Electrochemical Treatment Methods in Separation and Purification

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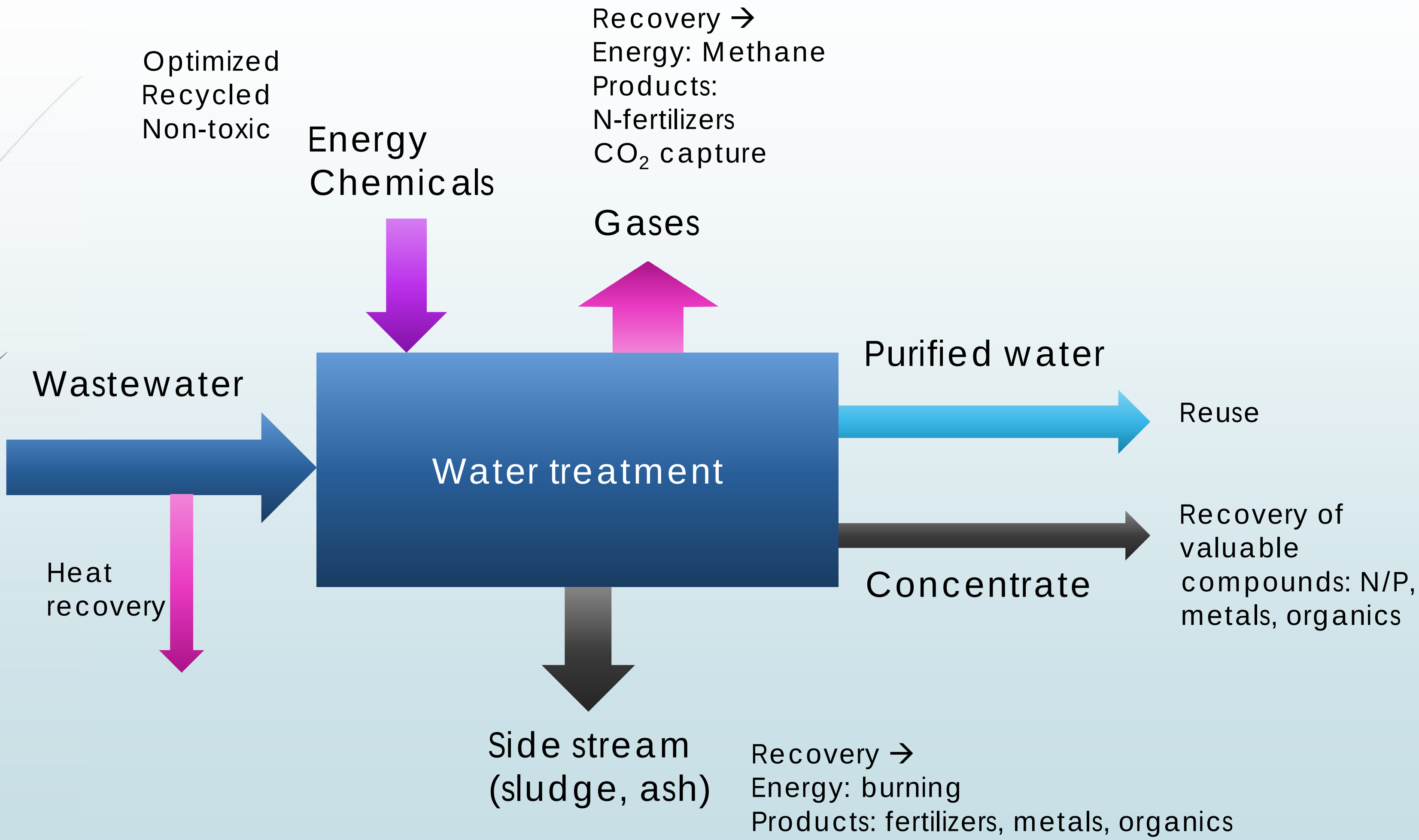
Two atoms are walking down the street. One of them says:

“Oh, no, I think I lost an electron.”

“Are you sure?”

“Yes, I’m positive.”



Optimized
Recycled
Non-toxic

Energy
Chemicals

Recovery →
Energy: Methane
Products:
N-fertilizers
CO_2 capture

Gases

Wastewater

Heat
recovery

Water treatment

Purified water

Reuse

Concentrate

Recovery of
valuable
compounds: N/P,
metals, organics

Side stream
(sludge, ash)

Recovery →
Energy: burning
Products: fertilizers, metals, organics

Purification Recovery/separation

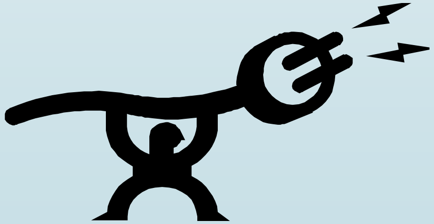
Electrical charges

- Are playing important role in every purification/separation technologies
  - Adsorption, catalysis, membrane based treatment etc.
  - Molecules and ions bearing negative or positive charges
  - Effect of pH
  - Effect of surfaces
  - Electrostatic attraction between a proton and electron is 10^{38} times stronger than that of mass-based gravitational attraction

What is electrochemistry?

Short definition:

> Electrochemistry deals with the charge transfer at the interface between an electrically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as with the reactions within the electrolytes and the resulting equilibrium



What is oxidation?

When a molecule/ion loses electrons
(becomes more positive)

Whatever is oxidized is the reducing agent

What is reduction?

When a molecule/ion gains electrons
(becomes more negative)

Whatever is reduced is the oxidizing agent

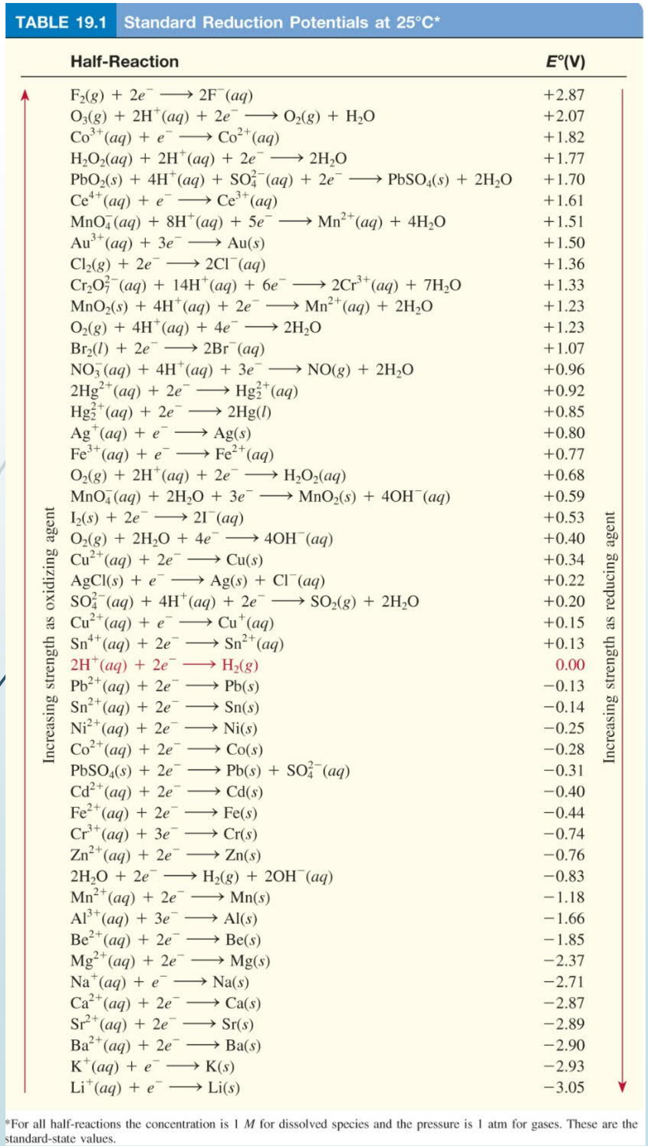


TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

http://highered.mheducation.com/olcweb/cgi/pluginpop.cgi?it=jpg::::::/sites/dl/free/0023654666/650262/Standard_Reduction_Potential_19_01.jpg::Standard%20reduction%20potentials

- E^0 is for the reaction as written
- The more positive E^0 the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E^0 changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction does not change the value of E^0

Cell potential

Half reactions:

$Zn \rightarrow Zn^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu$

Cell reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Cell potential:

$E^0_{cell} = E^0_{Zn\rightarrow Zn2+} + E^0_{Cu2+\rightarrow Cu} = +0{,}76\ V + 0{,}34\ V = 1{,}1\ V$ Positive: spontaneous

Electrolysis: forcing a current through a cell to produce a chemical change for which the cell potential is negative:

$Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$ $E^0_{cel} = -1{,}1\ V$

Gibbs energy and Nernst equation

- Gibbs energy and Nernst equation

$$\Delta G = \Delta G^\circ + RT\ln(Q)$$

$$\Delta G^\circ = -nFE^\circ$$

n = electrons transferred

$$-nFE = -nFE^\circ + RT\ln(Q)$$

$$E = E^\circ - \frac{RT}{nF}\ln(Q) \xrightarrow{T = 25\ ^oC} E = E^\circ - \frac{0.0591}{n}\ln(Q)$$

$$\alpha\,\mathrm{A} + \beta\,\mathrm{B} \Leftrightarrow \gamma\,\mathrm{C} + \mu\,\mathrm{D}$$

$$Q = \frac{[\mathrm{C}]^\gamma[\mathrm{D}]^\mu}{[\mathrm{A}]^\alpha[\mathrm{B}]^\beta}$$

Example: Electrochemical cell

Calculate the cell potential at 25 °C for the following reaction:

$2\ \text{Al} + 3\ \text{Mn}^{2+} \rightarrow 2\ \text{Al}^{3+} + 3\ \text{Mn}$ $E^{o}_{cell} = 0.48\ \text{V}$

$[\text{Mn}^{2+}] = 0.50\ \text{M}$ $[\text{Al}^{3+}] = 1.50\ \text{M}$

From half reactions: n = 6

$2\ \text{Al} \rightarrow 2\ \text{Al}^{3+} + 6\ e^{-}$ $3\ \text{Mn}^{2+} + 6\ e^{-} \rightarrow 3\ \text{Mn}^{2+}$

$$E = E^{\circ} - \frac{0.0591}{n}\ln\left(\frac{\left[\text{Al}^{3+}\right]^{2}}{\left[\text{Mn}^{2+}\right]^{3}}\right) = 0.48 - \frac{0.0591}{6}\ln\left(\frac{1.50^{2}}{0.50^{3}}\right) = 0.47\text{V}$$

Electrochemical treatment

Benefits of electrochemical technologies:

- Environmental compatibility
- Versatility
- Energy efficiency
- Safety
- Selectivity
- Cost effectiveness
- Less chemicals used

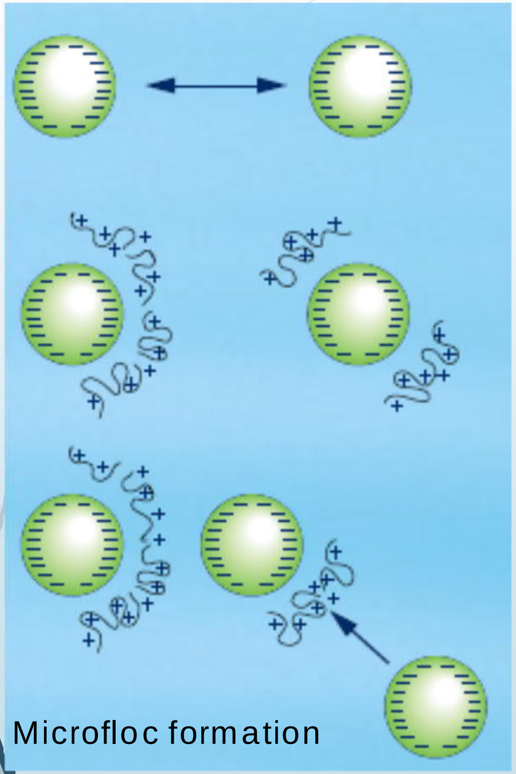
Methods:

- Electrochemical oxidation
- Electrocoagulation
- Electrochemical reduction
- Indirect electro-oxidation with strong oxidants
- Electrodeionization
- Capacitive deionization
- Photo or ultrasound assisted electrochemical methods
- Electro kinetics

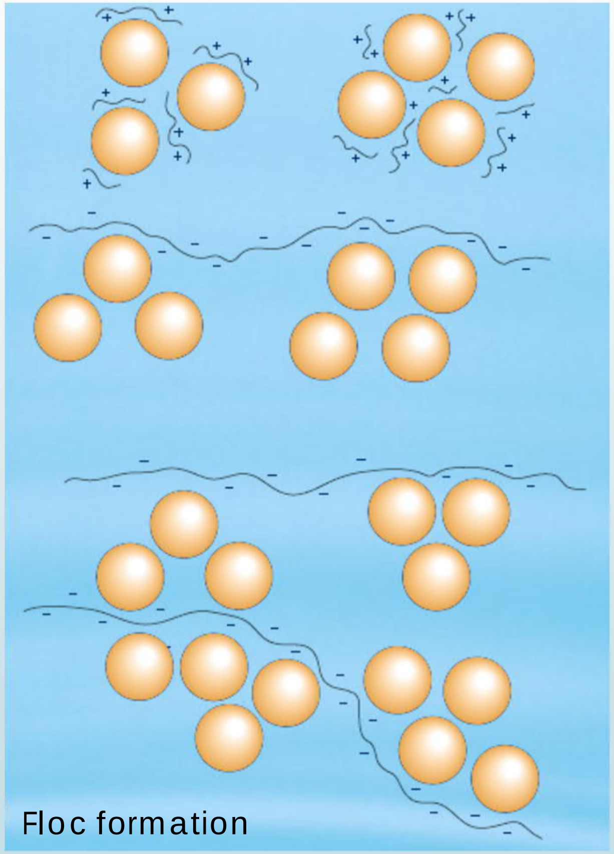
Group work

- Collect some interesting topics related to electrochemical purification or separation technologies
- Add your findings to: https://padlet.com/eveliinarepo/EC

Coagulation/flocculation


Microfloc formation

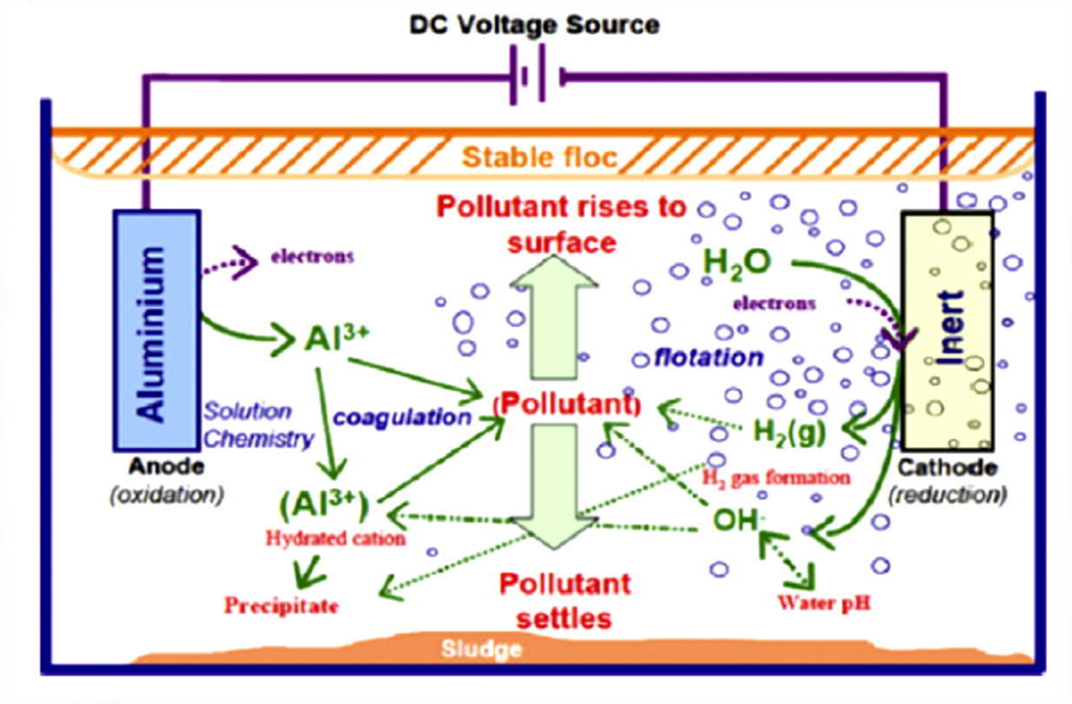
- Coagulation is the step where colloidal particles are destabilized.
- Flocculation is the step where destabilized colloidal particles are accumulated into aggregates.
- Coagulants: cause the neutralization of pollutants → repulsive forces between pollutant species disappear
- Flocculants: cause the aggregation of the destabilized colloidal particles
- Coagulant is always added before flocculant


Floc formation

SNF FLOERGER: coagulation flocculation http://www.snf.us/wp-content/uploads/2014/08/Coagulation-Flocculation.pdf

Electrocoagulation

Generation of coagulant species in situ by electrolytic oxidation of sacrificial anode materials



Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J. (2017). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1-21.

Sacrificial aluminum or iron anodes are the most common:

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

$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$ (at alkaline conditions)

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

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (at alkaline conditions)

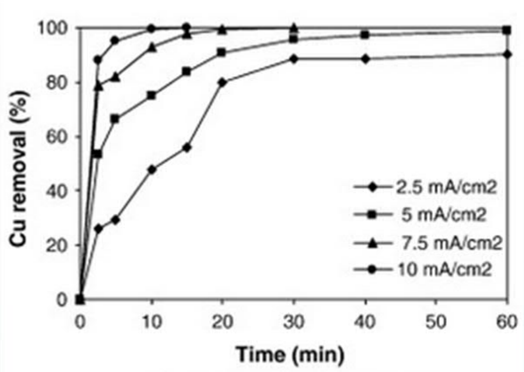
These metal ions are effective coagulants for the pollutants

Hydrogen gas released at the cathode helps to float the formed flocs out of the water

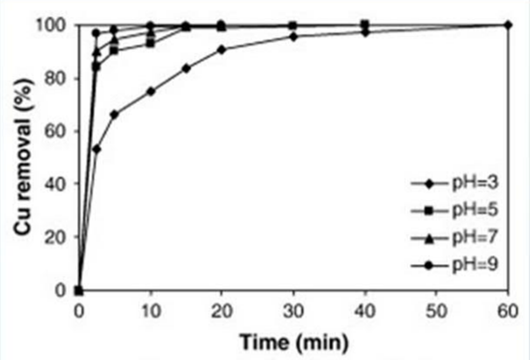
Electrocoagulation

Factors affecting electrocoagulation

1) Current density
2) Charge loading
3) Presence of salts in electrolyte solution, such us NaCl
4) pH
5) Temperature
6) Electrode position
7) Cell design



iron anode-aluminum cathode

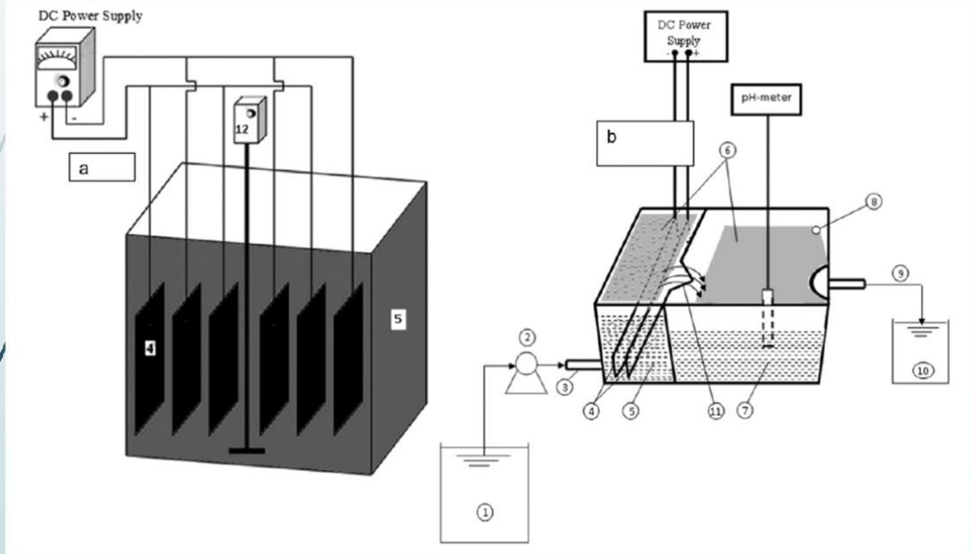


iron anode-aluminum cathode

Akbal, F., & Camcı, S. (2011). Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation. Desalination, 269(1), 214-222.

Electrocoagulation

Different kind of cell designs have been applied



Batch and continuous

Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J. (2017). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1-21.

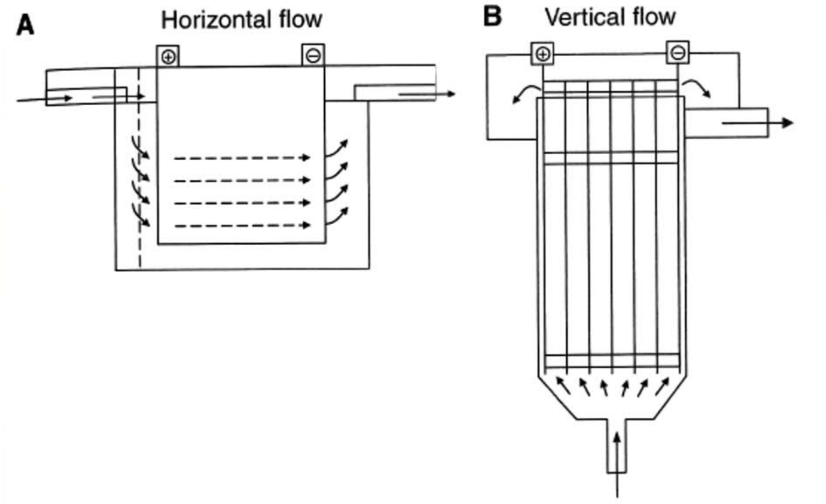


Fig. 10. Electrocoagulation units.

Wang, Hung & Shammas, Handbook of Environmental Engineering, Advanced physicochemical treatment technologies, Humana Press Inc. 2007

Electrocoagulation

Advantages

- Nonspecific method
- Address drinking water and wastewater
- Combines oxidation, coagulation and precipitation (results in lower capital costs [5])
- Reduced need for chemical reagents (replaced by either Al or Fe electrodes and electricity)
- Reduced operating cost
- Reduced risk of secondary pollution
- Low sludge production
- Without moving parts
- Low energy requirements
- Solar power can be used

Disadvantages

- Need for maintenance
- Electrode passivation over time
- Need for high-conductivity water
- Lack of systematic reactor design

Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J. (2017). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1-21.

Electrocoagulation

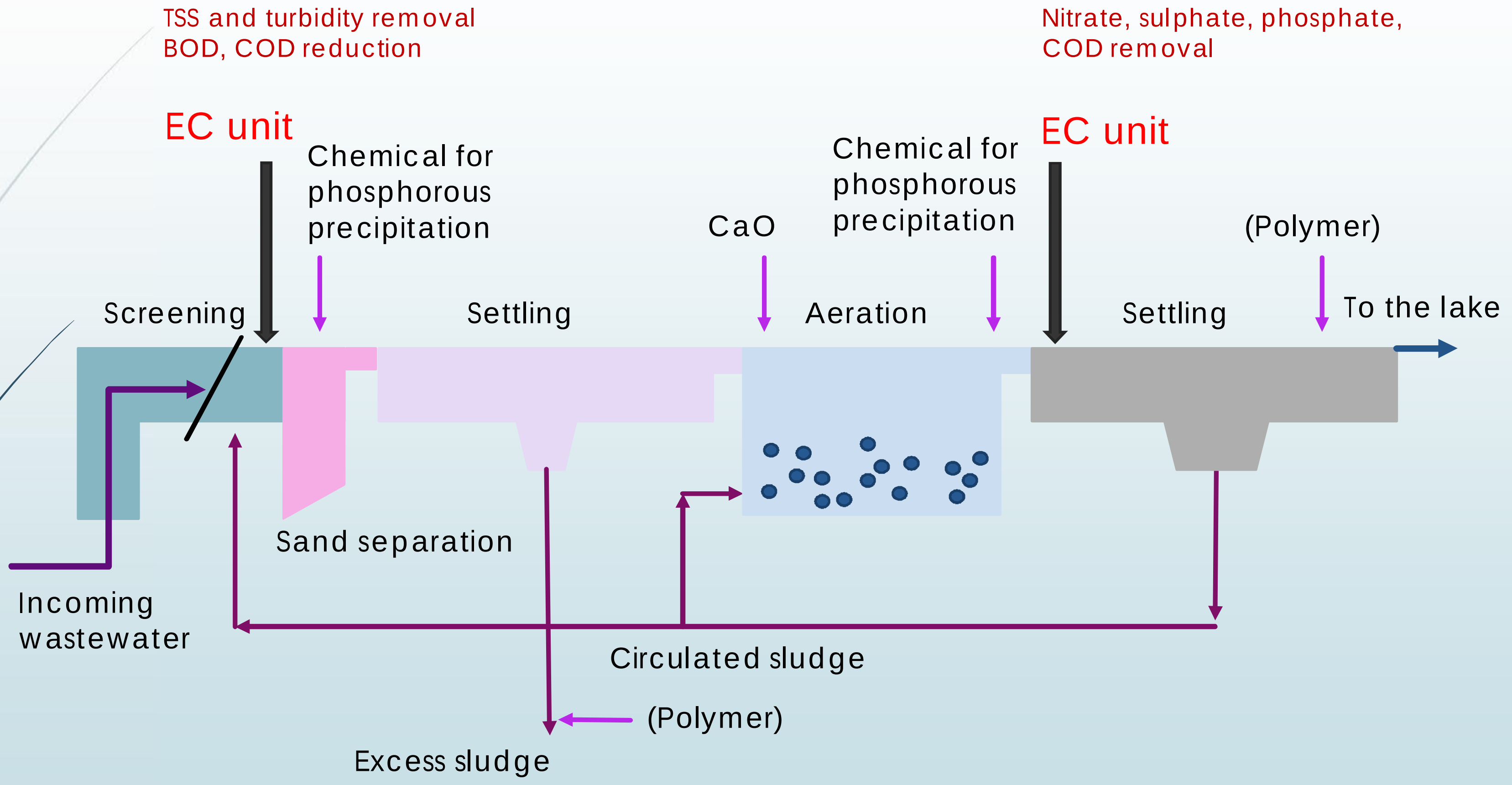
Effluents treated by electrocoagulation:

1) Suspended solids
2) Oil and grease
3) Colloids in natural waters
4) Algae and micro-organisms
5) Organic dyes
6) Municipal wastewater treatment
7) Heavy metals removal

A good review article:

Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J. (2017). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1-21.

Municipal wastewater treatment

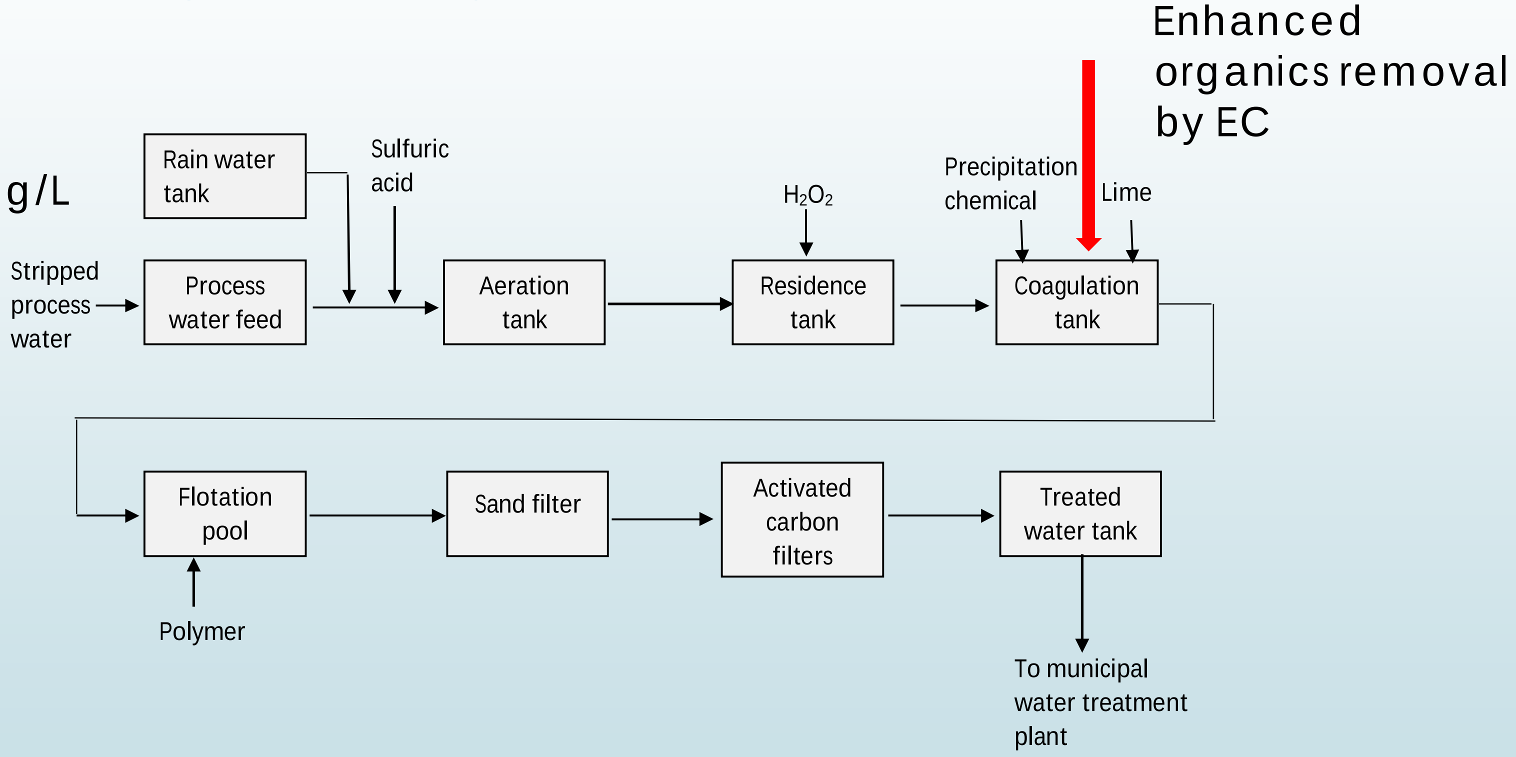


http://www.waterworld.com/articles/iww/print/volume-13/issue-5/features/embracing-closed-loop-technology-for-recycling-and-reuse.html

https://www.wateronline.com/doc/a-shocking-approach-to-wastewater-treatment-0001

Treatment of the process water in oil re-refining industry

COD: 11000 mg/L



Enhanced organics removal by EC

Rain water tank

Sulfuric acid

Stripped process water

Process water feed

Aeration tank

H_2O_2

Residence tank

Precipitation chemical

Lime

Coagulation tank

Flotation pool

Polymer

Sand filter

Activated carbon filters

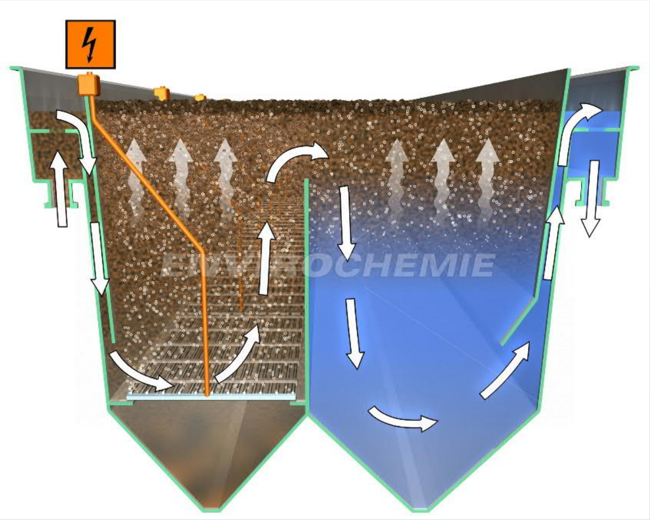
Treated water tank

To municipal water treatment plant

Electroflotation

- Tiny oxygen and hydrogen bubbles are formed at anode and cathode, respectively, during water electrolysis
- Bubbles attach to suspended matter → float to the surface (DAF)
- Graphite, titania or dimensionally stable anode (DSA) electrodes

Envirochemie designs and produces water treatment plants including Electroflotation systems



http://envirochemie.com/en/plants/flotation-plants/electroflotation/

Electroflotation

Factors affecting

1) Size of the bubbles
2) Cell design and arrangement of the electrodes
3) Electrode materials
4) Operating conditions, such us current density and water conductivity
5) pH

Applications

1) Separation of oil and low-density suspended solids from wastewaters
2) Used e.g. in mining, dairy and restaurant wastewater treatment

Electrochemical oxidation (EO)

- Indirect EO processes
  - Chlorine and hypochlorite generated anodically
  - Electrochemically generated hydrogen peroxide
  - Mediated EO where metal ions are oxidized on an anode to form high valence reactive species, which attack pollutants or generate hydroxyl radicals

- Direct or anodic oxidation
  - Generation of physically adsorbed “active oxygen” (adsorbed hydroxyl radicals) or chemisorbed “active oxygen” (oxygen in the oxide lattice)
  - Physically adsorbed “active oxygen” causes combustion of organic pollutants
  - Chemisorbed “active oxygen” participates in the formation of selective oxidation products

Electrochemical oxidation

Oxidants:

- Hydroxyl radicals (direct oxidation)
- Ozone and H_2O_2 (indirect oxidation)
- Chlorine and hypochlorous acid (indirect)
- Electric field (direct)

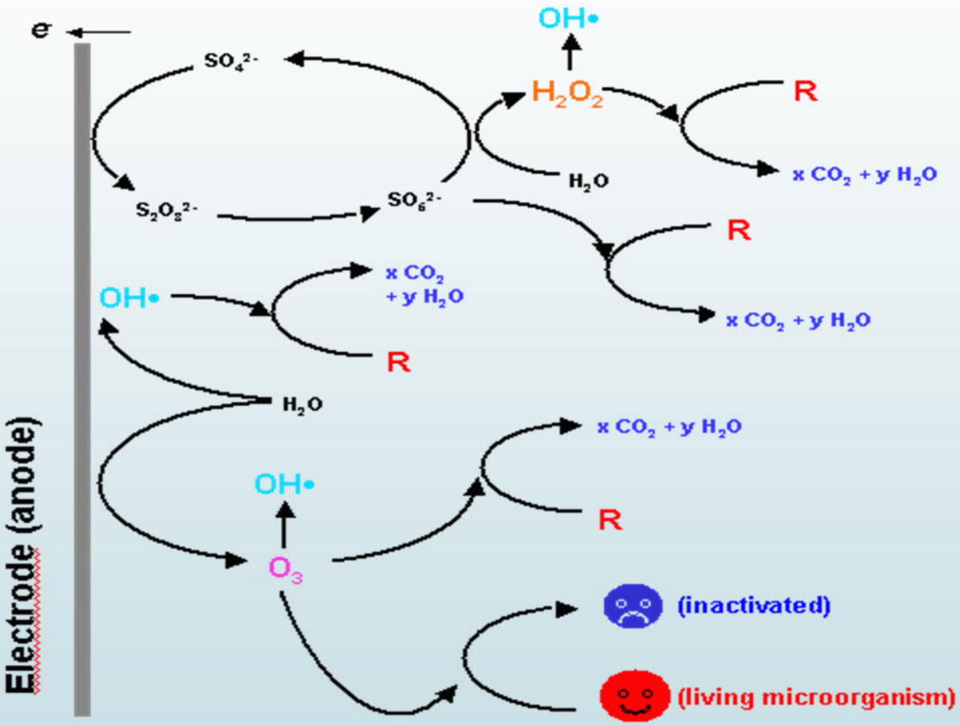
Important parameters:

- Electrolyte solution (conductivity, composition of ions)
- Current density (mA/cm^2)
- pH
- Pollutant concentration
- Electrode material

Formation potentials of different oxidants

$2\ H^+ + 2\ e^- \rightarrow H_2$	E0 = 0.0
$2\ H_2O \rightarrow O_2 + 4\ e^- + 4\ H^+$	E0 = + 1.23
$2\ Cl^- \rightarrow Cl_2 + 2e^-$	E0 = + 1.36
$Cl^- + H_2O \rightarrow HOCl + 2\ e^- + H^+$	E0 = + 1.49
$3\ H_2O \rightarrow O_3 + 6\ e^- + 6\ H^+$	E0 = + 1.51
$2\ H_2O \rightarrow H_2O_2 + 2\ e^- + 2\ H^+$	E0 = + 1.77
$O_2 + H_2O \rightarrow O_3 + 2\ e^- + 2\ H^+$	E0 = + 2.07
$H_2O \rightarrow OH^\bullet + e^- + H+$	E0 = + 2.85

Reactions:



Different oxidation reactions on the surface of the anode

Electrochemical oxidation: electrodes

Electrodes should have following characteristics:

- sufficient catalytic activity
- good stability
- high oxygen evolution overpotential
  - Oxygen evolution is a competitive reaction in the process of anodic oxidation of pollutants
- inert in tough conditions
- high corrosion stability

- PbO_2
- BDD (boron-doped diamond)
- MMO (mixed metal oxide)
- Graphite
- Pt

BDD:

- large working potential window
- high chemical stability even at strong acidic or alkaline conditions
- non-poisoning of the surface
- effective for degradation refractory or priority pollutants

Electrochemical oxidation: electrodes

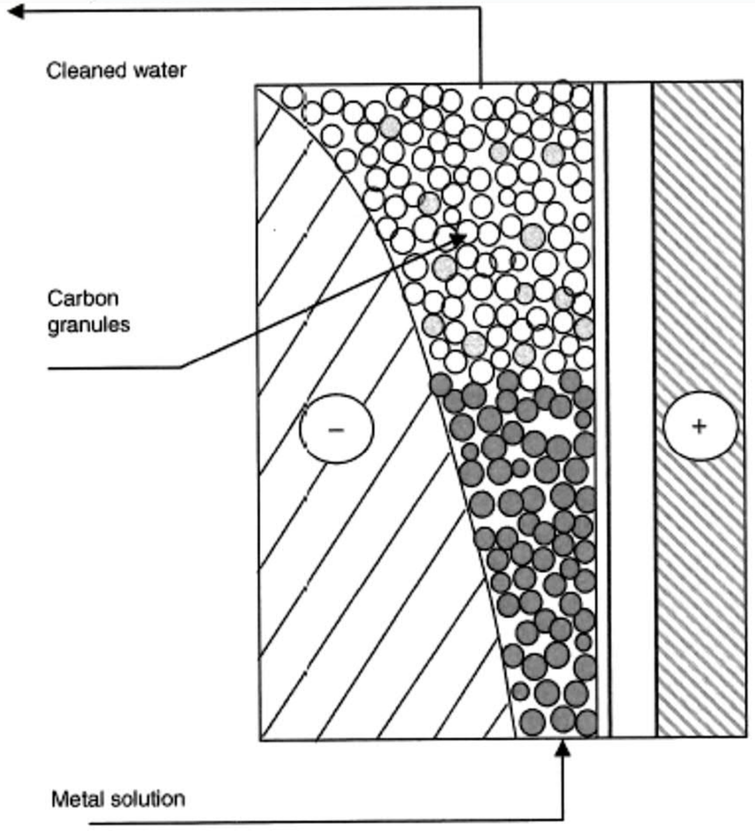
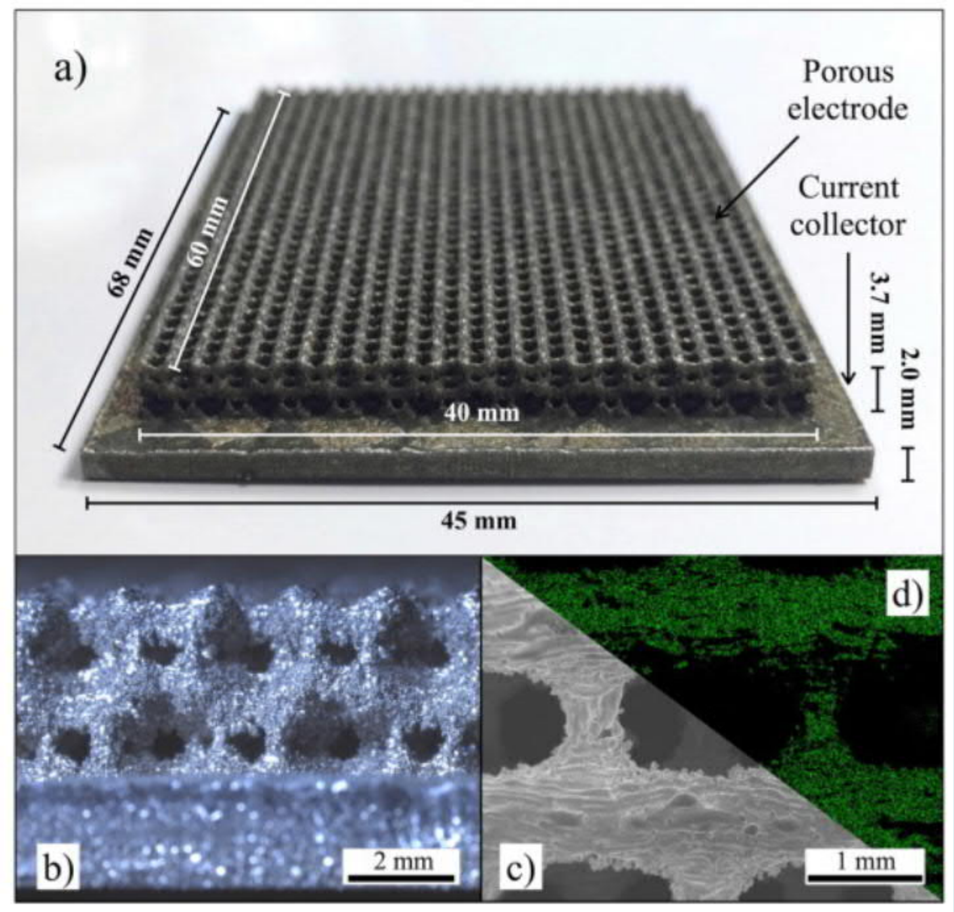


Fig. 8. Fixed bed reactor.

Wang, Hung & Shammas, Handbook of Environmental Engineering, Advanced physicochemical treatment technologies, Humana Press Inc. 2007

- Moving electrodes or turbulence promoters
    - Improved mass transport and thus increased current density
- Accommodation of large electrode area in a small cell volume
- Improved mass transfer coefficients and enlarged specific electrode area are provided by the use of three-dimensional electrodes

Electrochemical oxidation: electrodes



- 3D-printed electrodes
- Tailored composition, catalytic activity, active surface area, fluid flow characteristics and mass transport properties
- A high degree of surface roughness, local heterogeneity and surface micro-porosity

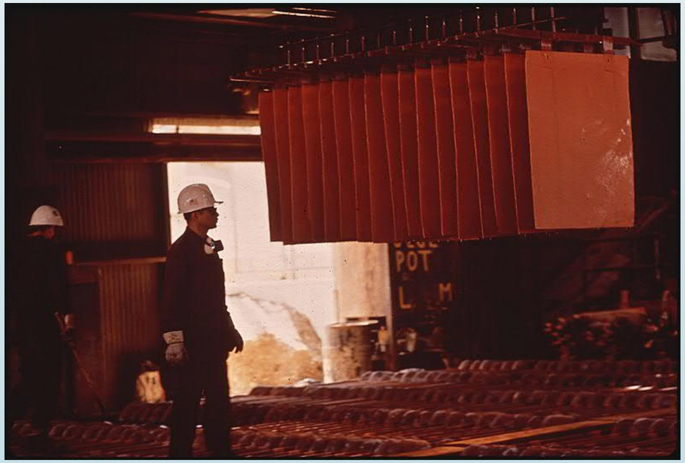
➡ A huge amount of possibilities in order to enhance purification and separation processes!

Arenas, L. F., de León, C. P., & Walsh, F. C. (2017). 3D-printed porous electrodes for advanced electrochemical flow reactors: A Ni/stainless steel electrode and its mass transport characteristics. Electrochemistry Communications, 77, 133-137.

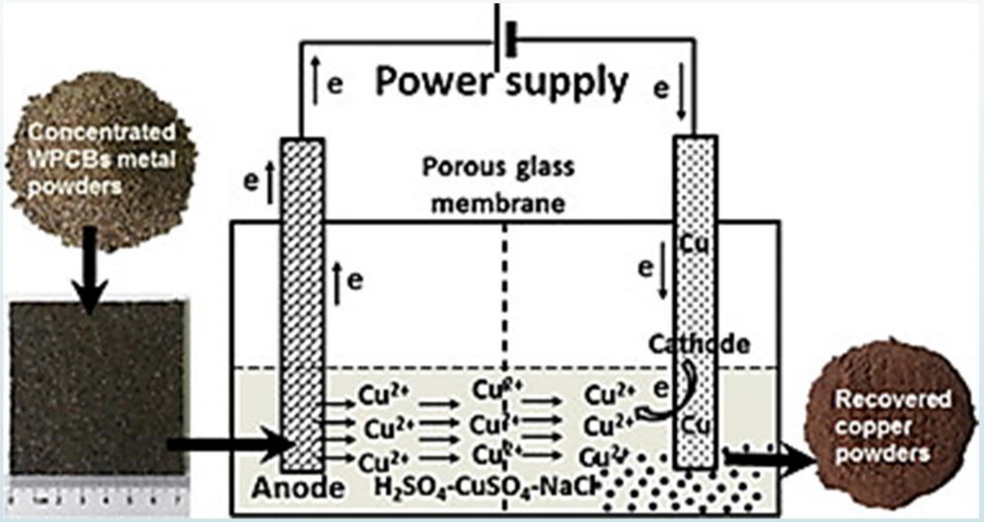
Electrochemical reduction

- For metal ion removal
- Metal ions in the solution are reduced to elemental form at cathode
- Suitable only for higher pollutant concentrations and as a pre-treatment method before other methods

- Electrochemical reduction is used in metal production (electrolysis)
- Electrorefining: metal ions dissolve from the anode and deposit on the cathode
- Electrowinning: dissolved metals deposit on the cathode



Electroleaching + reduction (electrolysis)

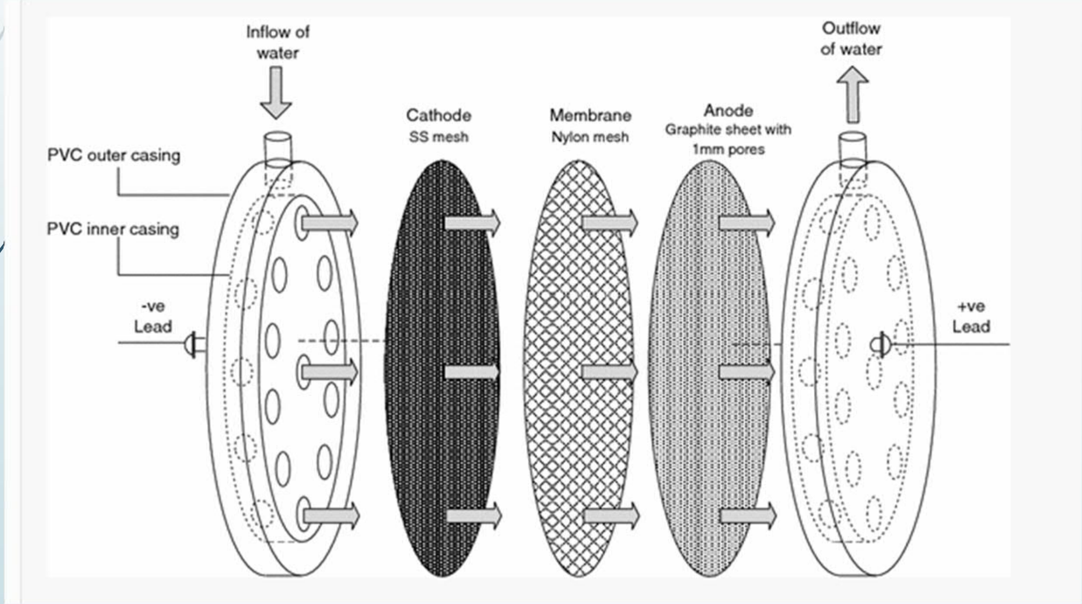


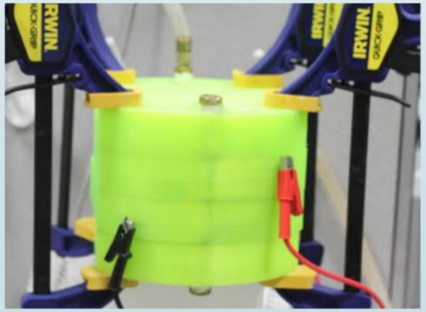
Leaching from the raw material and recovery in a single cell

Chu, Y., Chen, M., Chen, S., Wang, B., Fu, K., & Chen, H. (2015). Micro-copper powders recovered from waste printed circuit boards by electrolysis. Hydrometallurgy, 156, 152-157.

Perforated electrode flow through cell: PEFT

- To improve the efficiency and reduce the cost of chlorine electrogeneration
- NaCl used as electrolyte
- Used especially for disinfection of water



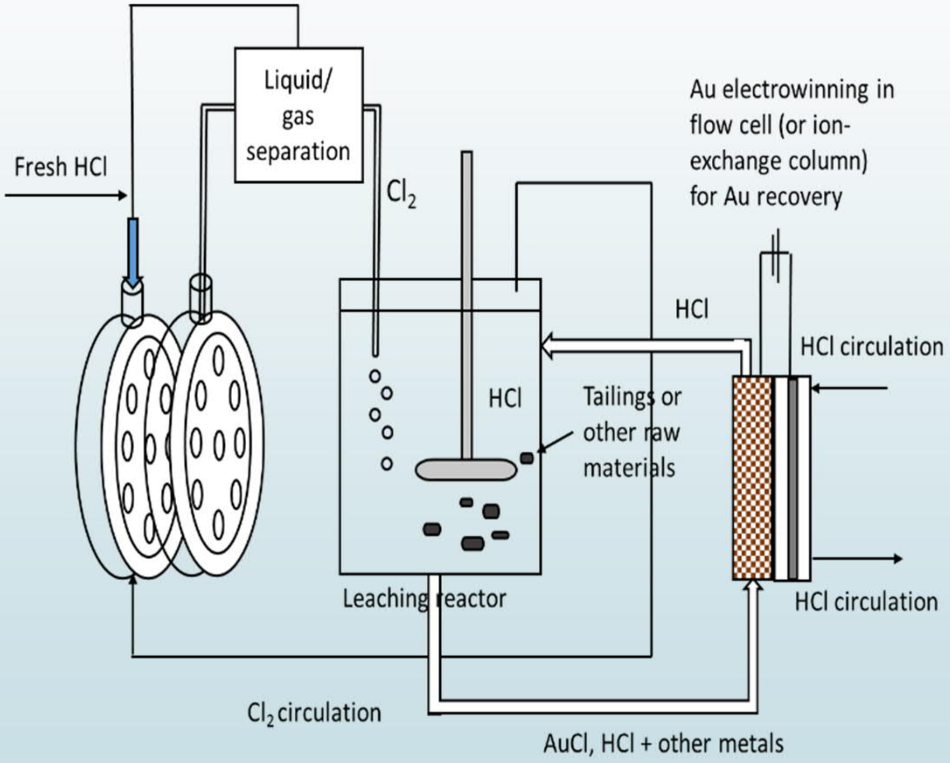


Nath, H., Wang, X., Torrens, R., & Langdon, A. (2011). A novel perforated electrode flow through cell design for chlorine generation. Journal of Applied Electrochemistry, 41(4), 389-395.

Hettiarachchi, J. (2017). Treating Water Using a Perforated Electrode Flow Through Cell (Doctoral dissertation, University of Waikato).

Gold recovery by electrogenerated chlorine

- New electrochemical reactor designs for gold recovery
- Additive manufacturing (AM, 3D-printing) utilized in the fabrication of electrodes
- Electro-efficiency of the recovery systems maximized
- Main result is an environmentally friendly closed-loop gold recovery system



Electro-Fenton

- Hydrogen peroxide H_2O_2 is a weak oxidant alone in treating effluents
- To improve this, H_2O_2 is commonly activated in acidic effluents with Fe^{2+} (ferrous) ion as catalyst (Fenton´s reagent) to give homogenous hydroxyl radicals as strong oxidant of organics

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$

- In Electro-Fenton, H_2O_2 is directly electrogenerated at the cathode of the cell from O_2 gas reduction as follows:

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (E^0 = 0{,}68 \text{ V vs. SHE})$$

Electro-Fenton

Main advantages of Electro-Fenton method:

- The on-site production of H_2O_2 avoids its dangerous transport and storage
- Higher degradation rate of organic pollutants than in traditional Fenton method because of the continuous regeneration of the Fe^{2+} at the cathode

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+$$

- The feasibility of overall mineralization with relative low cost if operational parameters are optimized

Photoelectro-Fenton

- Simultaneous use of electro generated H_2O_2 in the presence of Fe^{2+} (EF conditions) and UV illumination of the solution

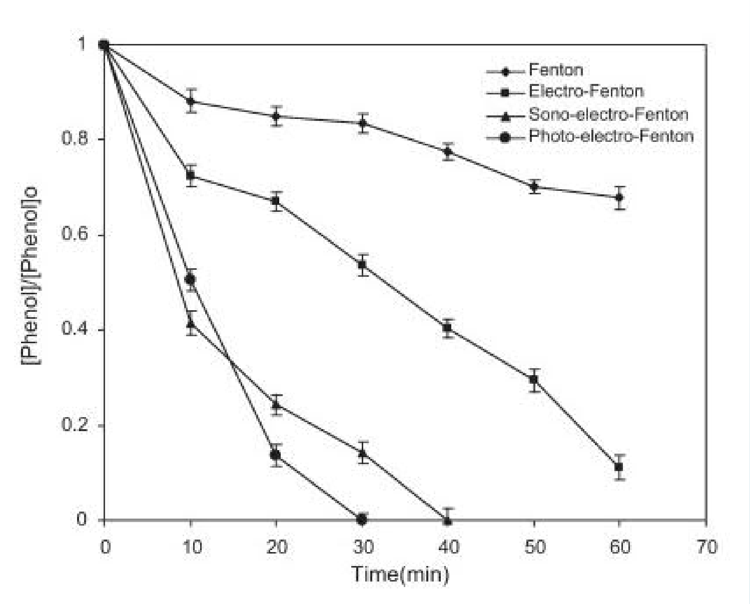
$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \bullet OH$

$H_2O_2 + hv \rightarrow 2\ \bullet OH$

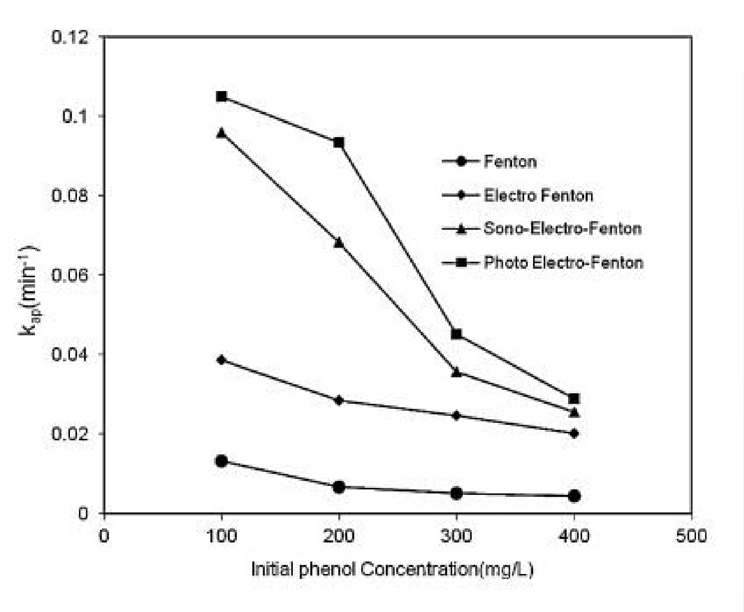
Sonoelectro-Fenton

- Ultrasound accelerates the regeneration of ferrous ions and enhances the radical formation further

Examples



Phenol degradation as a function of time

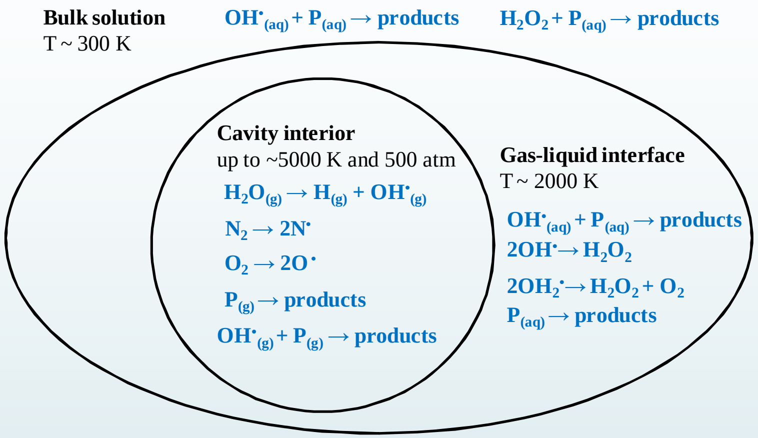


Phenol degradation constants as function of initial concentration

Babuponnusami, A., & Muthukumar, K. (2012). Advanced oxidation of phenol: a comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes. Chemical Engineering Journal, 183, 1-9.

Sonoelectrocatalysis

Ultrasound treatment is energy intensive and therefore expensive alone



Bulk solution
T ~ 300 K

$OH^{\bullet}_{(aq)} + P_{(aq)} \rightarrow$ products

$H_2O_2 + P_{(aq)} \rightarrow$ products

Cavity interior
up to ~5000 K and 500 atm

$H_2O_{(g)} \rightarrow H_{(g)} + OH^{\bullet}_{(g)}$

$N_2 \rightarrow 2N^{\bullet}$

$O_2 \rightarrow 2O^{\bullet}$

$P_{(g)} \rightarrow$ products

$OH^{\bullet}_{(g)} + P_{(g)} \rightarrow$ products

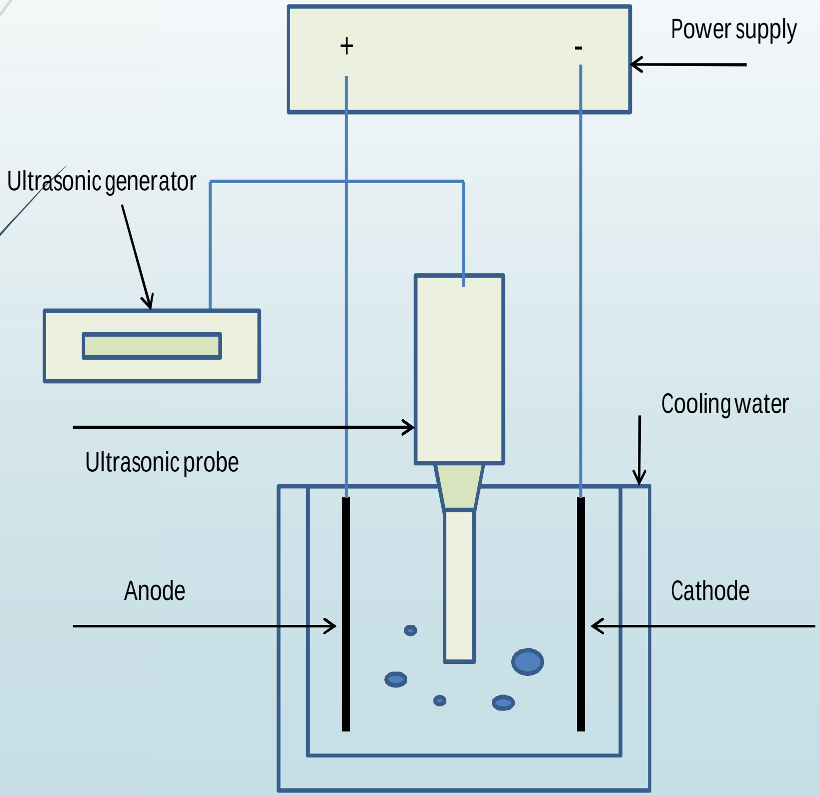
Gas-liquid interface
T ~ 2000 K

$OH^{\bullet}_{(aq)} + P_{(aq)} \rightarrow$ products

$2OH^{\bullet} \rightarrow H_2O_2$

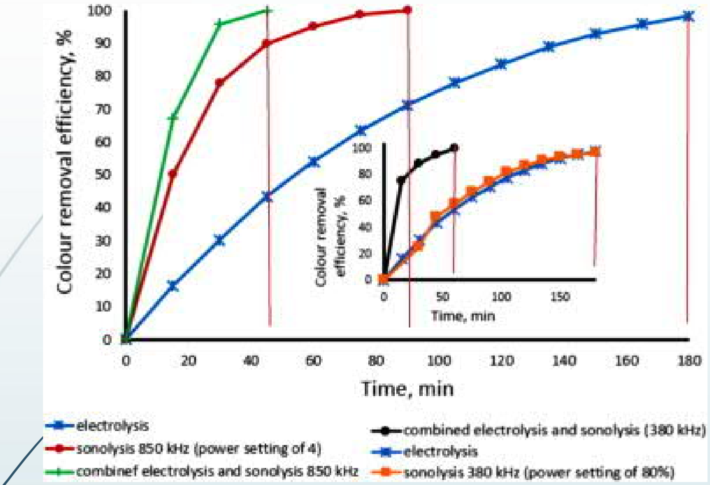
$2OH_2^{\bullet} \rightarrow H_2O_2 + O_2$

$P_{(aq)} \rightarrow$ products

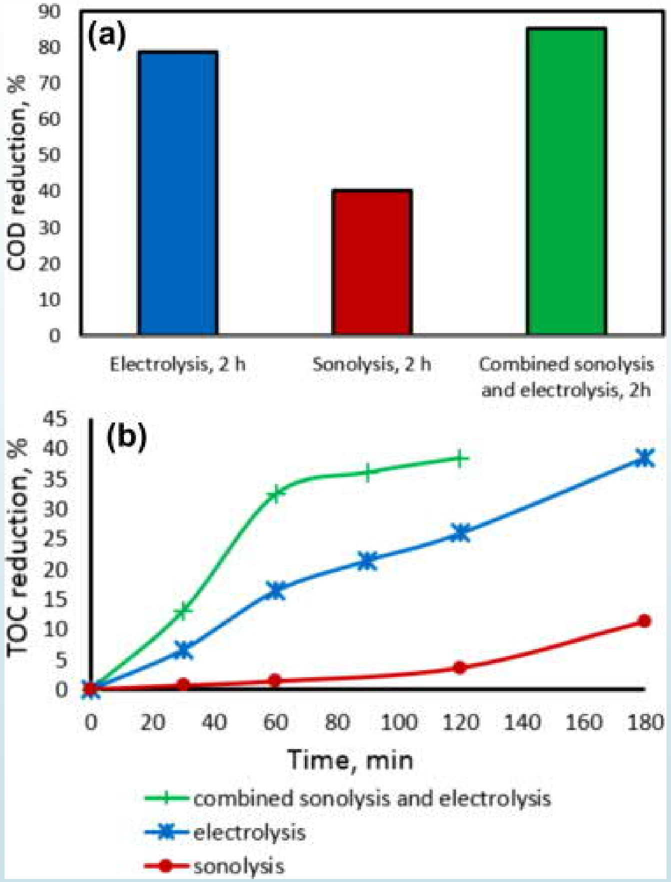


- Ultrasound keeps the electrode surface clean and enhances mass transport
- Suitable for dirty “dark” wastewaters

Shestakova, M., Vinatoru, M., Mason, T. J., & Sillanpää, M. (2014). Sonoelectrocatalytic decomposition of methylene blue using Ti/Ta2O5-SnO2 electrodes. Ultrasonics sonochemistry.

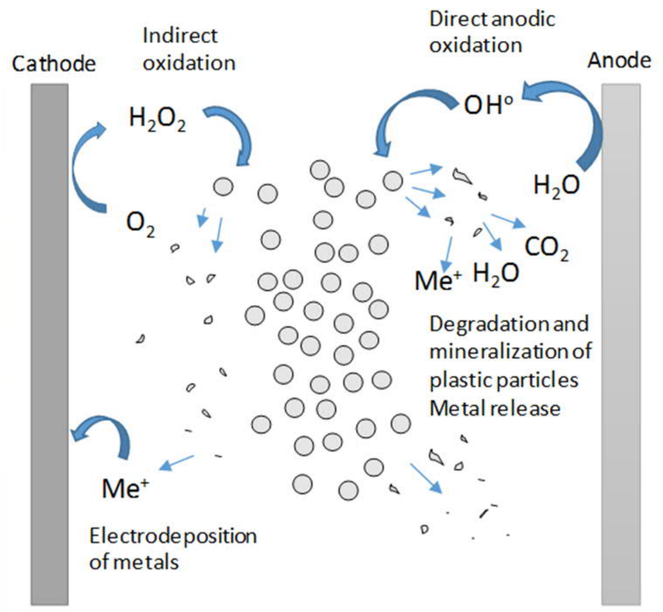


Comparison of sonolysis, electrolysis and combined sonolysis processes and electrolysis on the decolourisation of MB solution.



COD (a) and TOC (b) reduction during electrolysis sonolysis and combined electrolysis and sonolysis, i = 20 mA, frequency: 850 kHz; power setting 4.

Degradation of microplastics/oily wastewater with ultrasound enhanced electro-oxidation



$H_2O \rightarrow OH^o + H^+ + e^-$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

OH^o + MP → organic intermediates + metals

H_2O_2 + MP → organic intermediates + metals

OH^o + organic intermediates → $CO_2 + H_2O$

$Me^{n+} + ne^- \rightarrow Me(s)$ (electrodeposition)

Enhancement by ultrasound:

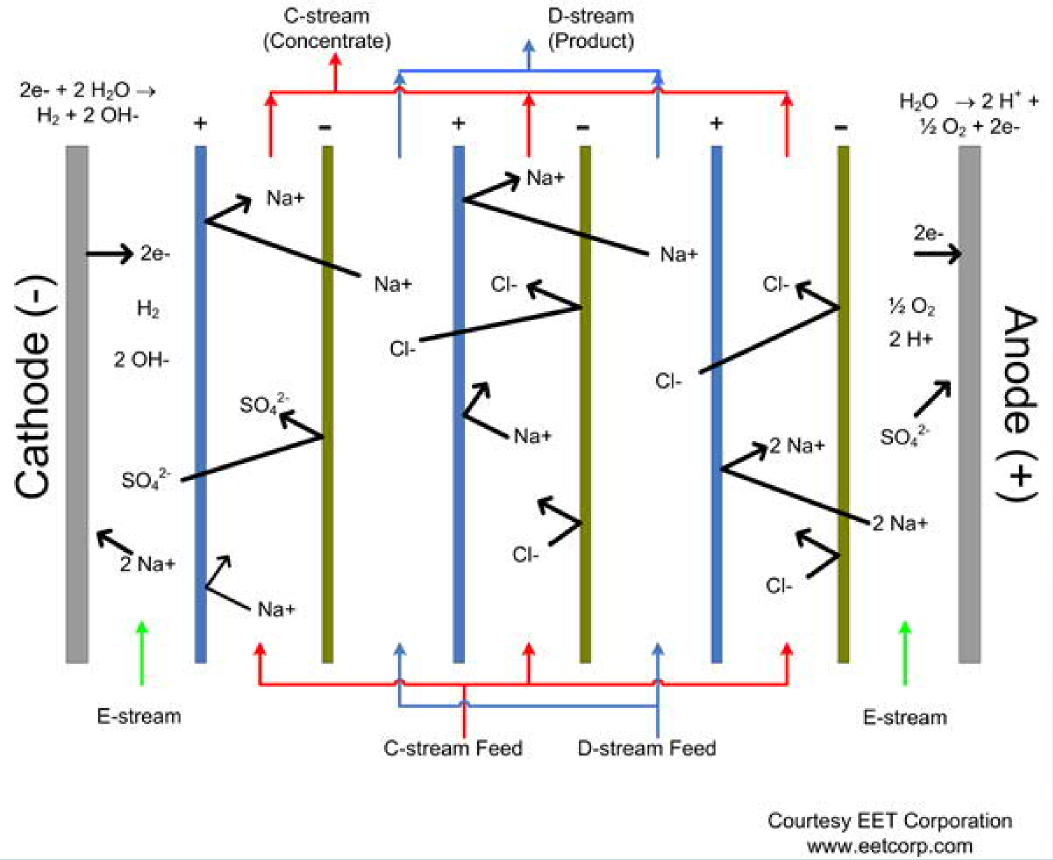
O_2 + (((→ $2O^o$

$O^o + H_2O \rightarrow 2\ OH^o$ + other strong oxidants

+ side reactions

Electrodialysis

- Membrane process driven by a difference in electrical potential over a membrane stack
- Membranes are cation or anion selective
- Cationic and anionic membranes are placed in a row allowing the purification of the wastewater



Courtesy EET Corporation
www.eetcorp.com

https://commons.wikimedia.org/wiki/File:Electrodialysis.jpg, cc-license

Electrodialysis

Advantages

- Mature and reliable technology: desalination or concentration of electrolyte solutions
- Can be used for concentration of metals from the diluted solutions

Cost efficient in water desalination in a certain range of feed water salinity and product water quality.

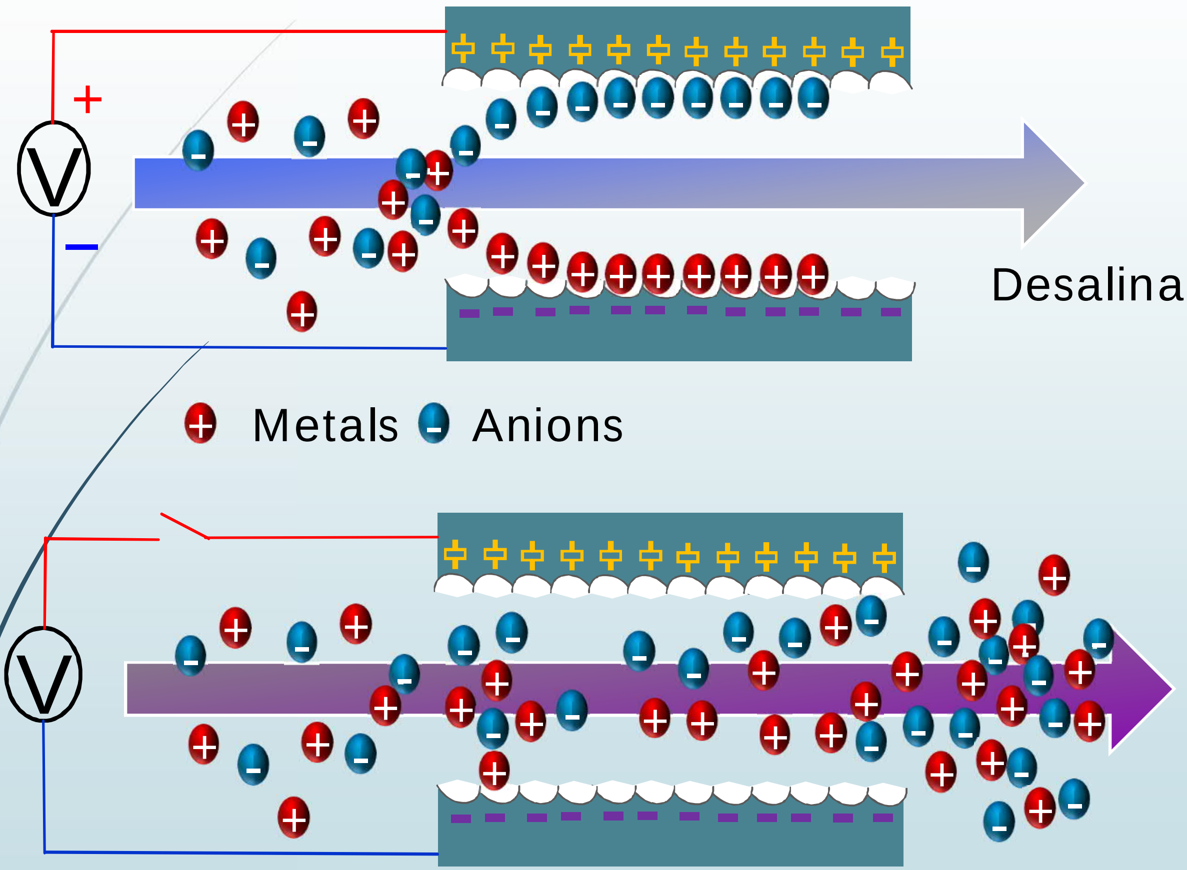
Disadvantages

- High cost of electrodes and ion exchange membranes
- Relatively short life time of membranes when working in high-density electrical field
- Organic matter, colloids and silicon dioxide are not removed by ED system
- Influent water pre-treatment is necessary to prevent fouling (depends on the composition)
- Selection of materials of construction for membranes and stack is important to ensure compatibility with the feed stream

Strathmann, H. (2010). Electrodialysis, a mature technology with a multitude of new applications. Desalination, 264(3), 268-288.

Xu, T., & Huang, C. (2008). Electrodialysis-based separation technologies: A critical review. AIChE journal, 54(12), 3147-3159.

Capacitive deionization (electrosorption)



Deionization occurs by applying a voltage over two porous carbon electrodes

After the electrodes are saturated he potential difference between electrodes is reversed when ions leave the electrode pores and can be flushed out of the CDI cell

Capacitive deionization

- Solar energy can be applied
- Novel three-dimensional electrodes: activated carbon, graphene, biocarbon, carbon aerogels, composites/coatings
- Flow-trough reactors: entire electrode area contributes, faster, lower energy cost, higher capacity

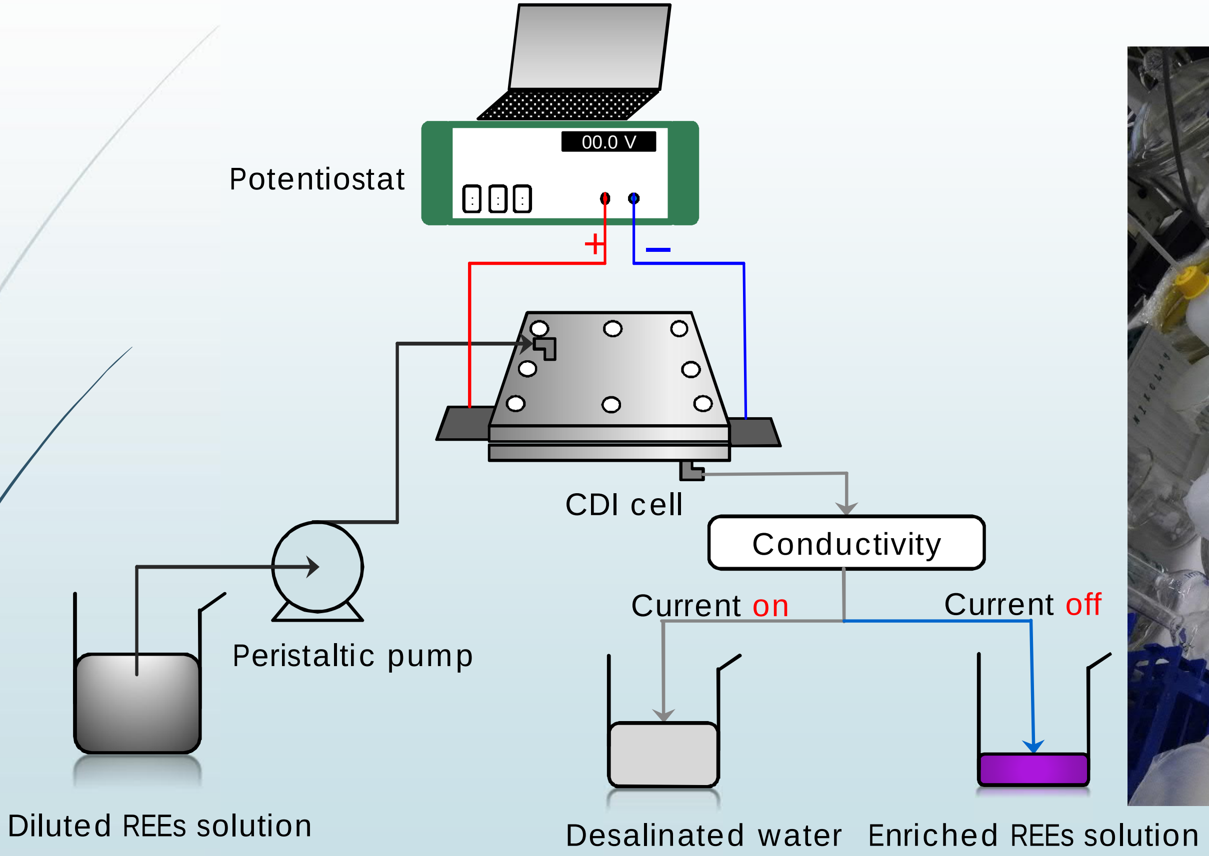
Desalination comparison

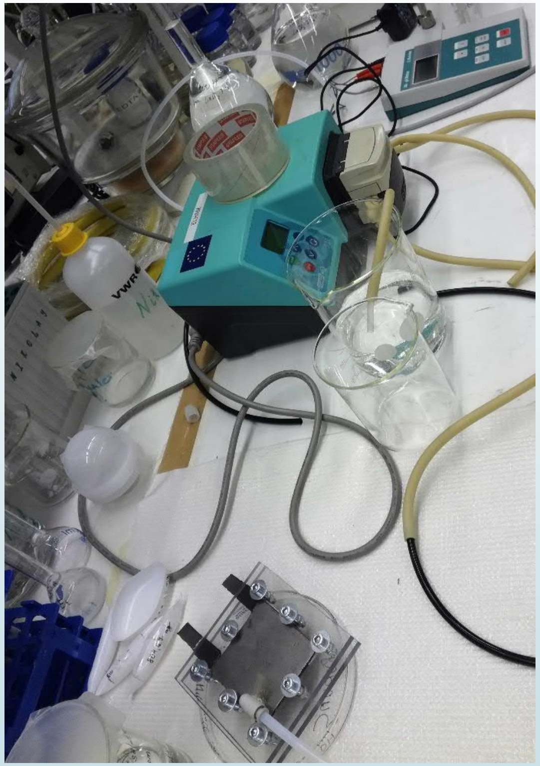
Reverse osmosis drawbacks	CDI advantages
Requires high pressure	Can be operated gravity fed
Efficiency drops with size	Size-independent efficiency
Fragile polymer membranes	Robust carbon electrodes
Method limits recovery	Solubility limits recovery

CDI investment cost 1/3 of that of RO!

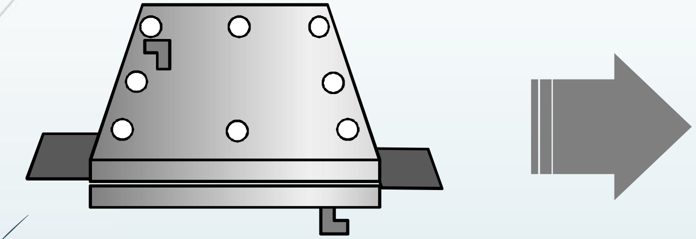
https://www.youtube.com/watch?v=PstkfJoIBUU

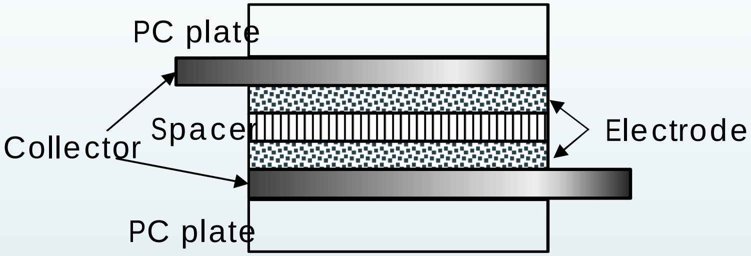
LUT CDI system for REEs recovery

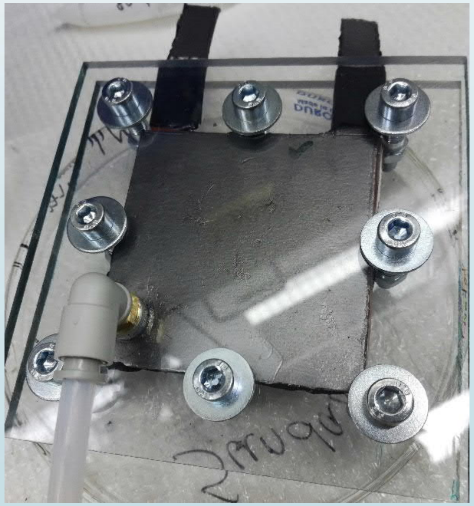


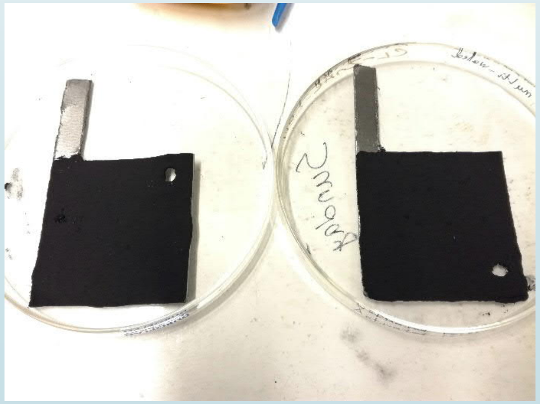


Capacitive Deionization cell

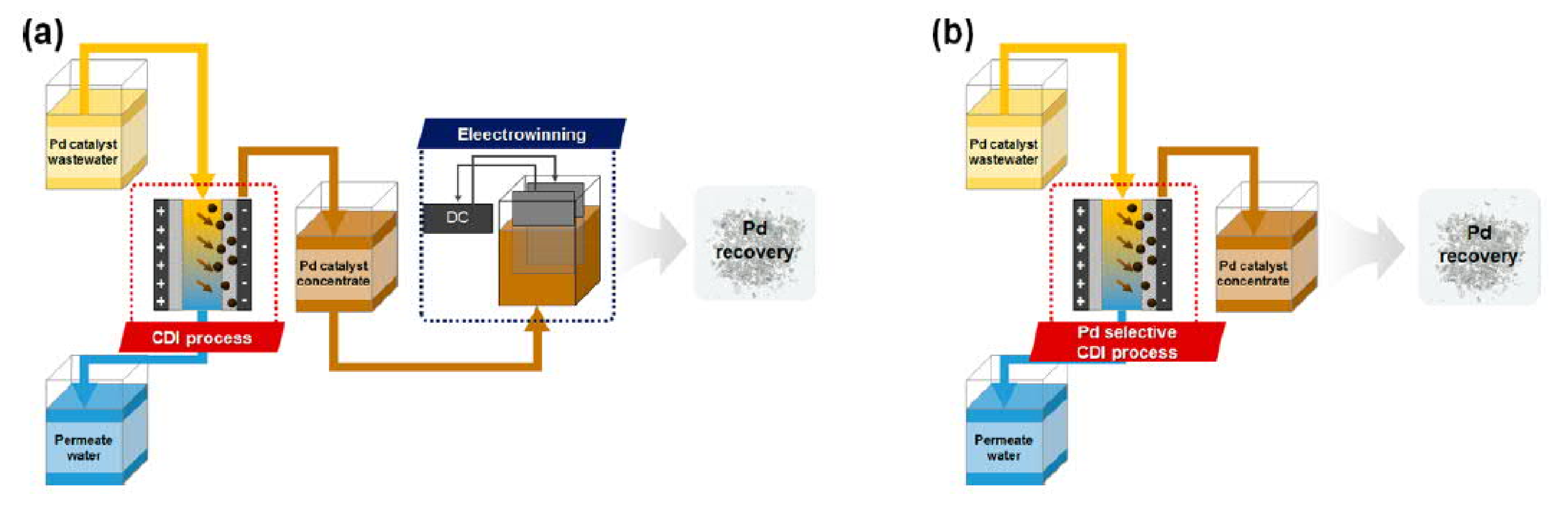






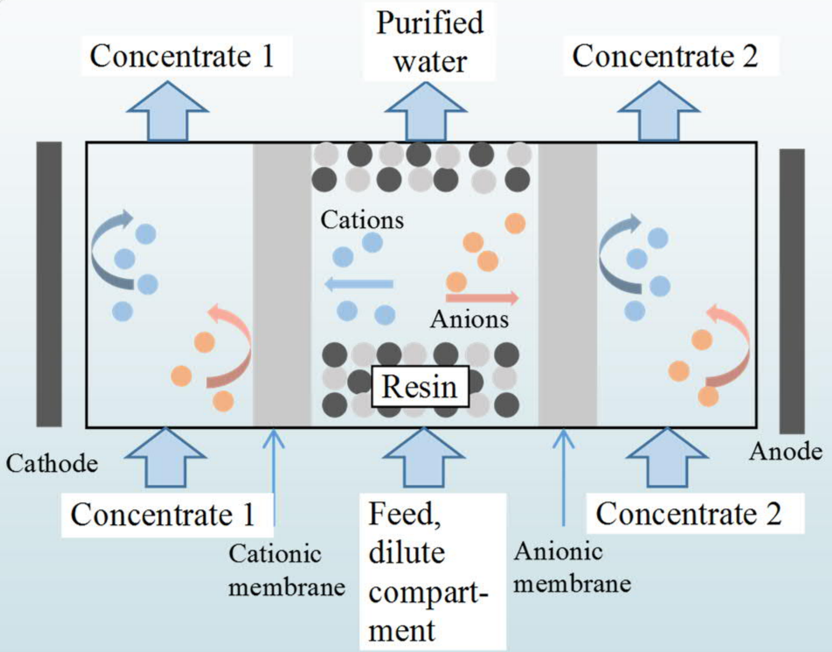


Capacitive deionization – Pd recovery



Kim, D., Gwak, G., Dorji, P., He, D., Phuntsho, S., Hong, S., & Shon, H. (2017). Palladium recovery through membrane capacitive deionization (MCDI) from metal plating wastewater. ACS Sustainable Chemistry & Engineering.

Electrodeionization

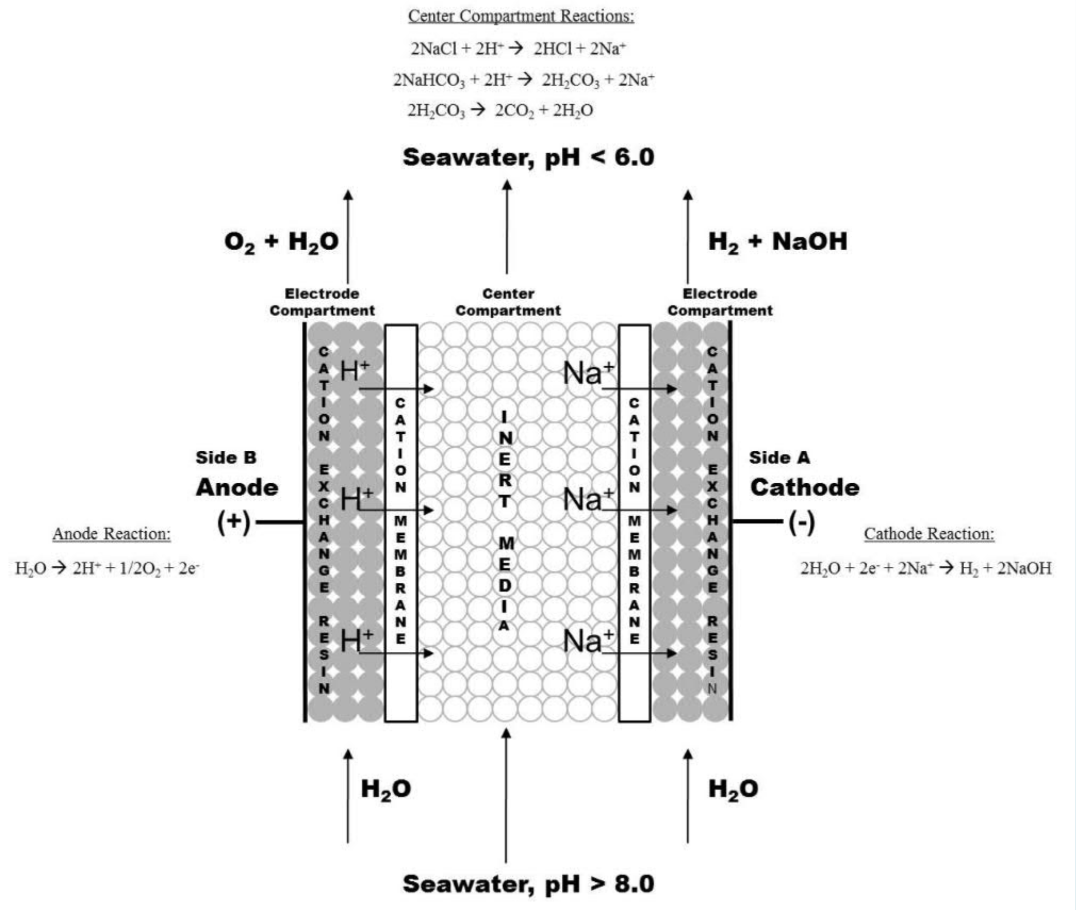


- Anions and cations can be separated
- Can be used for the recovery of valuable elements
- Can be applied without membranes as well
- Ion-exchange resin is regenerated continuously

Arar, Ö., Yüksel, Ü., Kabay, N., & Yüksel, M. (2014). Various applications of electrodeionization (EDI) method for water treatment—A short review. Desalination, 342, 16-22.

Electrodeionization - CO_2 extraction from seawater

- Total CO_2 concentration of the world's oceans is about 100 mg/L
- 2–3% of this in the form of a dissolved gas, 97–98% is as bicarbonate and carbonate
- Indirect removal of CO_2 from atmosphere (treated seawater can absorb from the air)



Center Compartment Reactions:

$2NaCl + 2H^+ \rightarrow 2HCl + 2Na^+$

$2NaHCO_3 + 2H^+ \rightarrow 2H_2CO_3 + 2Na^+$

$2H_2CO_3 \rightarrow 2CO_2 + 2H_2O$

Anode Reaction:

$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^-$

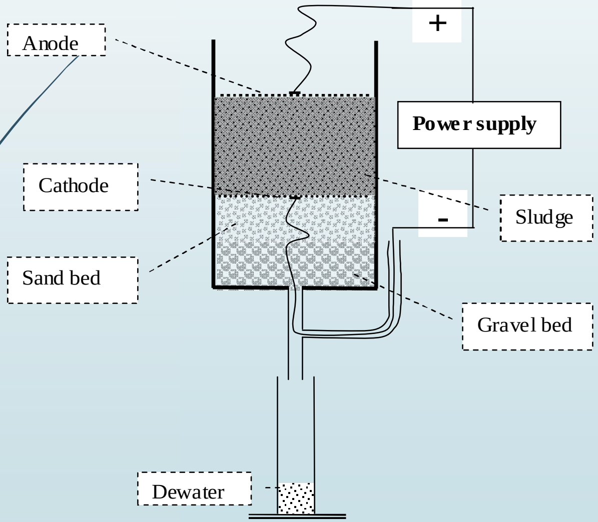
Cathode Reaction:

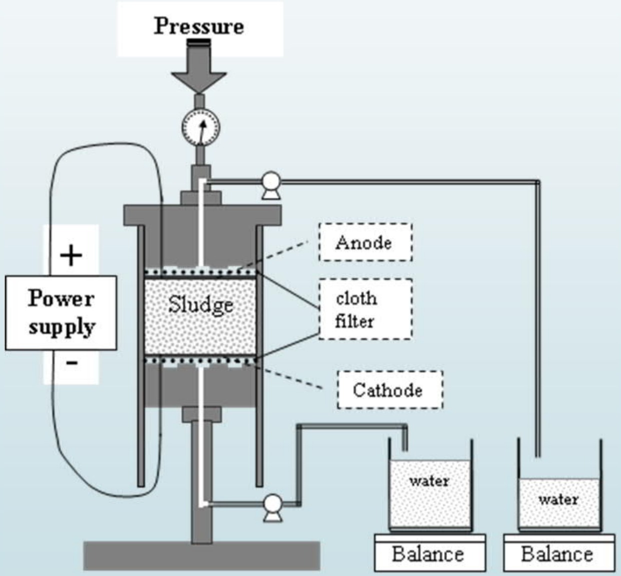
$2H_2O + 2e^- + 2Na^+ \rightarrow H_2 + 2NaOH$

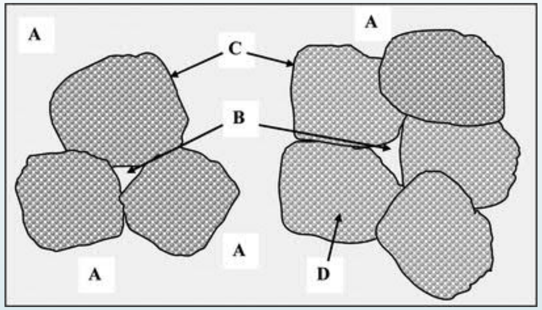
Willauer, H. D., et al. (2014). Feasibility of CO2 extraction from seawater and simultaneous hydrogen gas generation using a novel and robust electrolytic cation exchange module based on continuous electrodeionization technology. Industrial & Engineering Chemistry Research, 53(31), 12192-12200.

Sludge treatment: dewatering

- Conventional mechanical techniques such as centrifuge, vacuum, and belt pressure filter are only removing free water and interstitial water → electrochemical treatment enhances the removal of interstitial water and removes surface water as well







A: free water
B: interstitial water
C: surface water
D: intercellular water

Schematic representation of the laboratory scale electro-dewatering reactors

Tuan, P. A., et al.(2012). Sewage sludge electro-dewatering treatment—A review. Drying Technology, 30(7), 691-706.

Summary

- Electrochemical methods are generally cost-efficient and environmentally benign purification processes (less chemicals needed)
- Enhancement of the methods are often related to the material development (novel electrodes)
- Optimization of the treatment is highly important and especially pH effects significantly on the most of the processes
- Especially desalination could become much cheaper in the future by utilizing electrochemical methods

- New book: Electrochemical Water Treatment Methods, 1st Edition, Fundamentals, Methods and Full Scale Applications, Authors: Mika Sillanpää Marina Shestakova

  https://www.elsevier.com/books/electrochemical-water-treatment-methods/sillanpaa/978-0-12-811462-9

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