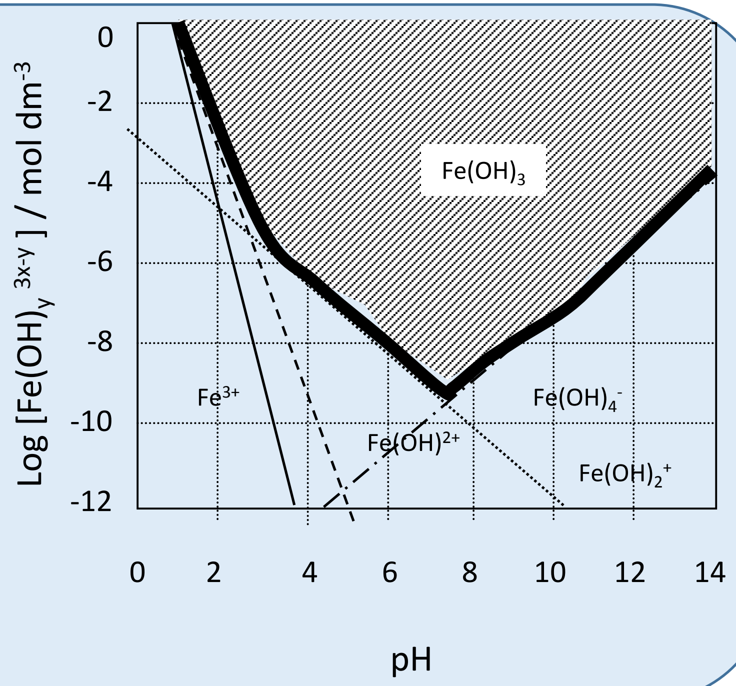
However, the main drawback is the decomposition of the hydroperoxide anion that it is favoured at alkaline conditions.

$$HO_2^- \rightarrow 2OH^- + O_2$$

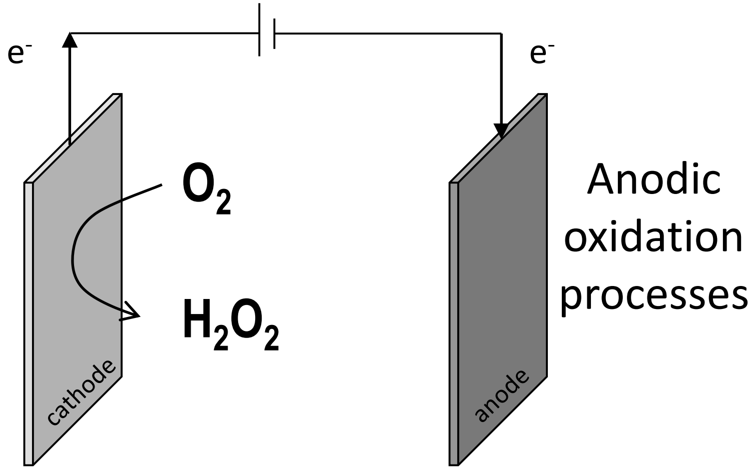
Cathodic reduction of iron (III) is required because iron(II) is a catalyst

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

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

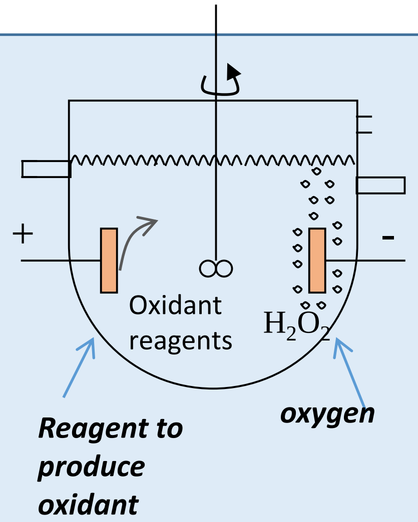



✓Best pH: around 3.0.

✓Cathode material: carbon felt, graphite, porous carbon…

✓Not neccesary iron anodes. With iron anodes no Electro-Fenton but peroxicoagulation occurs

✓Very good results in the combination with Conductive Diamond anodes (complementary electrochemical technologies)



# Electrochemical Advanced Oxidation Processes

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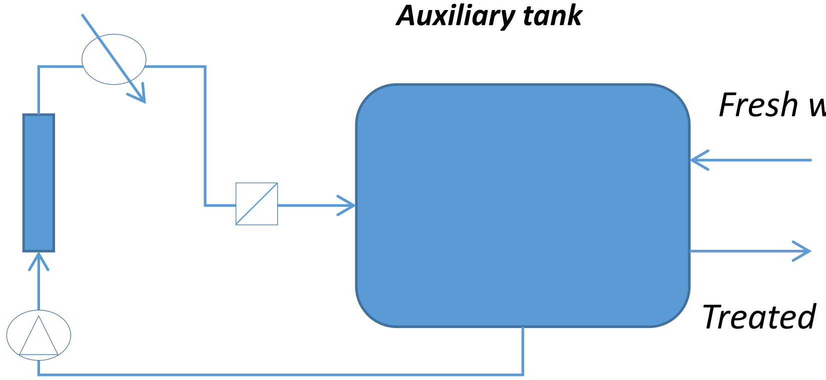
# REMARKS ON THE APPLICATION OF ELECTROLYSIS TO WATER & WASTEWATER TREATMENT

What do we know about full scale wastewater electrolytic processes?

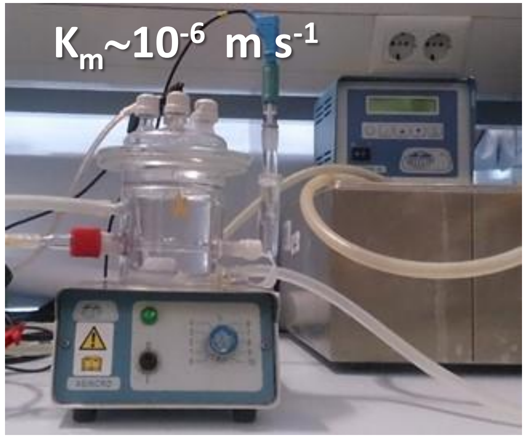
☑ **Layout of a continuous electrolytic cell**




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

## ☑ Flow pattern

Mixed tank vs Filter press flow





## ☑ Commercial cells

- ✓ Designed for electrosynthesis, not for wastewater treatment

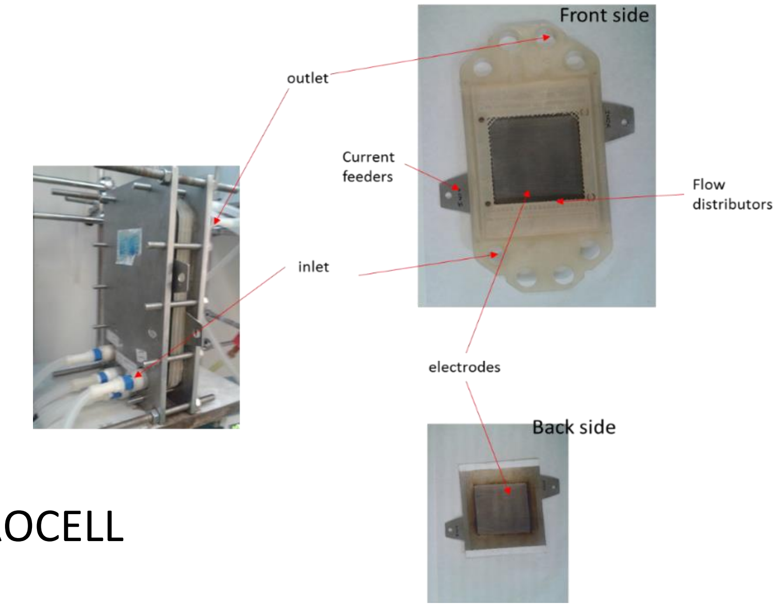
  ELECTROCELL (ElectroCell A/S, Denmark)
  FC01-LC ( former ICI Chemicals and Polymers Ltd., now INEOS Chlor-chemicals, UK)

- ✓ Designed specifically for diamond. Applied commercially for disinfection

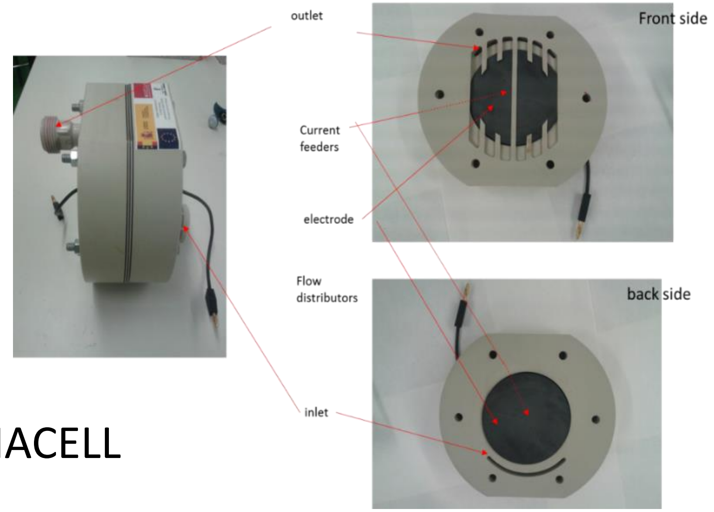
  DIACELL (former ADAMANT TECH, Switzerland, now WaterDiam)
  CONDIAS' Cells for target applications

☑ Mechanical design

- ✓ Inlet & outlet
- ✓ Flow distributors
- ✓ Current feeders

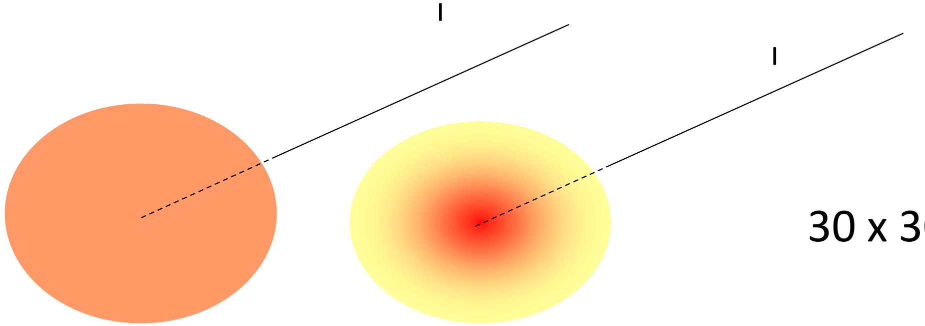



ELECTROCELL




DIACELL

☑ Increase electrode size




Uniform current distribution

Non-uniform current distribution

30 x 30 $cm^2$ ?

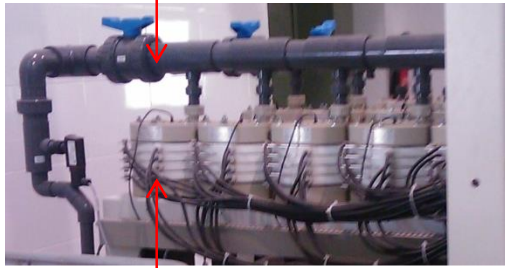
☑ stacking

Stack of ELECTROCELL

Stack of DIACELL

☑ Auxiliary equipments

piping



Electrical connections

Power supply

SCADA

Stack of cells

Recirculation tank

filter

pumps

Electrovalves
Regulation valves
Resistances

Regulation devices

SCADA,

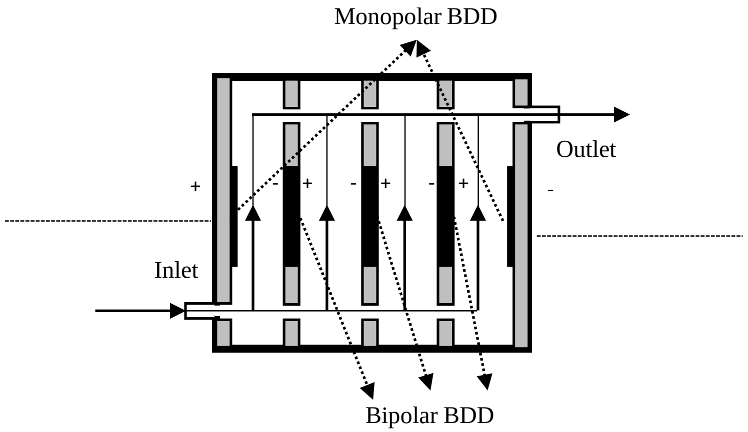
fieldbus

Measument devices (temperature, flowrate, concentration, level, pressure)

Stacks of electrolytic cells

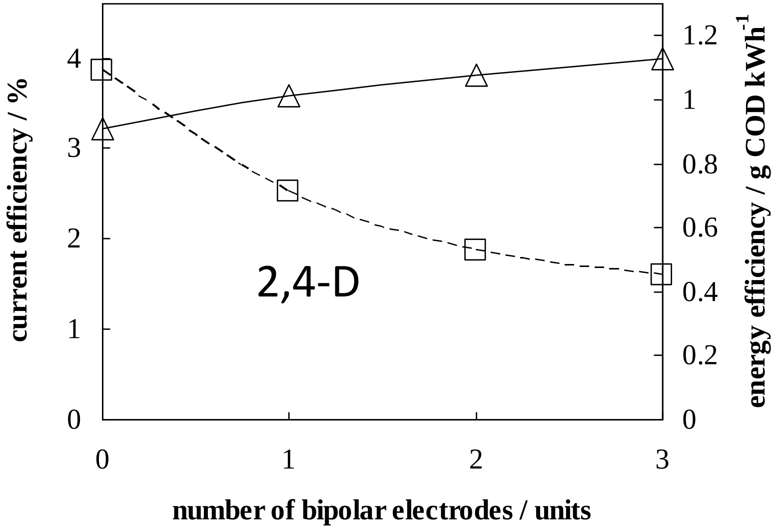
Heat exchanger

## ☑ Does the cell really influence?



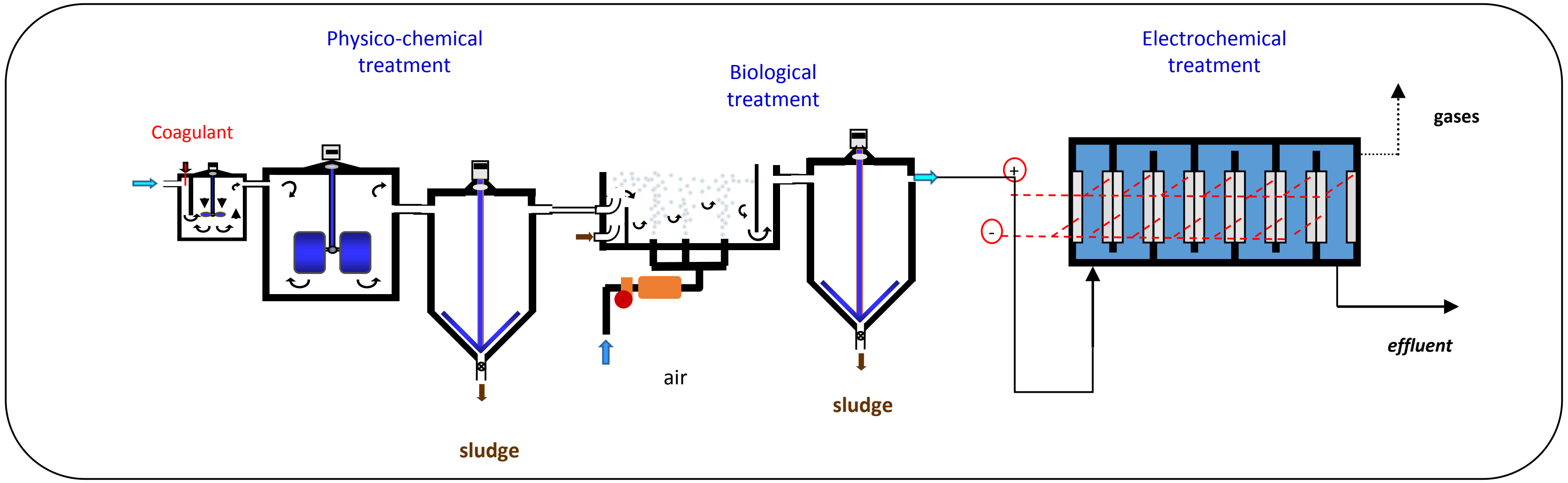

Electrochemical cell

Diacell type 401



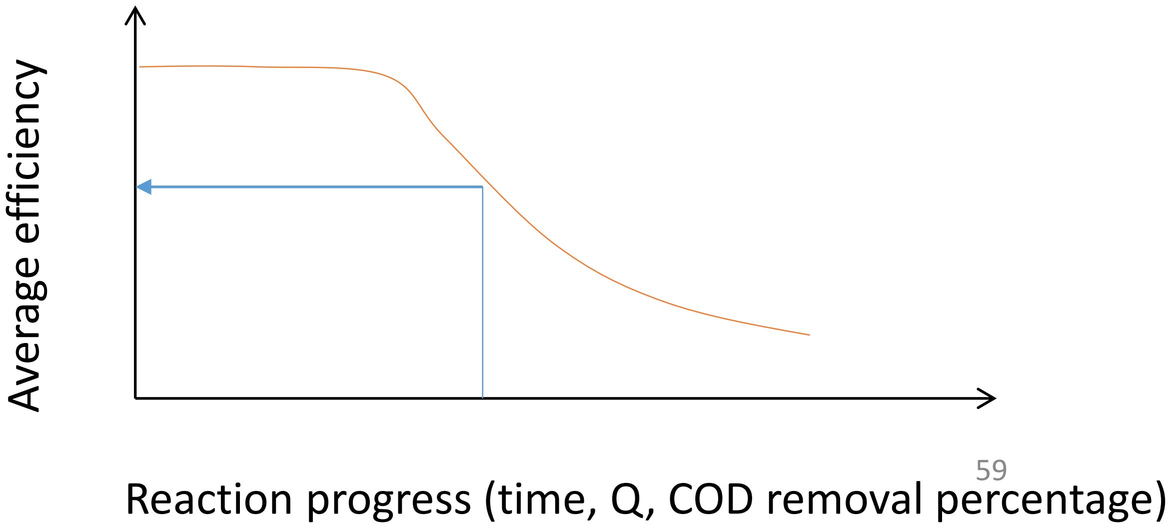
## ☑ Practical cases

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



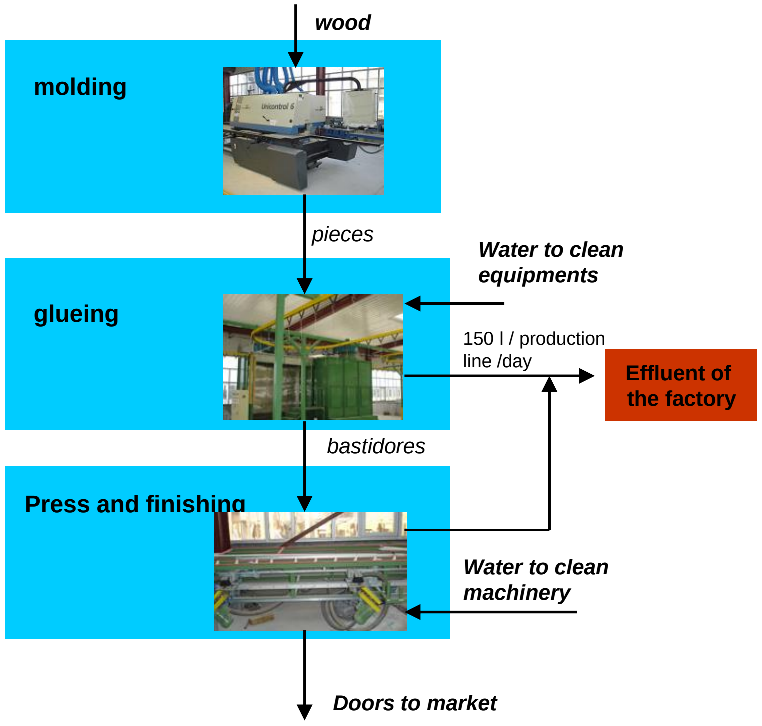

✓Sizing requires experimental data always!. Look for

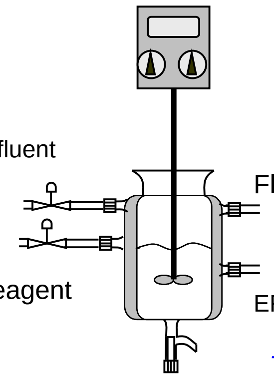
- ➢Feasibility
- ➢Getting data for design (optimum current density, cell voltage, etc.)
- ➢efficiency for a given degree of treatment
- ➢Operation problems



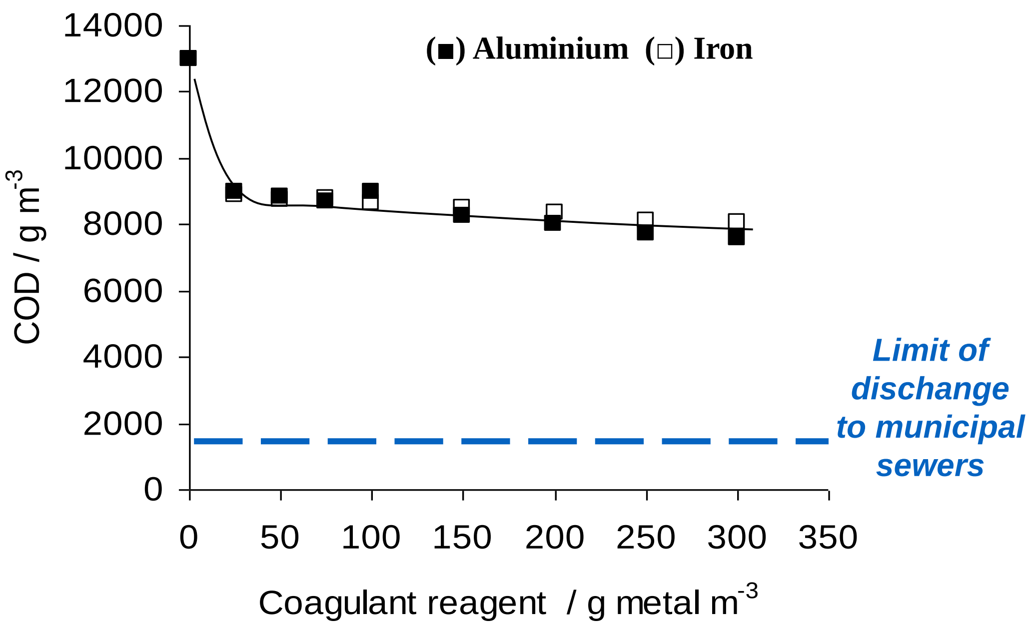
# ☑ Case study: wooden-door manufacting factories

| Parameter | Effluent 1 | Effluent 2 | Effluent 3 |
|---|---|---|---|
| $COD_0$ (mg $dm^{-3}$) | 13.068 | 15.310 | 7.110 |
| pH | 7,2 | 6,4 | 6,5 |
| Conductivity (mS $cm^{-1}$ ) | 7,5 | 4,9 | 4,1 |
| Total nitrogen (mg N $dm^{-3}$) | 347 | 410 | 184 |
| Suspended solids (mg $dm^{-3}$) | 13.574 | 3.766 | 2.040 |
| Main pollutants | Formaldehyde /urea | Formaldehyde /resorcine | Polyvinyl acetate |



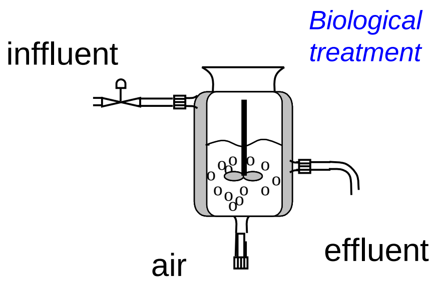


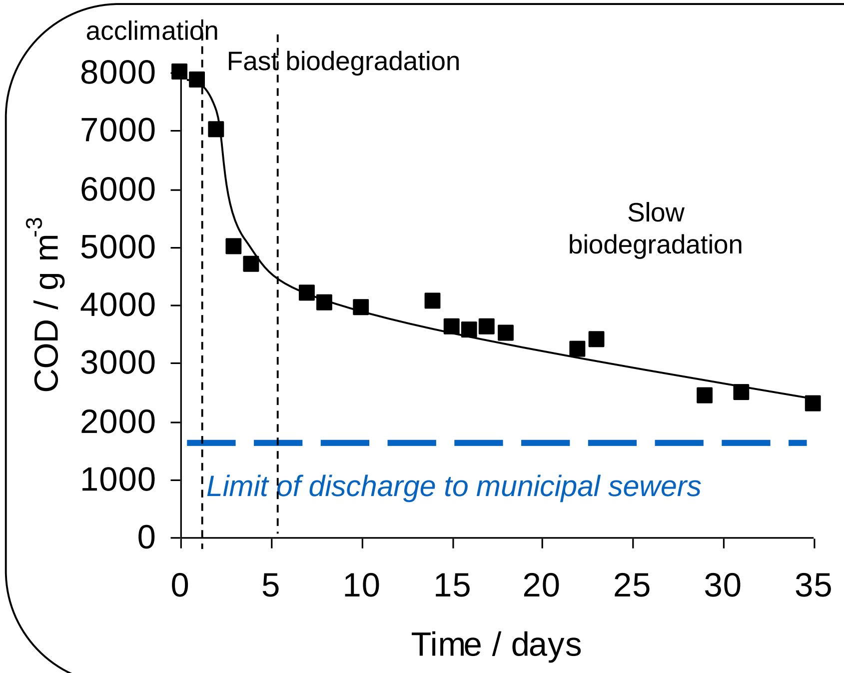

*Tratamiento físico-químico*

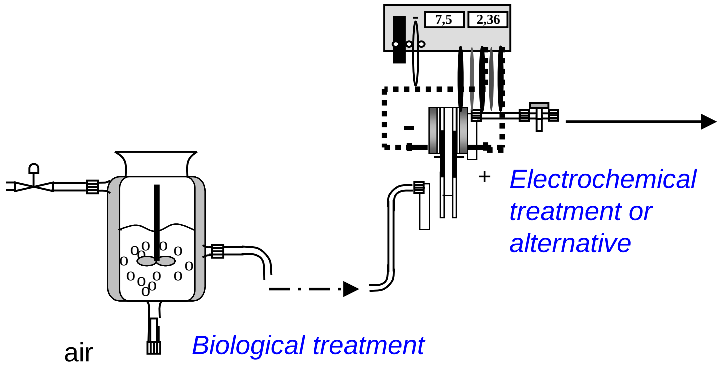


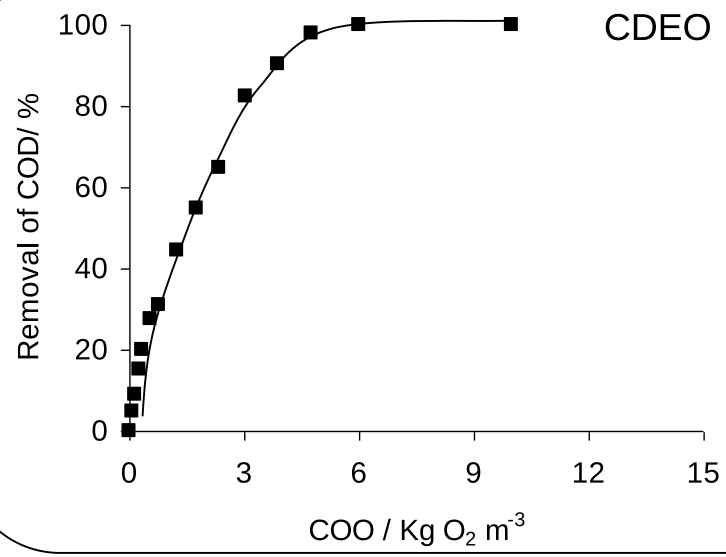

| Parameter | Effluent 1 | Effluent 2 | Effluent 3 |
|---|---|---|---|
| $COD_0$ (mg dm$^{-3}$) | 13.068 | 15.310 | 7.110 |
| Coagulant | aluminium | iron | aluminium |
| Concentration (mmol dm$^{-3}$) | 5,5 | 3,6 | 5,5 |
| $COD_f$ (mg dm$^{-3}$) | 8.120 | 9.640 | 4.770 |
| COD removal (%) | 38 | 37 | 33 |

❶ BIOLOGICAL TREATMENT+ CDEO



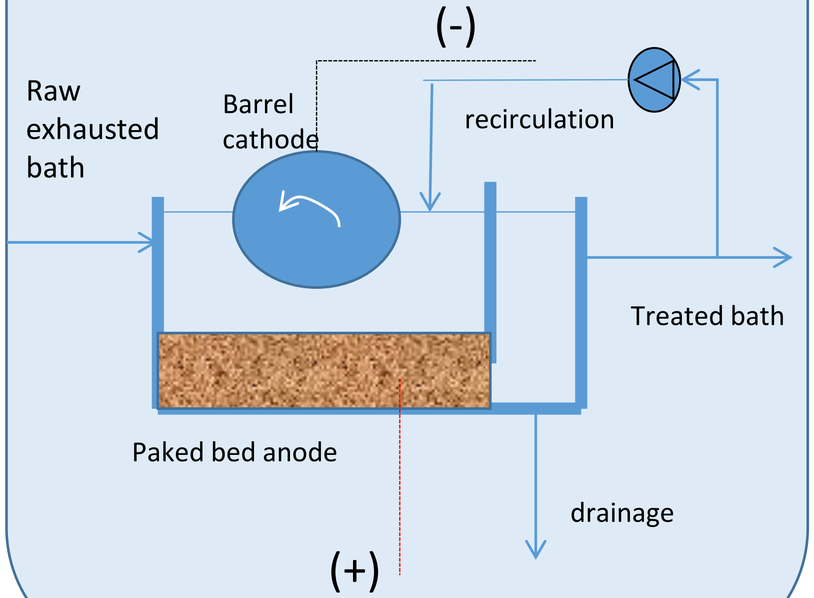
## ☑ Applications of Electrolysis

Industrial wastewater

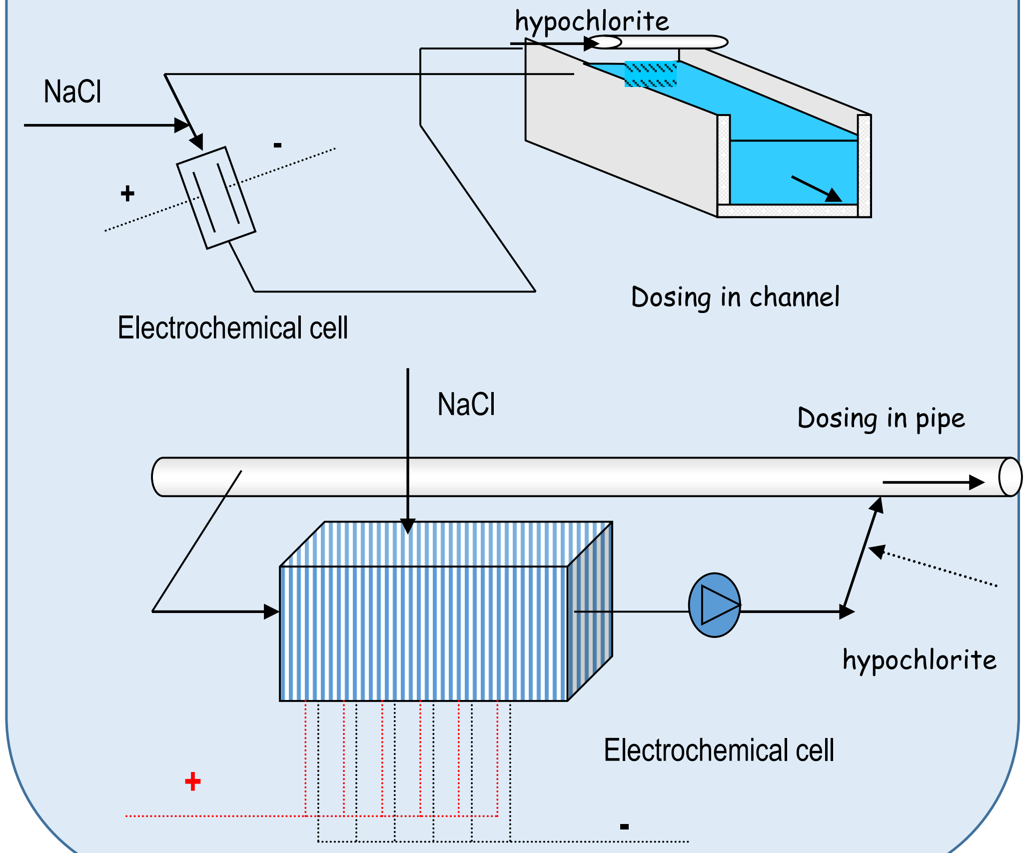
- Pharmaceutical industries
- Ink manufacturing
- Hospital
- Food processing
- Metalworking fluids
- Petrochemical
- Melanoidins

| | Range (COD) |
|---|---|
| Direct electrolysis | 1500-20000 mg $dm^{-3}$ |
| Enhanced Mediated Electrolysis | <1500 mg $dm^{-3}$ |

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



# CONCLUSIONS AND REMARKS

People from academia

it works!, needs to be promoted

too expensive?, low efficiency?, not promising?,

People from industry

## ☑ 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 feability 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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# TO LEARN MORE…


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# 8 ANNEX: PRE- SIZING AN ELECTROCHEMICAL PROCESS

**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**

$$R \pm ne^- \rightarrow \ldots$$

$$r\left(\frac{\mathrm{mol\,R}}{\mathrm{s}}\right) = \frac{\mathrm{I(A)}}{n\left(\frac{\mathrm{mol\,e^-}}{\mathrm{mol\,R}}\right)F\left(\frac{96500\mathrm{C}}{\mathrm{mol\,R}}\right)}$$

Continuous processes

Specific applied current charge

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

Current density

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

Specific Power consumption

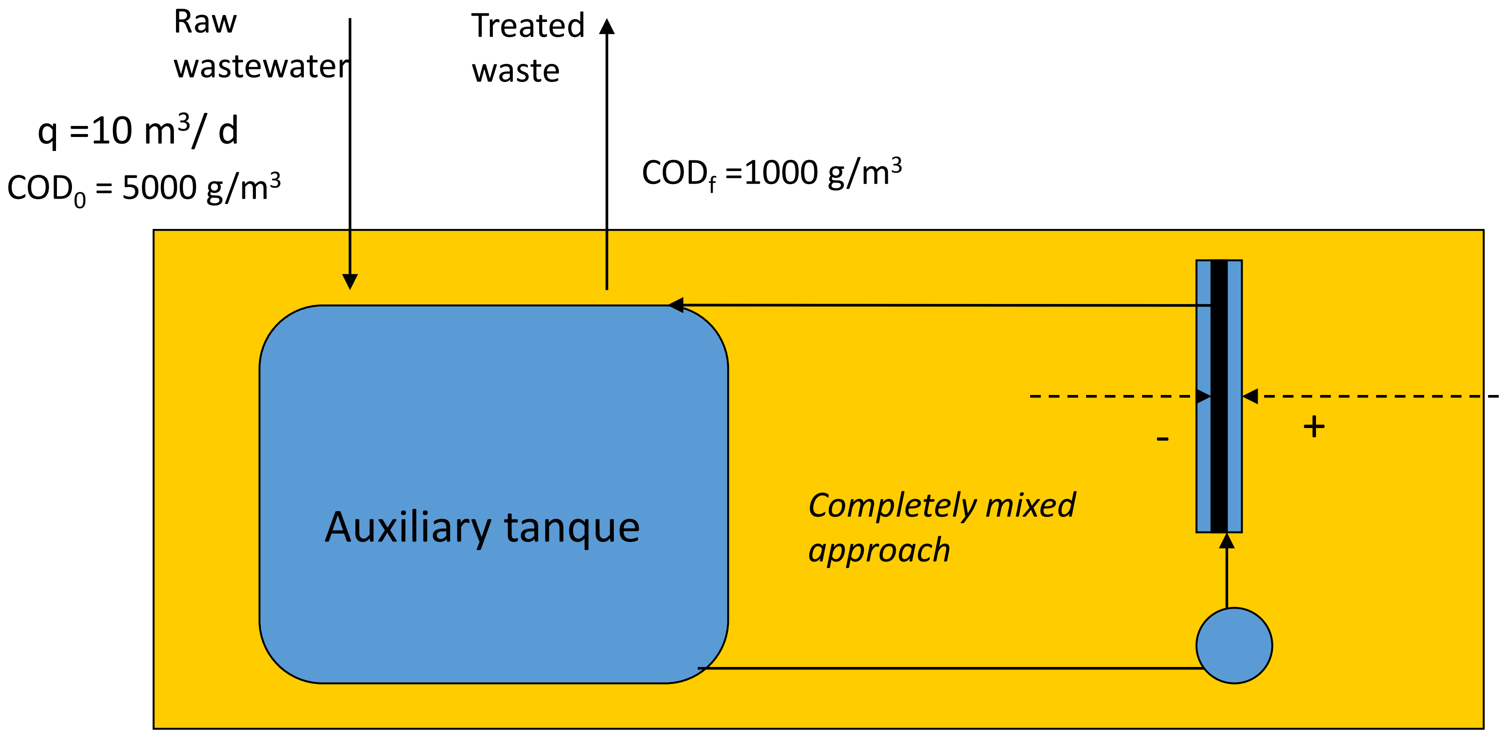
$$W\left(\frac{kWh}{m^3}\right) = q\left(\frac{kAh}{m^3}\right) \cdot E(V)$$

**Case 1.** A waste stream (10 $m^3$/ d) in a pharmaceutical company is going to be treated by electrolysis with conductive –diamond anodes. Chemical Oxygen Demand ($COD_0$) of the effluent is 5000 mg/l and concentration at the discharge of the treatment process ($COD_f$) 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 $A/m^{-2}$



## COD removal rate

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

**COD removal rate**= q* ($COD_0$-$COD_f$)= 10 ($m^3/d$)* (5000-1000) $g/m^3$= 40000 g/d**= 0.463 g/s**

## Estimation of intensity

**For a 100% current efficiency**

**r = I/ (nF) = mol DQO/s**

**I→ A =c/s**

**F=96500 C/mol e-**

**For COD oxidation**

**$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$**

**$m_{DQO}$= 32 g/mol**

**n = 4 mol e-/ mol COD**

Then:

r= 0.463 g/ s of COD to be removed

$$r = (I\ m_{DQO}) / (nF) = 0.463\ g/\ s$$

$$(I \cdot 32) / (4 \cdot 96400) = 0.463\ g/\ s \longrightarrow I=5585\ A$$

**From Experimental data**
**Efficiency= 80%**

$\eta = I_{stoichiometric} / I_{actual}$

efficiency =80%

→ $I_{actual}$ =5585/0.8=6980 A

## Estimation of electrode area

**From Experimental data**
**j= 1000 A/m⁻²**

$I = j \cdot S$

$S = 6980/1000\ m^2 = 7\ m^2$

…And a very rough economic estimation

Price= 20000 $A^{0.78}$ = 91200 euros

Investment= 4,2* 91200= 384000 euros

Amortization = 384000 /10/ 365= 105 euros/d

## Estimation of energy consumption

**From experimental data: V= 5 Volts**

W= I·V= 6980 ·5= 34900 watts = 35 kW

Specific Power= W/q= 83 kwh/ $m^3$

…And a very rough economic estimation

Energy cost= 35 kWd/d =840 kWh/d= 92.4 euros/d (0.11 €/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.

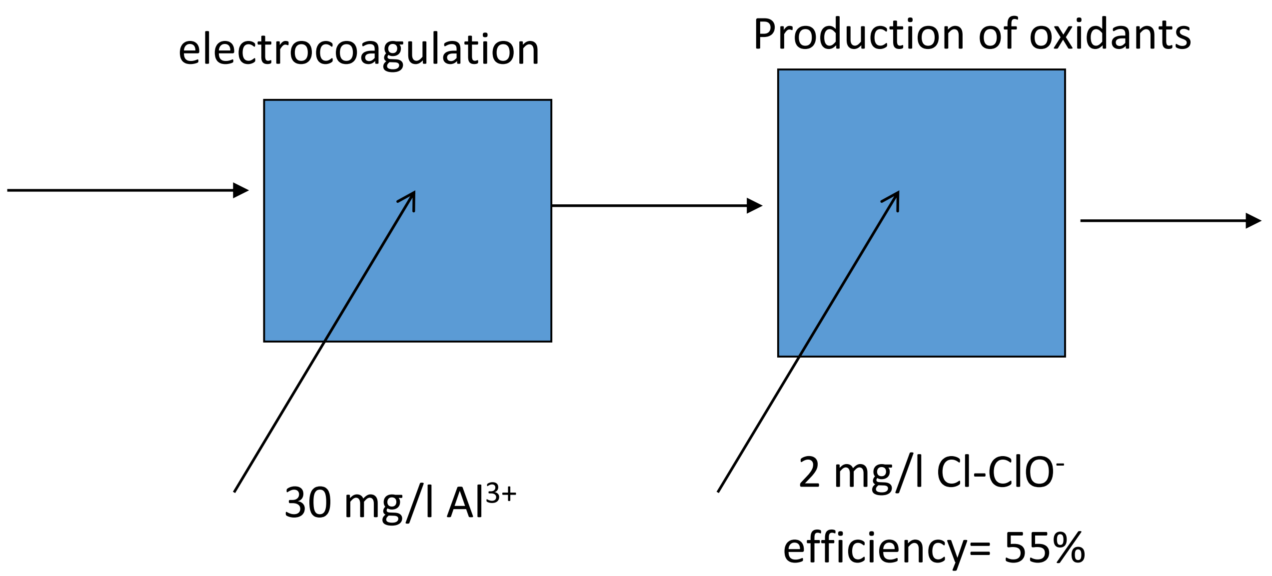
Consider that specific water demand for this population is 250 l /p.e./d

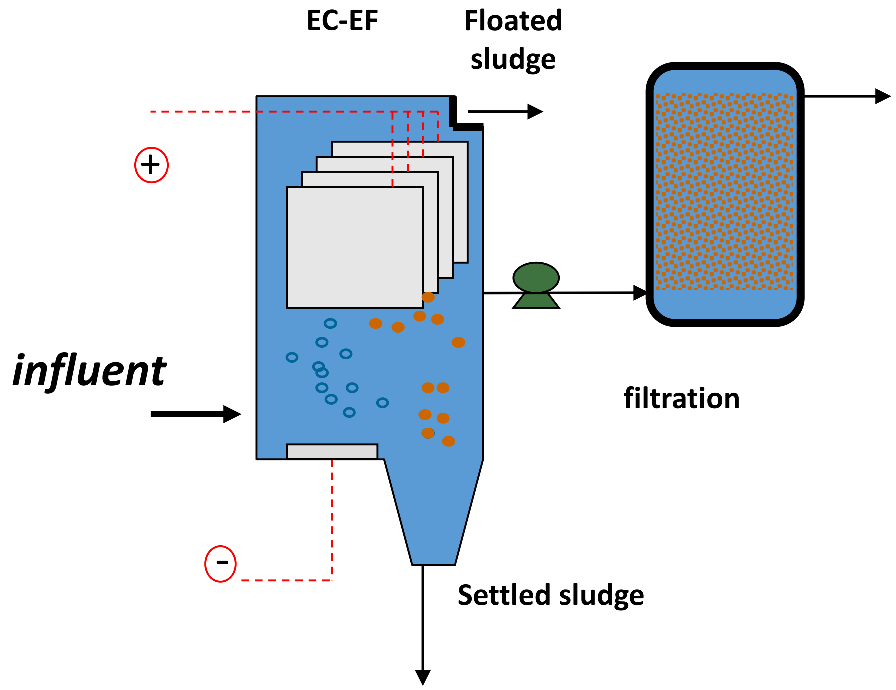
The dose of aluminium and hypochlorite were determined experimentally in a bech scale plant study being 30 mg $Al^{3+}$/ l and 2 mg Cl-$ClO^-$ of hypochlorite. Ti/$RuO_2$ anodes for chlorine production and aluminium plates were used in that study. Calculate operation cost and electrode area requirements

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 efficienty = 55%; j= 100 mA $cm^{-2}$;V= 5 V








**Estimation of the amount of aluminium that should be dosed daily:**

r (g/d)= 3000 (h.e.) * 250 (l/h.e./d)* 30 mg Al / l=22500 g/d = 22.5 kg /d Al

r (mol/d)= 22500 g/d * 1 mol $Al^{3+}$ /26.9 g $Al^{3+}$ = 836.4 mol $Al^{3+}$/d

## Estimation of the intensity that should be applied

$r = I/nF$

$I = r \cdot n \cdot F = 836.4$ mol $Al^{3+}$/d · 3mol $e^-$/mol $Al^{3+}$· 96500 C/mol $e^-$ · 1d/86400s= 2802.6 A

**For COD oxidation**

**$Al \rightarrow Al^{3+} + 3e^-$**

**$m_{DQO}$= 32 g/mol**

**n = 3 mol e-/ mol $Al^{3+}$**

## Estimation of energy consumption

**From experimental data**
**V= 2.5 V**

Power= I·V=2802.6·2.5= **7 kW**=

Energy consumption=7kW·24 h/d= **168 kWh/d**

## Estimation of the anode area required

**From experimental data**
**j= 5 mA $cm^{-2}$**

I= 2802.6 A

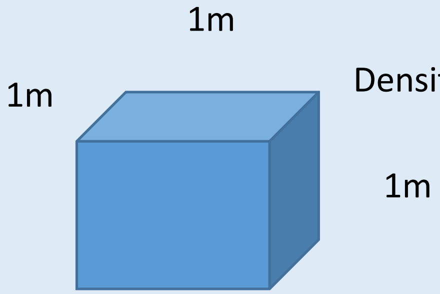
j= 5 mA $cm^{-2}$ = 50 A $m^{-2}$

Electrode area= I/j= 2802.6/ 50= 56.05 $m^2$

10 anodes de 2.4·2.4 m

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.

## Replacement of the sacrifice electrode




Density of aluminium: 2700 kg/$m^3$

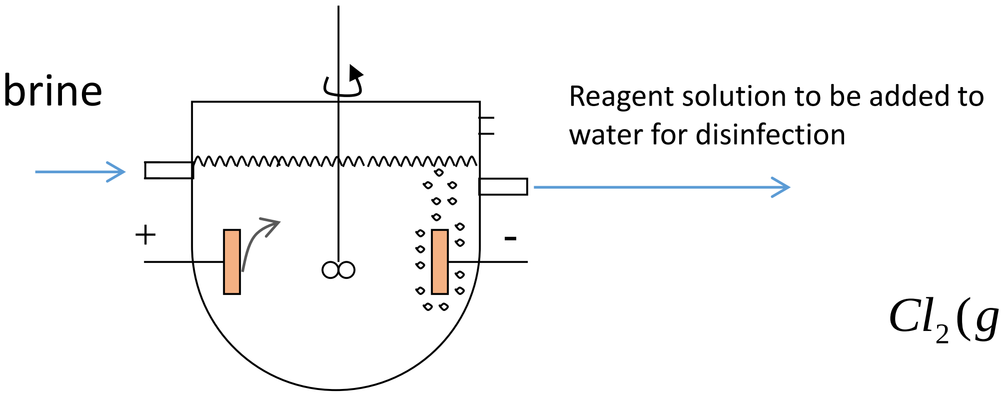
For an initial width of 1cm => 27 kg/$m^2$

Width: 1 mm
Weight: 2.7 kg/$m^2$/mm

Weight per electrode (2.4·2.4 $m^2$)= 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




$$2Cl^- \rightarrow Cl_2(g) + 2e^-$$

$$Cl_2(g) + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$$

**Estimation of the amount of hypochlorite to be dosed to water**

r (g/d)= 3000 (h.e.) * 250 (l/h.e./d)· 2 mg Cl-ClO$^-$ / l= 1500 g/d = 1.5 kg /d Cl-ClO$^-$

r(mol/d)= (1500 g/d )· /(1 mol Cl-ClO$^-$ /35.5 g Cl-ClO$^-$ )= 42.25 mol Cl-ClO$^-$ /d

**Estimation of intensity**

**From experimental data**
**j= 100 mA cm$^{-2}$= 1000 A m$^{-2}$**
**V= 5 V**
**efficiency= 55%**

$$2Cl^- \rightarrow Cl_2(g) + 2e^-$$

$$Cl_2(g) + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$$

n=2 moles de e$^-$/mol Cl-ClO$^-$

r= 42.25 mol Cl-ClO$^-$/d

I= r·n·F=42.25 mol Cl-ClO$^-$/d · 2mol e$^-$/mol Cl-ClO$^-$ ·96500 C/mol e$^-$ · 1d/86400s= 94.4 A

I real = I / eficiency= 94.4/0.55= 171.6 A

**Estimation of electrode area**

Anode area= I/j 171.6/1000= 0.17 m$^2$

**Estimation of energy requirements**

W= I·V= 171.6·5 W= **858 W**
Energy requierements = 858W·(24 h/d)/(1000 w/kW)= 20.6 kWh/d