

Dr. Ljiljana Rajic

ELECTROCHEMICAL PROCESSES FOR WATER TREATMENT: ELECTROREDUCTION AND ELECTROSORPTION

Focus of today's lecture

- Electroreduction and indirect oxidation processes, and their use for groundwater treatment
- Electrosorption: Salts removal for water desalination (process called Capacitive Deionization or CDI) and organics removal

Part 1

PROCESSES DRIVEN BY FARADAIC REACTIONS AT THE CATHODE

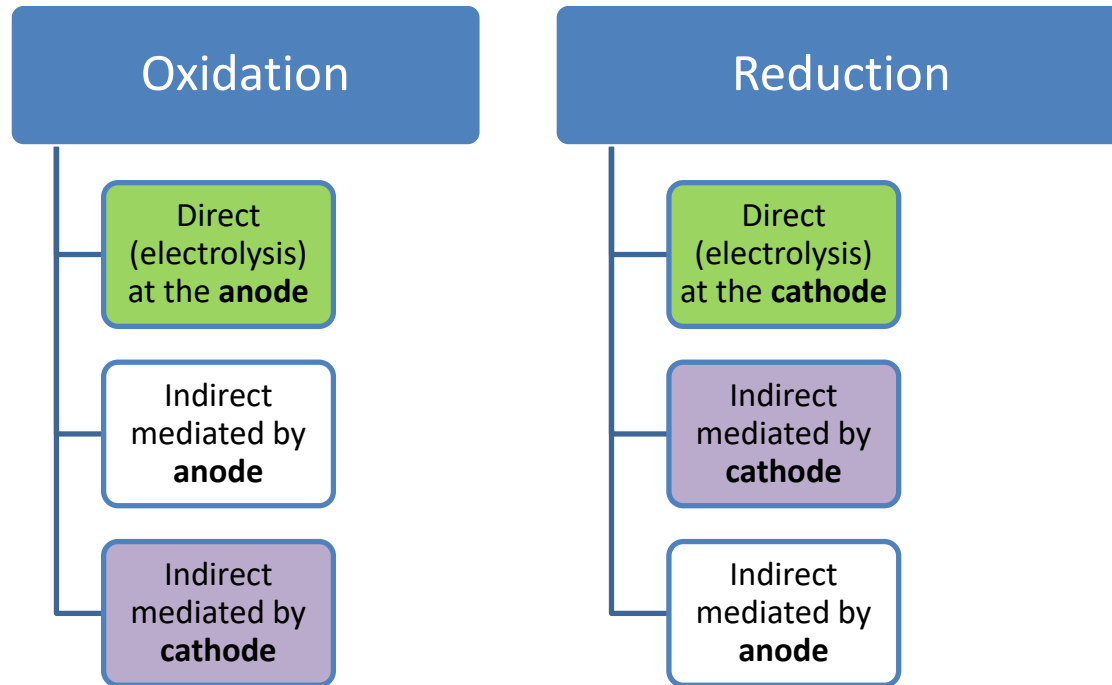
Faradaic reactions

Occur when charges (e.g., electrons) are transferred across the metal-solution interface. Electron transfer causes oxidation or reduction to occur (these are governed by Faraday Law's).

Give few examples?

When it comes to electrochemical transformation/removal of water pollutants...

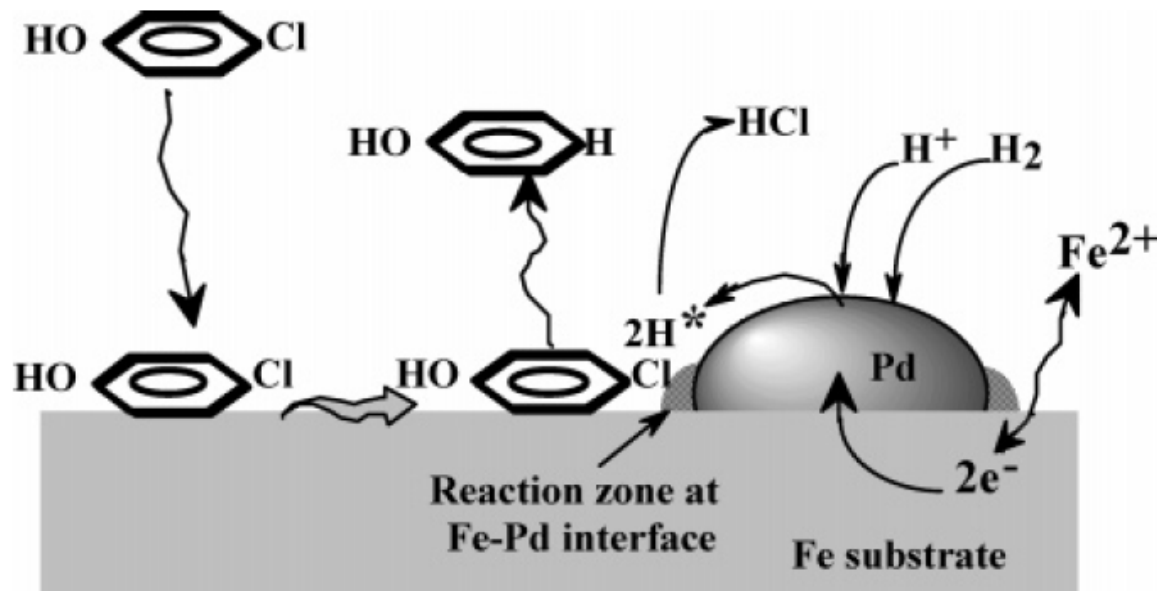
Direct and indirect degradation processes induced by Faradaic reactions



INDIRECT REDUCTION MEDIATED BY CATHODE

Hydrodechlorination or HDC

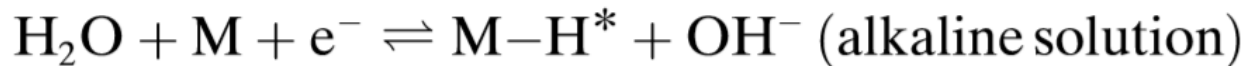
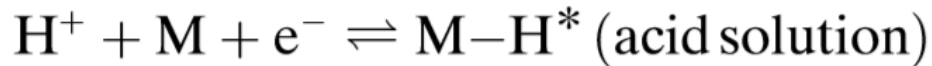
- e.g. tetrachloroethylene, trichloroethylene, chlorophenol, chlorobenzene



Hydrodechlorination or HDC

Electrochemical reduction through hydrodechlorination (HDC) occurs at the cathode due to water electrolysis (hydrogen evolution reaction or HER).

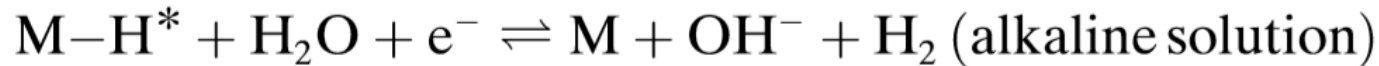
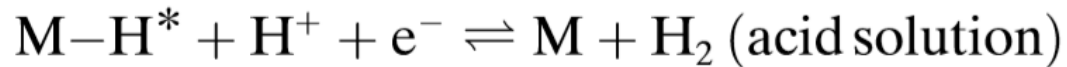
Step 1: Process starts with electrochemical hydrogen adsorption (Volmer reaction) where atomic hydrogen (H_a) is chemically adsorbed on active site of the electrode surface (M)



Hydrodechlorination or HDC

Electrochemical reduction through hydrodechlorination (HDC) occurs at the cathode due to water electrolysis.

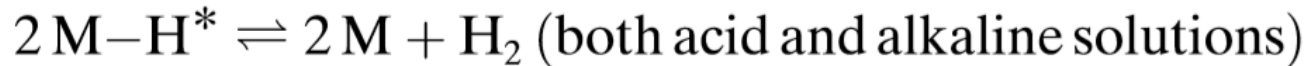
Step 2: The H_a further involves in electrochemical desorption (Heyrovsky reaction)



Hydrodechlorination or HDC

Electrochemical reduction through hydrodechlorination (HDC) occurs at the cathode due to water electrolysis.

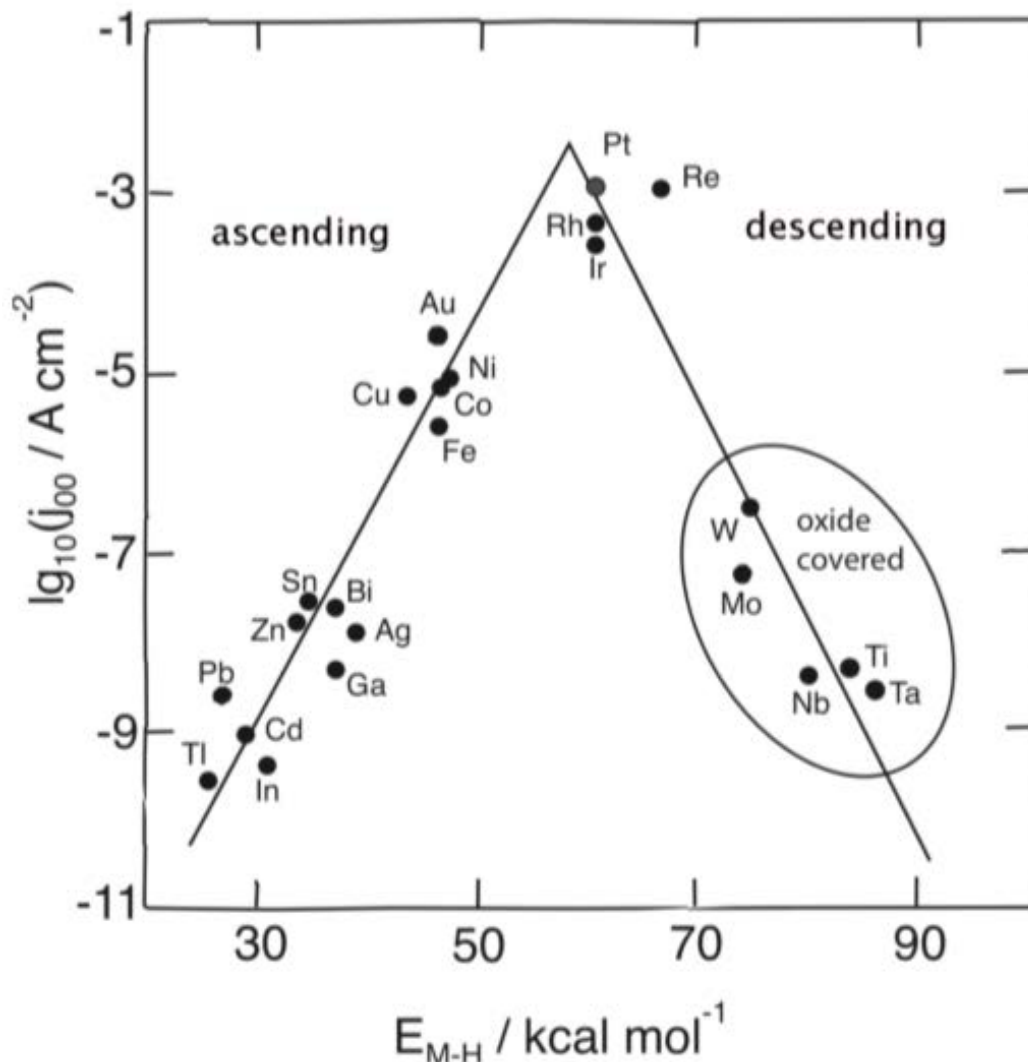
Step 2: OR chemical desorption (Tafel reaction) to create hydrogen gas or **interacts with the reducible molecules like chlorinated substances, which leads to HDC.**



Influence of cathode material

The good HDC catalyst should have strong bond with H_a to allow proton-electron transfer process but weak enough to ensure the bond breaking and the product release.

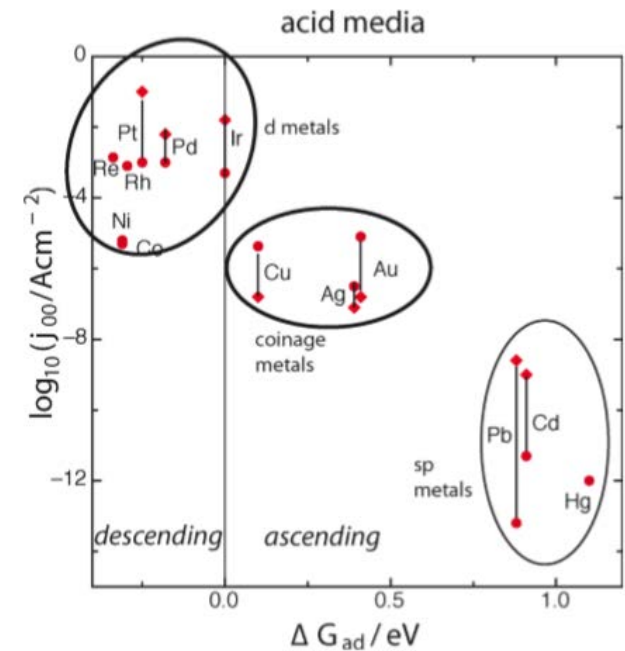
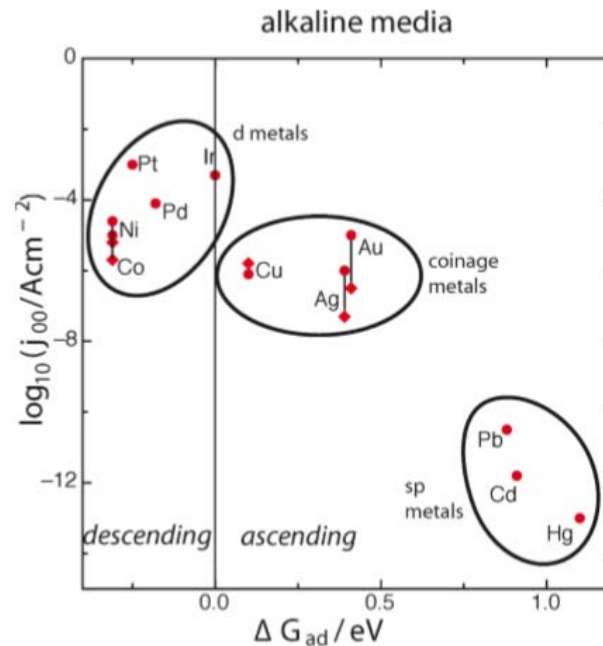
If the hydrogen-metal surface (H_a -M) binding energy is too high, adsorption is slow and limits the overall rate but if it is too low, desorption is slow.



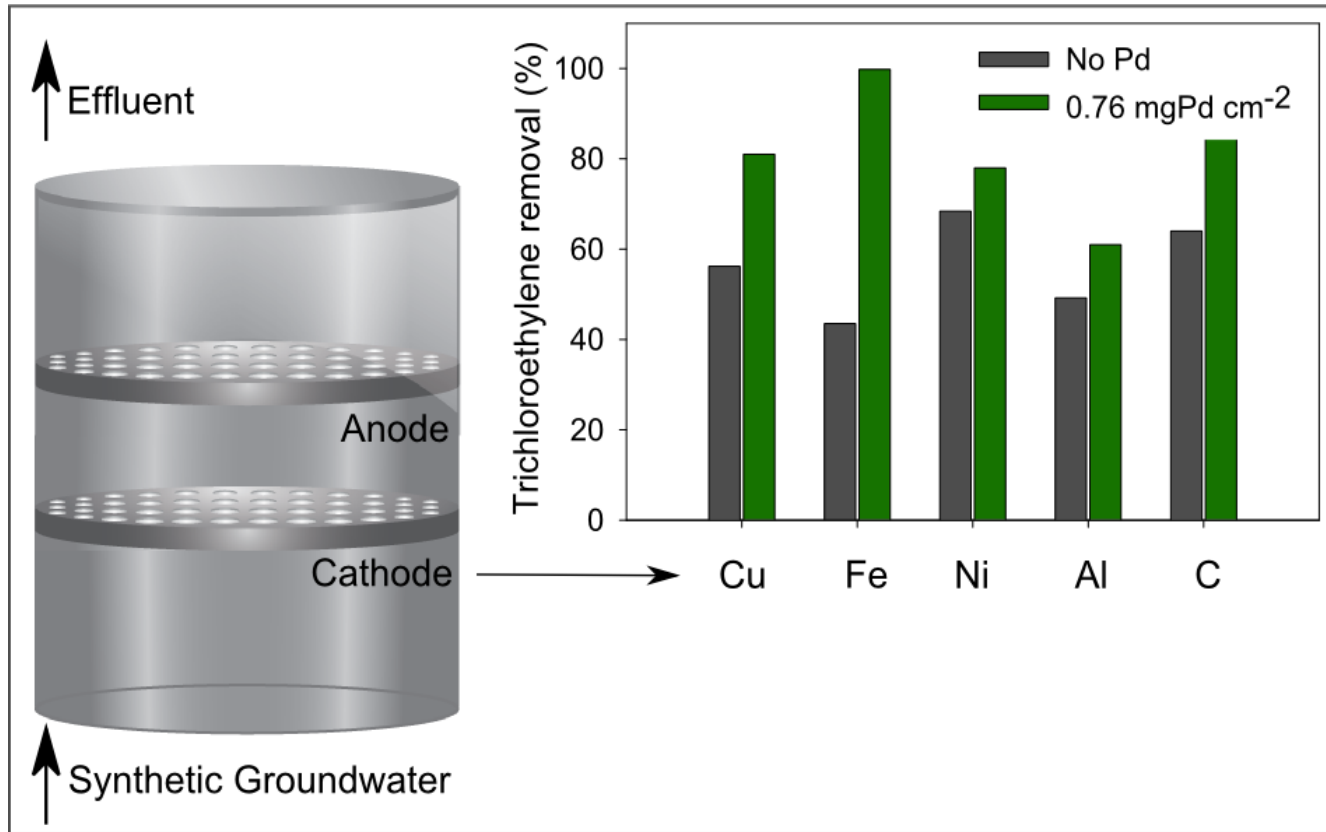
Trassati's volcano plot for the HER in acid solutions. j_{00} denotes the exchange current density, and E_{MH} the energy of hydride formation

Modern “Volcano” plots

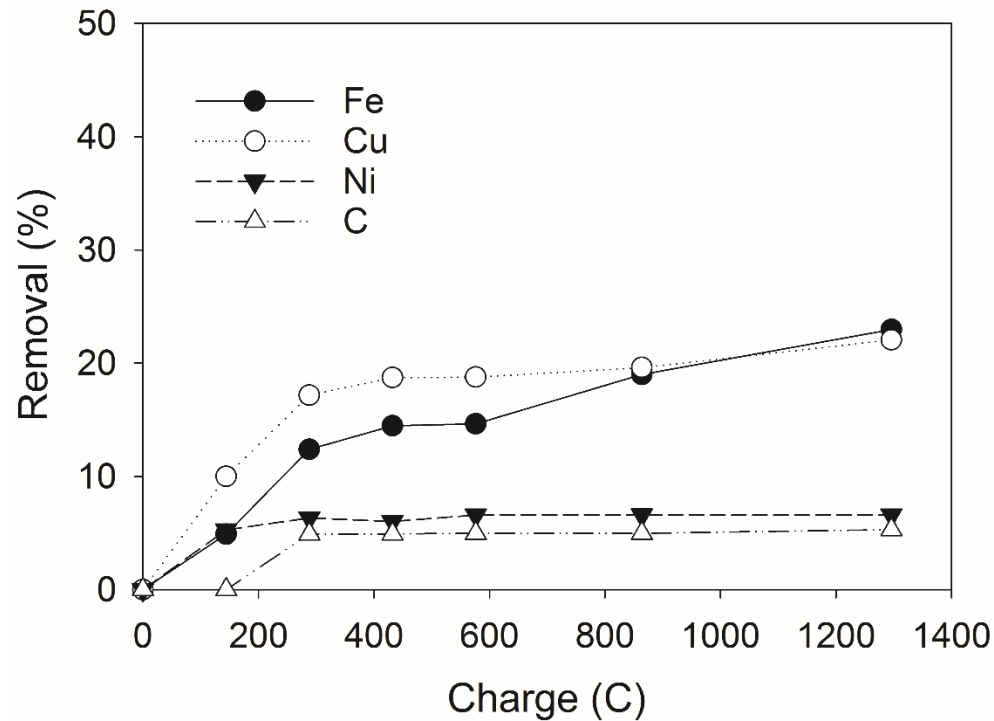
There is a clear separation into three groups: sp metals, which are the worst catalysts, coinage metals, which are intermediate, and the d metals, which contain the best catalysts, but also Ni and Co, which are mediocre.



What has major effect on HDC?

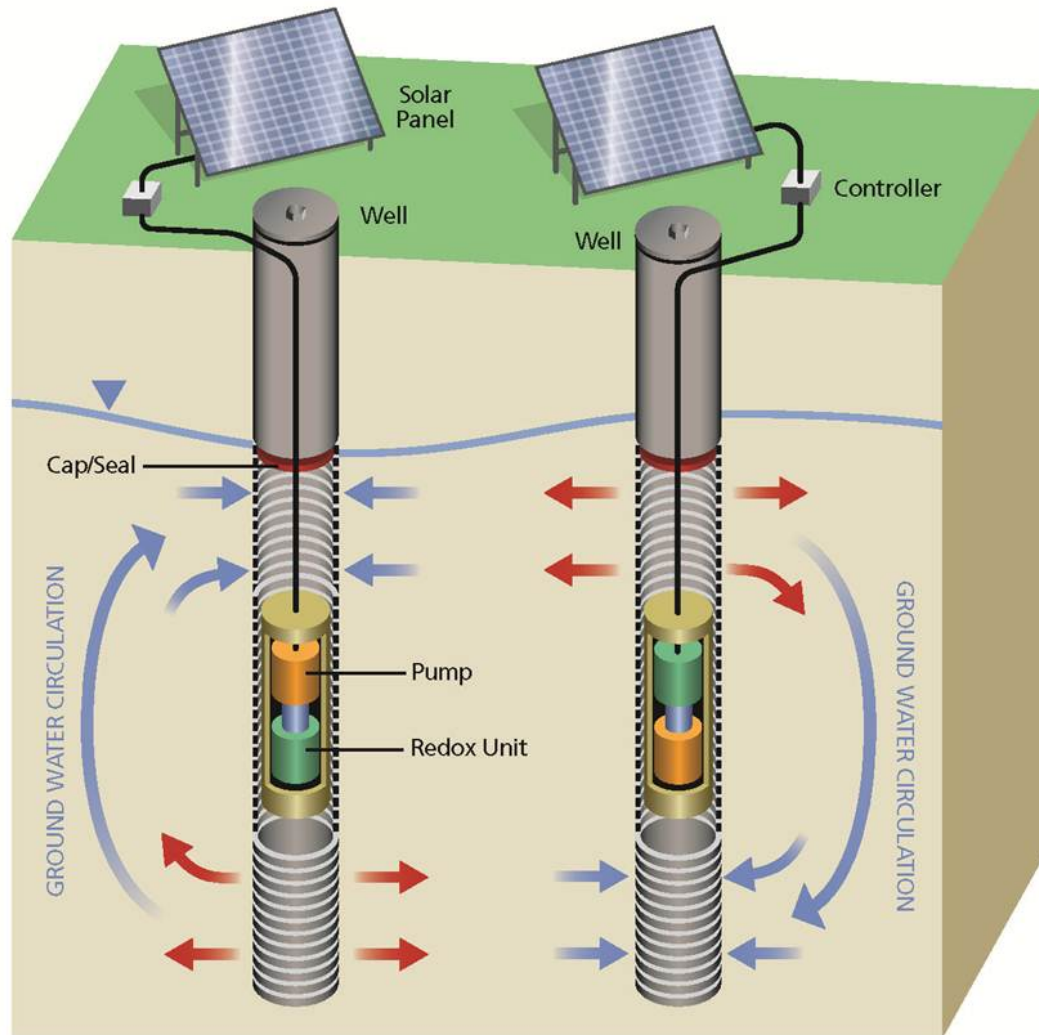


Same cathodes and process but for different contaminant removal?

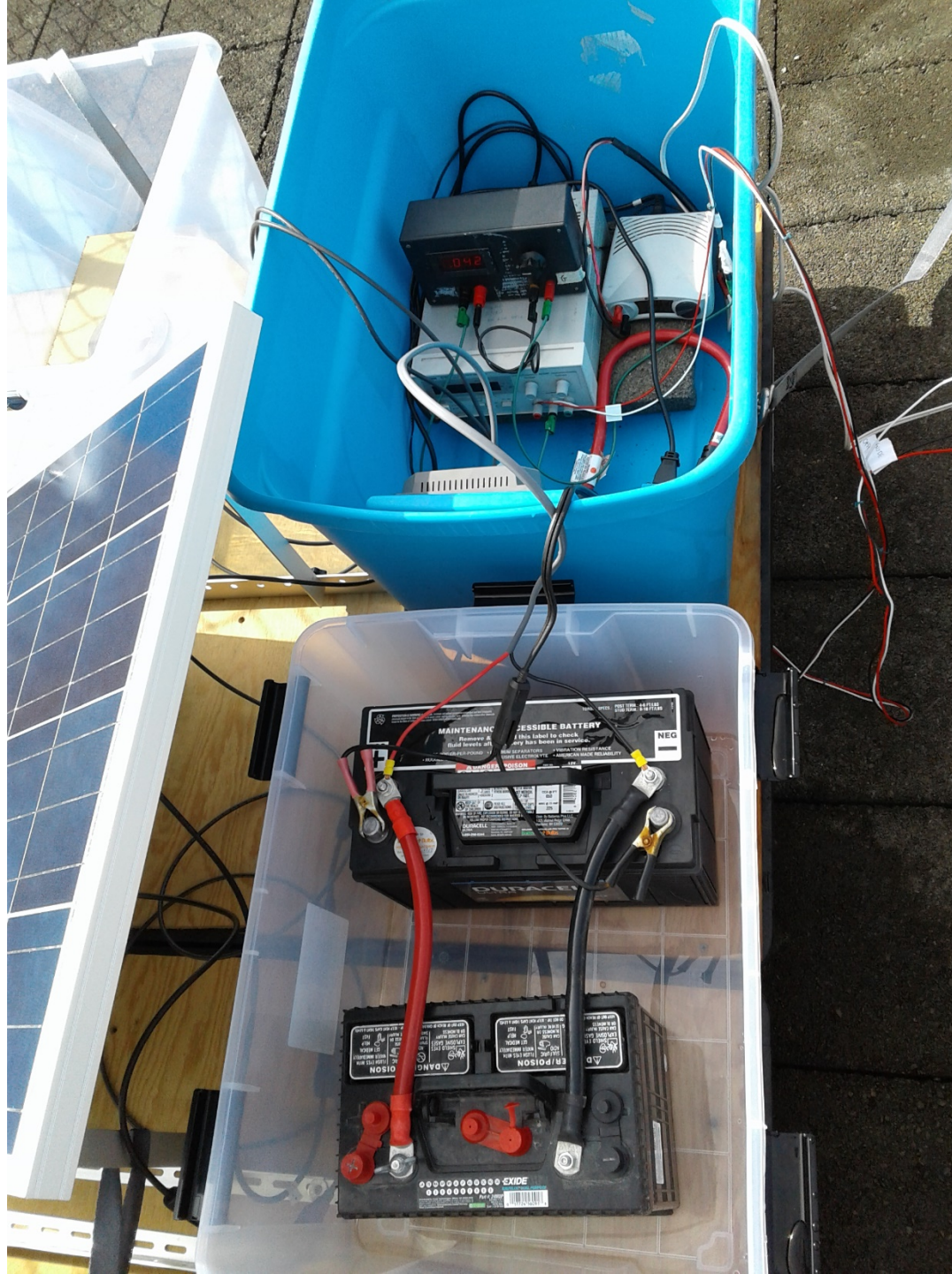


PRACTICAL APPLICATIONS

Approach 1



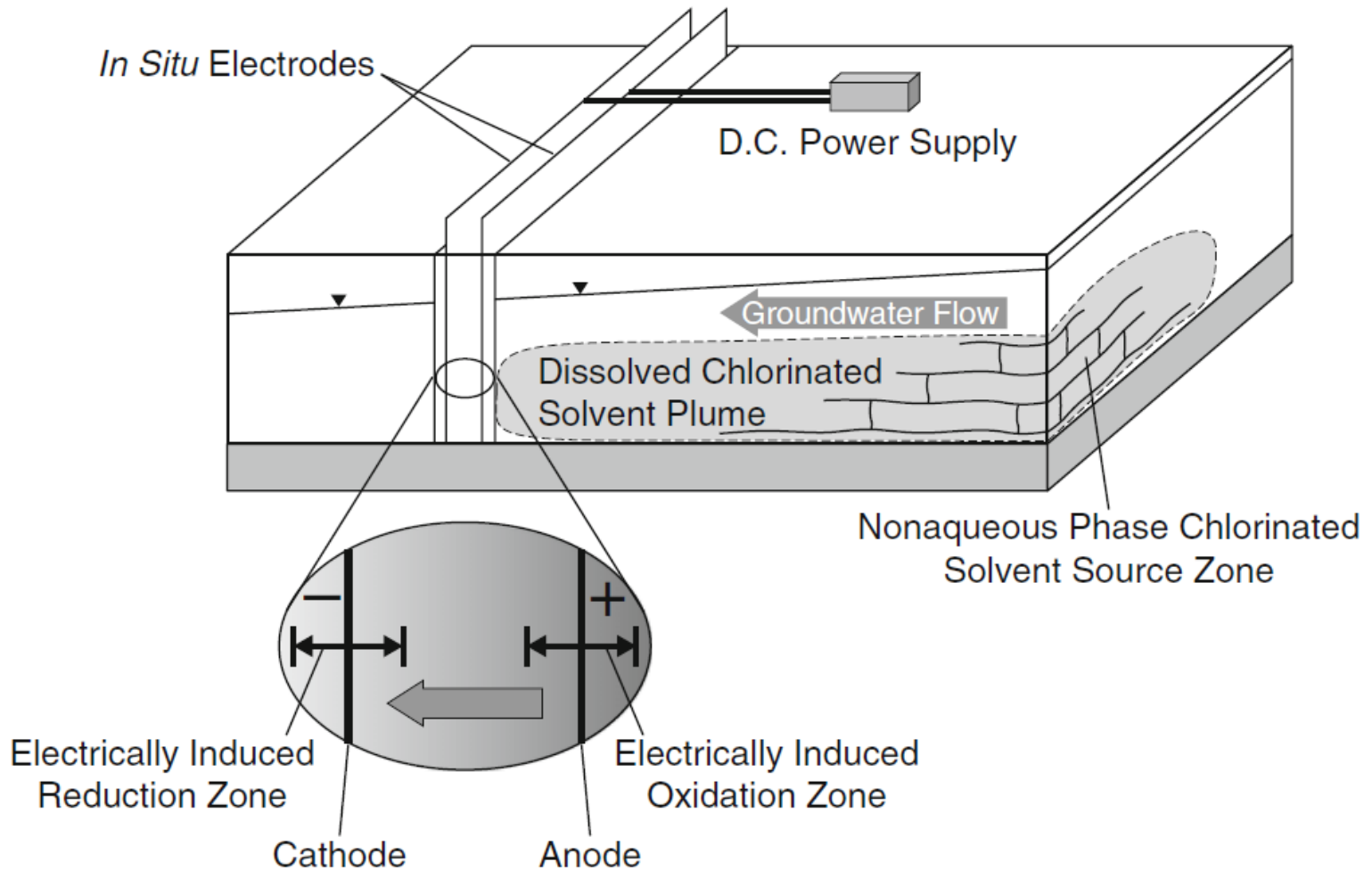






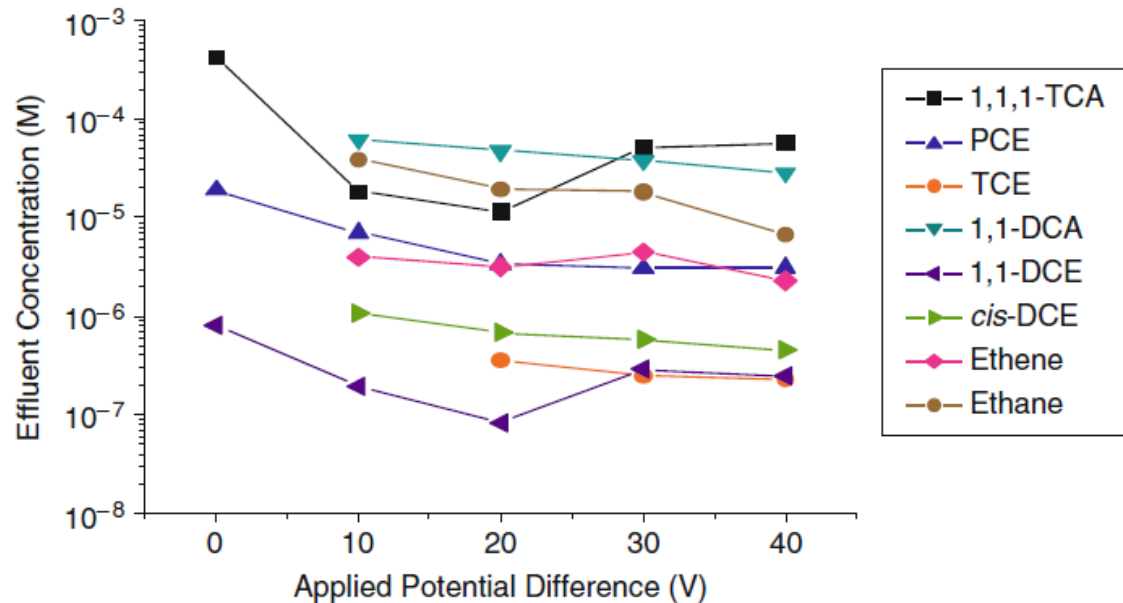
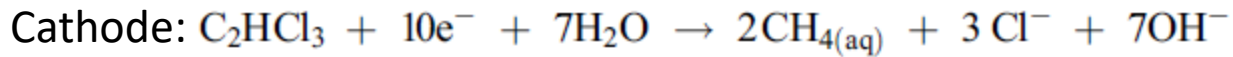
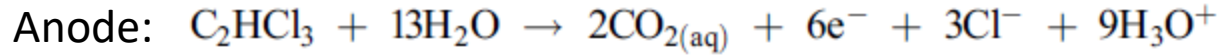


Approach 2





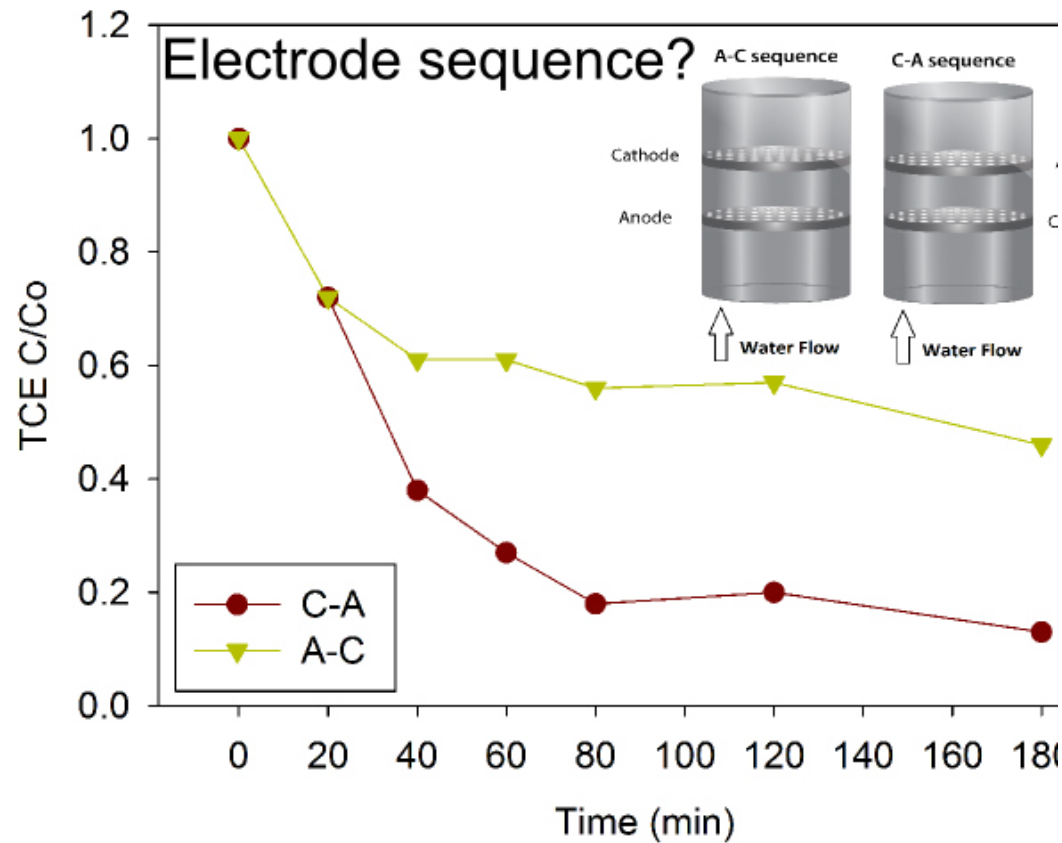
Results



Over 90% degradation of TCE can be achieved without formation of DCE or VC

Another effect on HDC?

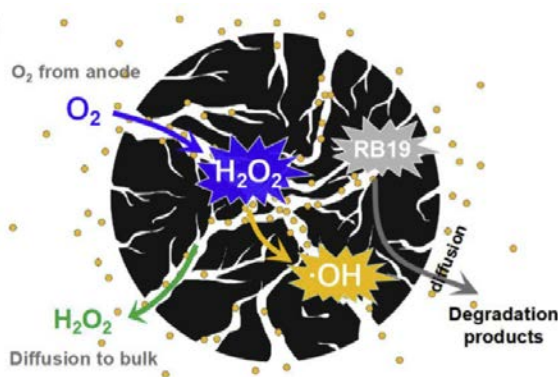
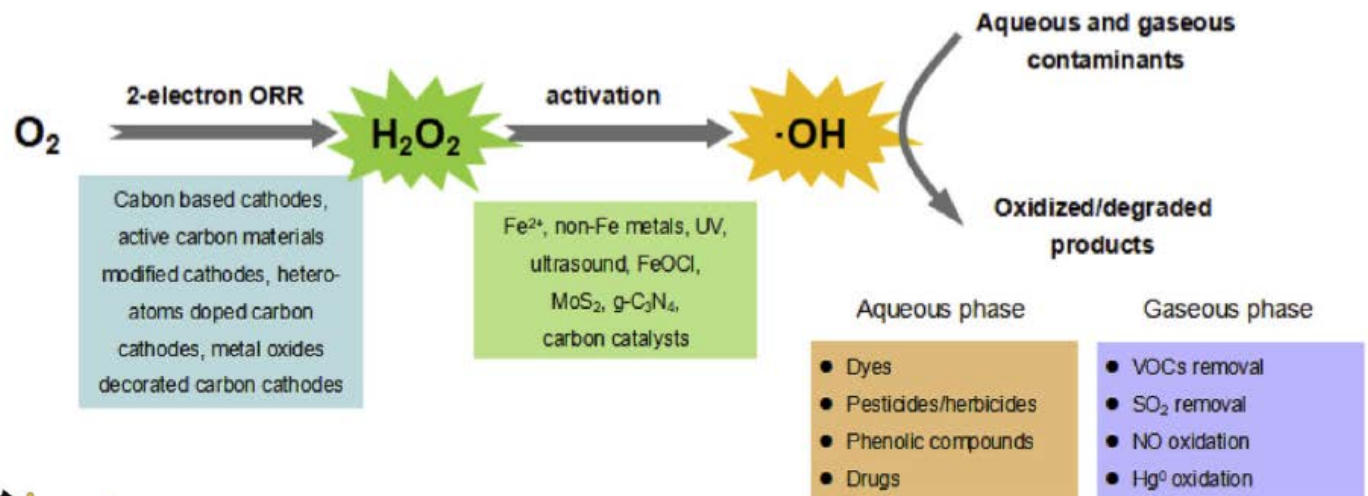
Competitive reactions: O₂ reduction!



INDIRECT OXIDATION MEDIATED BY CATHODE

Indirect oxidation processes

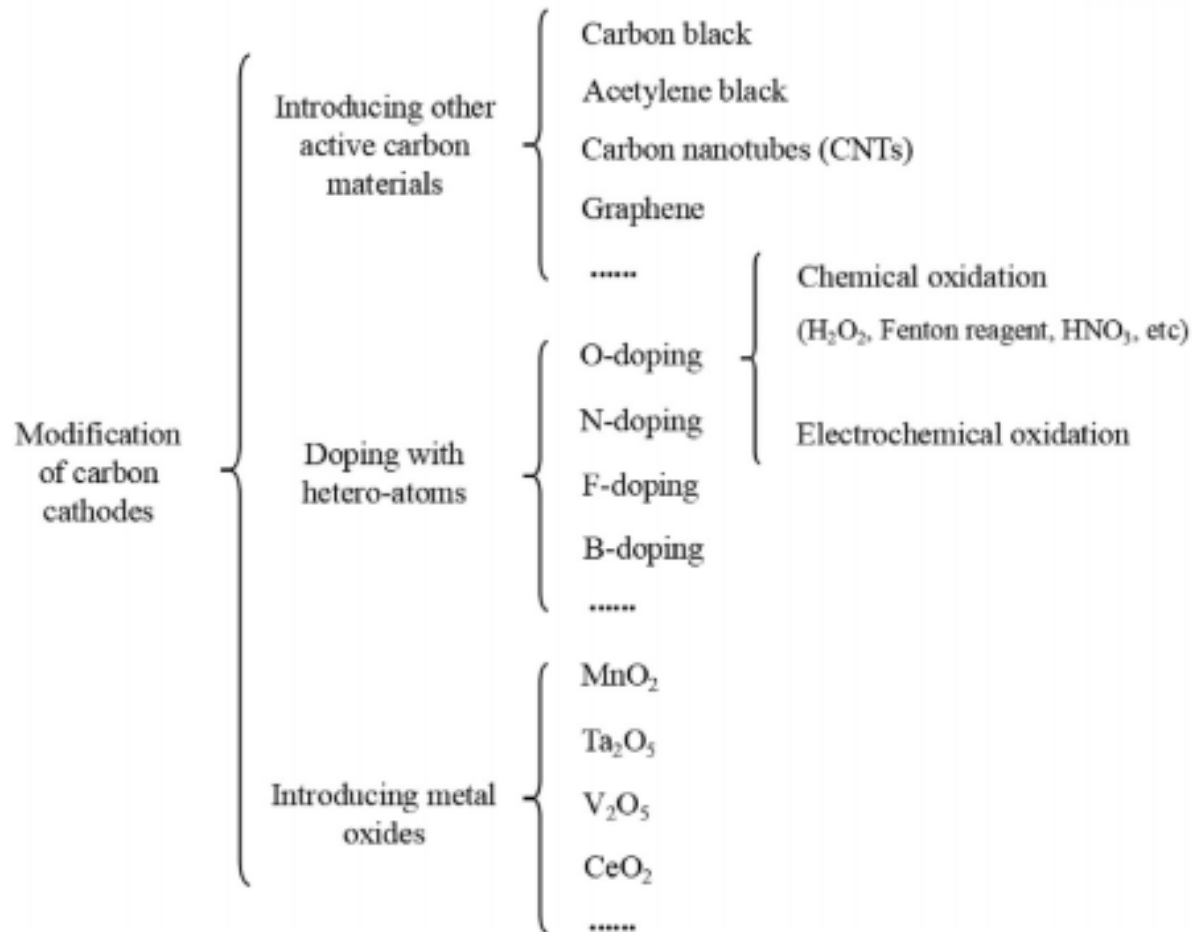
Cathodes can support formation of H_2O_2 via 2-electron O_2 reduction reaction ($2e$ ORR)



Cathode material

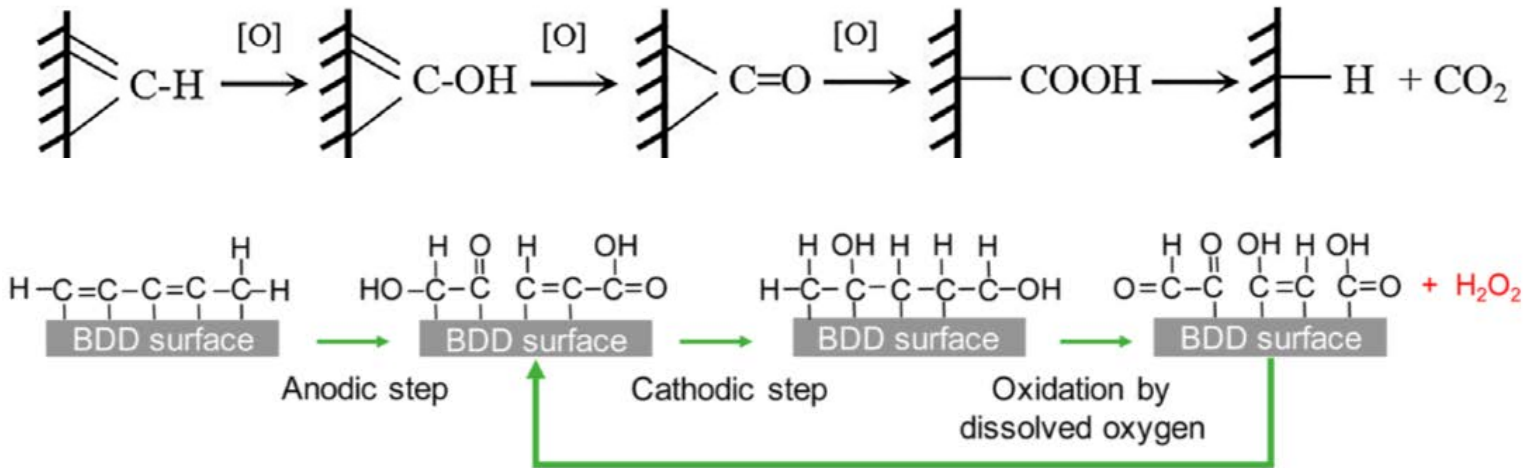


Cathode material



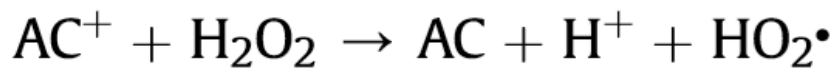
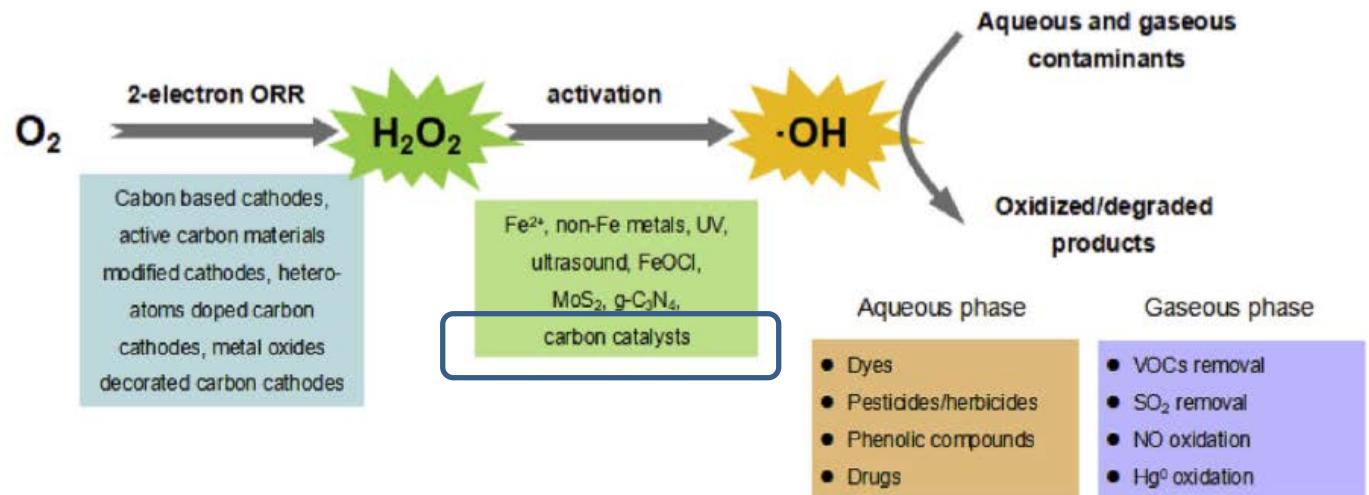
Cathode material

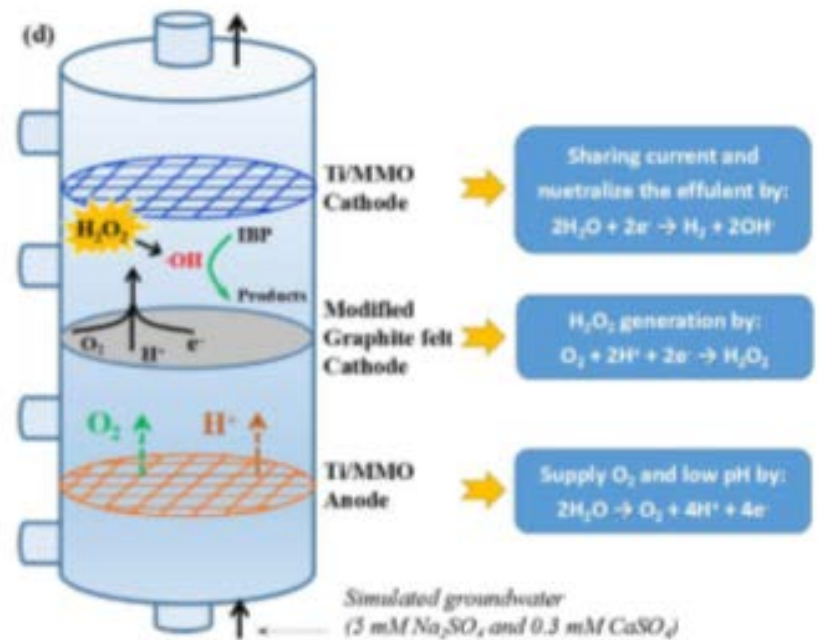
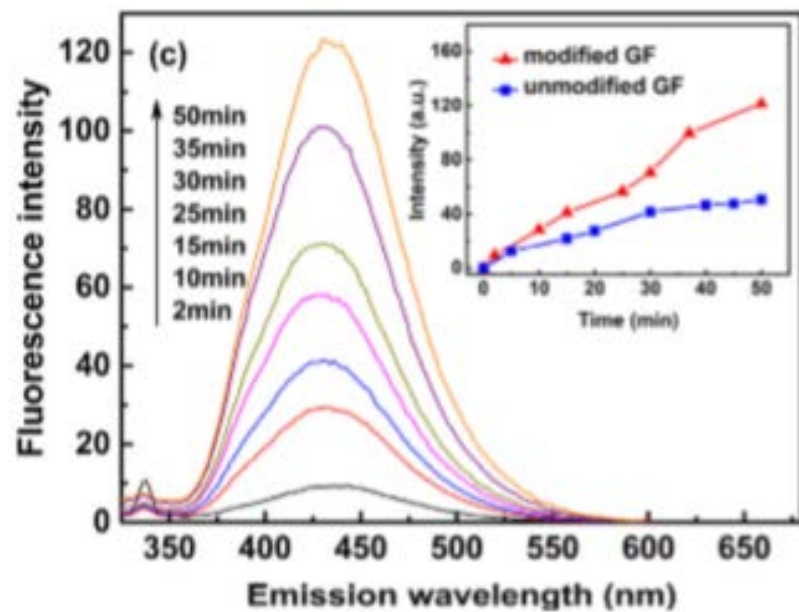
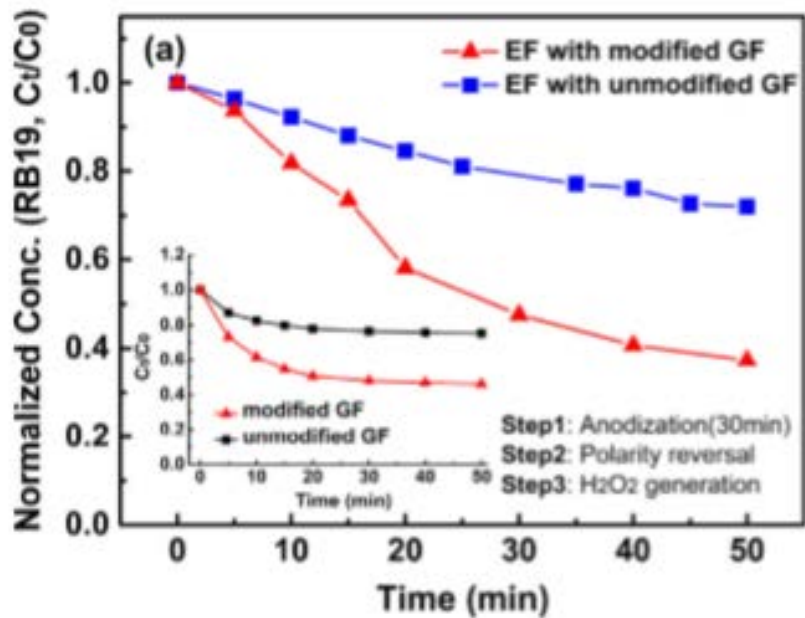
Modifications: heteroatom-doping (i.e. oxygen-containing functional groups)



Hydrogen peroxide generation

Cathode material

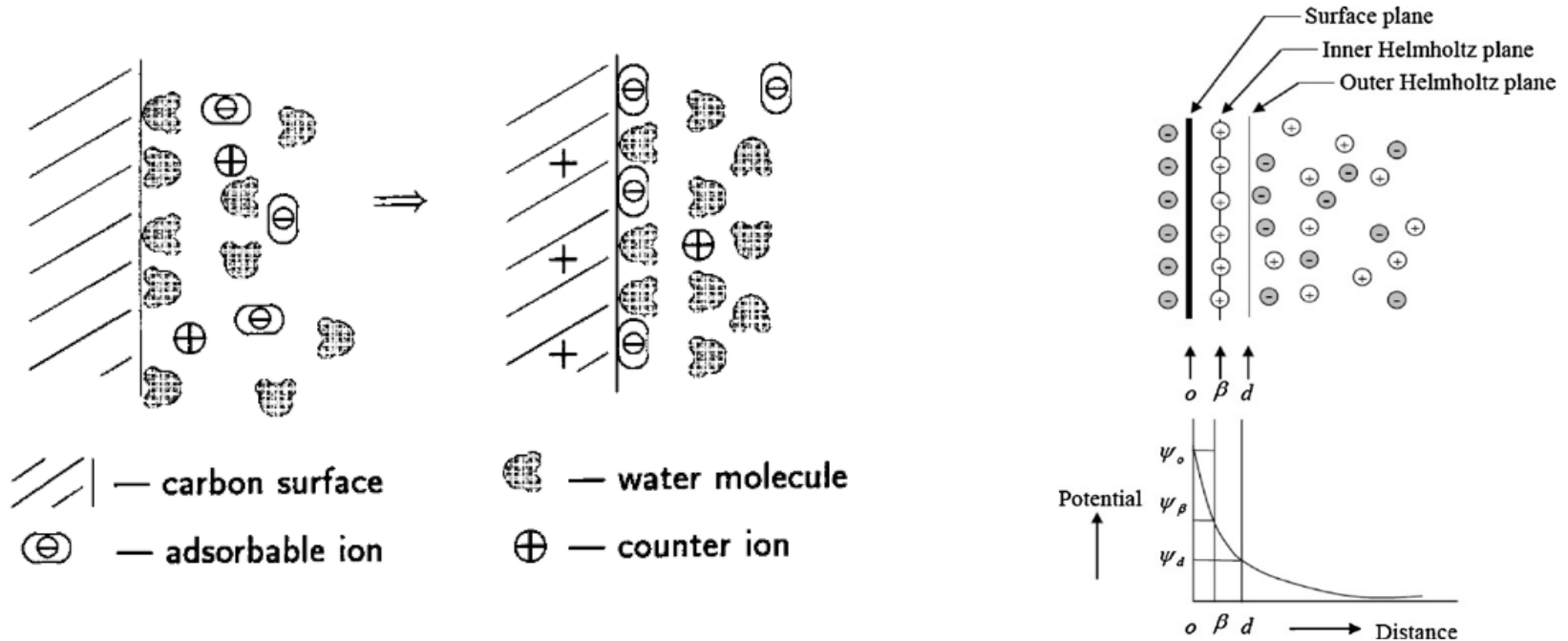




Part 2

**ELECTROSORPTION: SALTS REMOVAL
FOR WATER DESALINATION (PROCESS
CALLED CAPACITIVE DEIONIZATION OR
CDI) AND ORGANICS REMOVAL**

Electrosorption



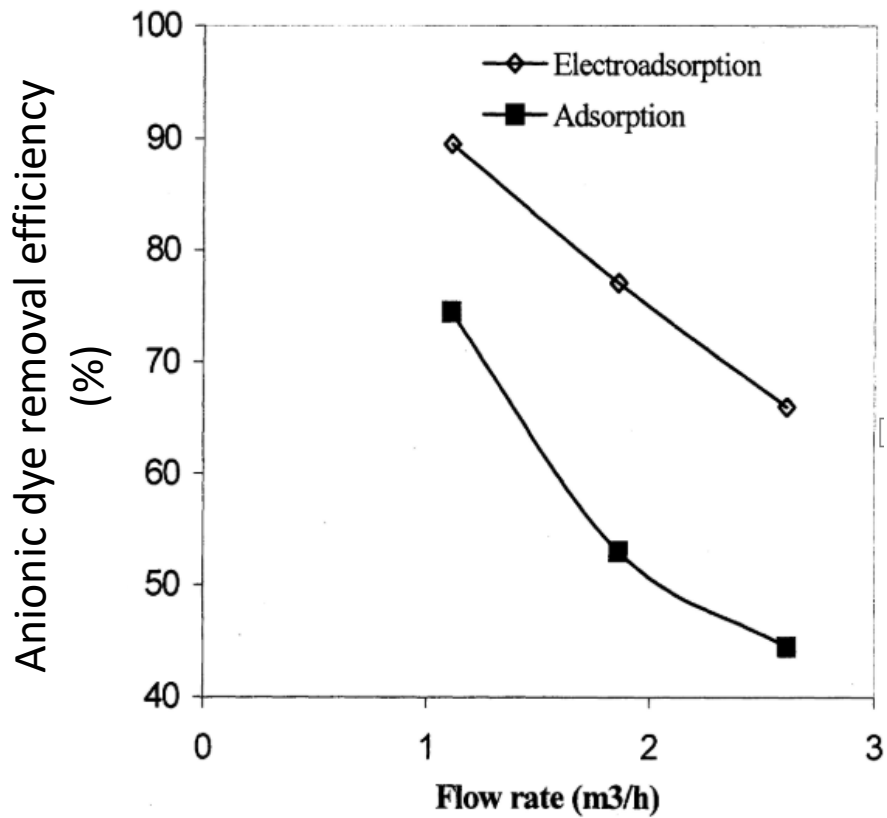
- Charge separates across the interface, resulting in the formation of strong electrical double layers (EDL) near the high conductivity and high surface area surfaces. When the electrode is charged and put into a solution with ions, the interface of the charged electrode and ions rich solution will be occupied with counter ions as a result of the Coulomb force, forming EDL.
- *Under some conditions, a given electrode-solution interface will show a range of potentials where no charge-transfer reactions occur because such reactions are thermodynamically or kinetically unfavorable. Charge does not cross the interface but external currents can flow!*

Electrosorption

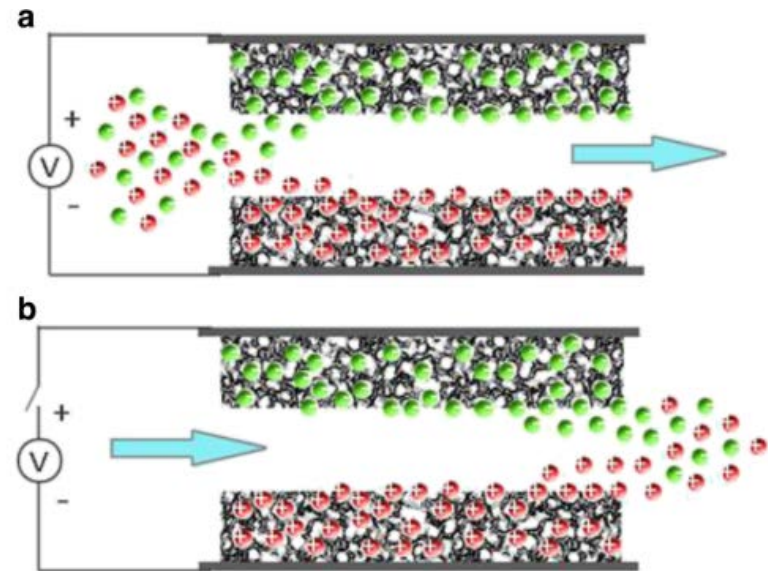
Adsorbent/precursor	Adsorbate	Maximum adsorption capacity (mg/g)
Activated carbon fibers (commercial)	Acid Orange 7 dye	644.59
Polyacrylonitrile resin	Phenol	225.86
Activated carbon fibers (commercial)	Naphthalenesulfonic acid	320.00
	Benzyl alcohol	210.00
	Naphthoic acid	200.00
Activated carbon cloth (commercial)	Bentazone	30.47
Spectracarb 2225 (commercial)	Chromium (VI)	7.28
Activated carbon fibers (commercial)	Phenoxide ions	207.04
	<i>p</i> -Nitrophenol	407.59
	Sodium dodecylbenzene sulfonate	766.66
Activated carbon fibers (commercial)	Uranium	5.02
Polyacrylonitrile resin	Aniline	315.71
Polyacrylonitrile resin	<i>m</i> -Cresol	367.68
NFEN 12915 (commercial)	Metribuzin pesticide	210.00
Spectracarb 2225 (commercial)	Nitrate	1.12
	Nitrite	0.83
Coconut charcoal	Phenol	188.00
Spectracarb 225 (commercial)	Ethyl xanthate	1120.55
	Thiocyanate	823.25

Electrosorption

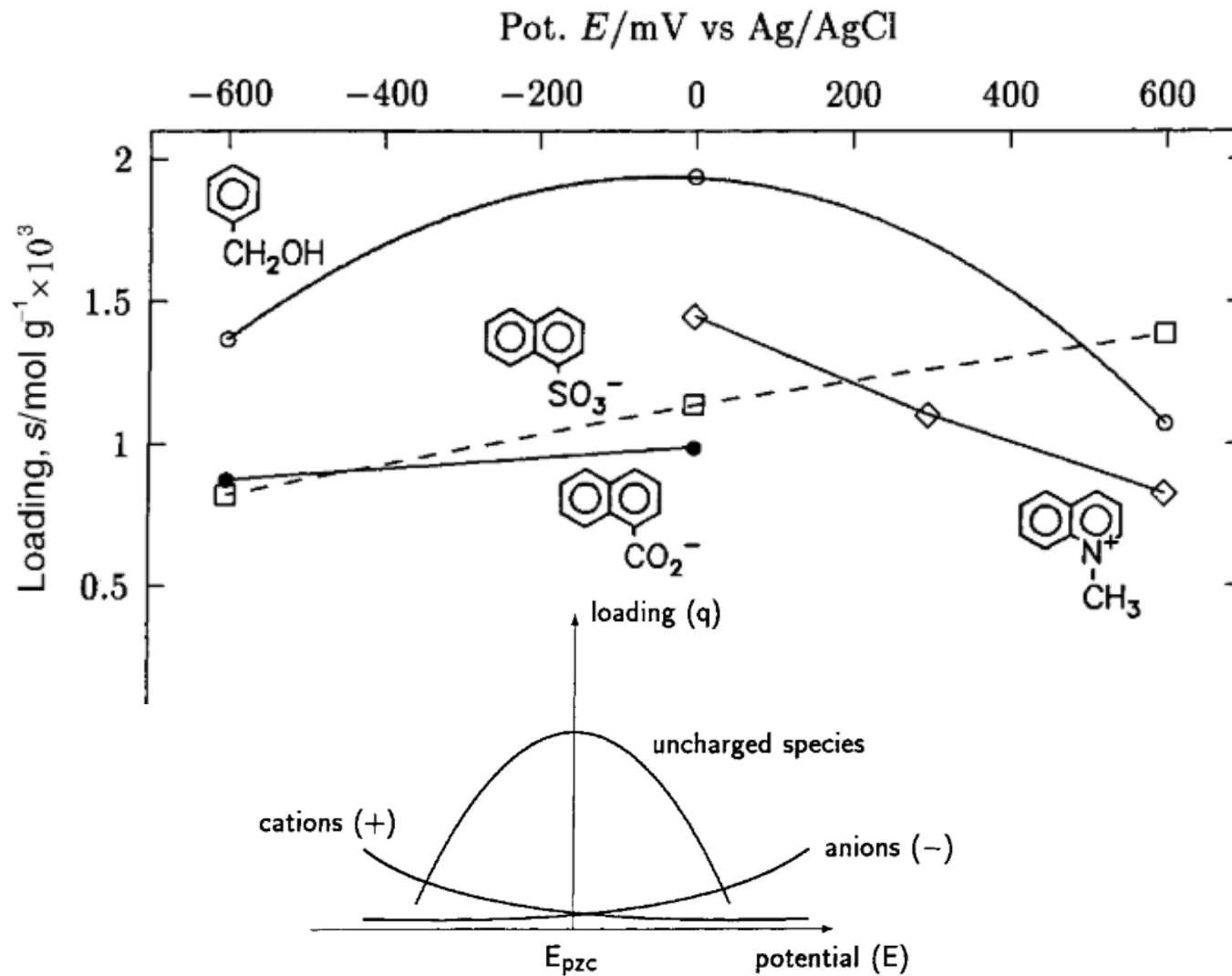
Accelerating the adsorption rate



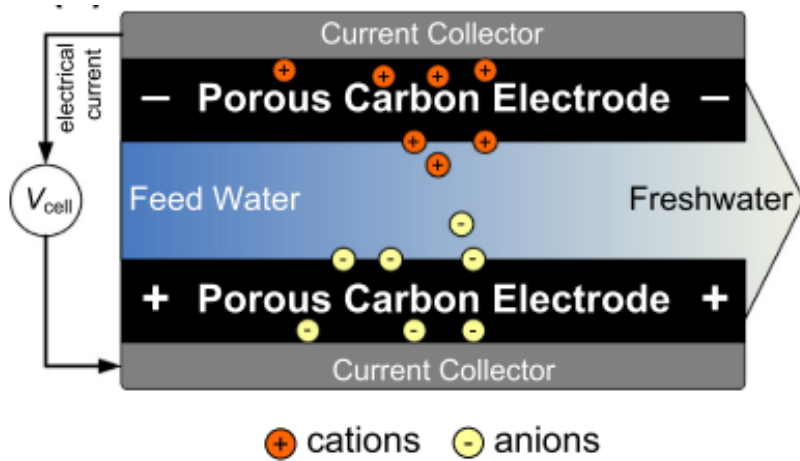
Ability for regeneration



Electrosorption

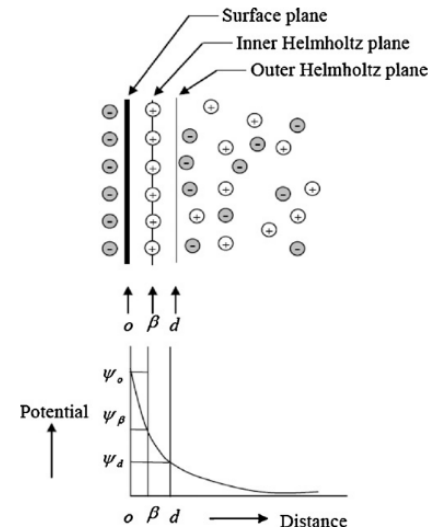
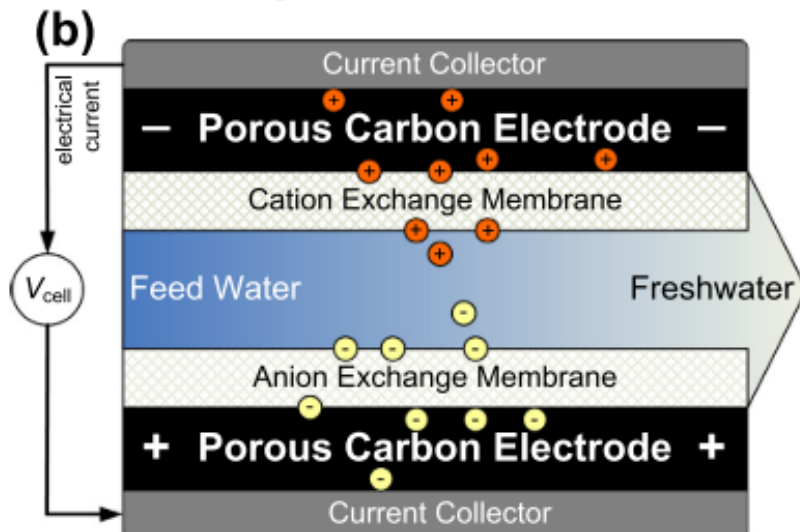


Capacitive deionization or CDI



Upon applying a voltage difference between two porous carbon electrodes, ions are attracted to the oppositely charged electrode.

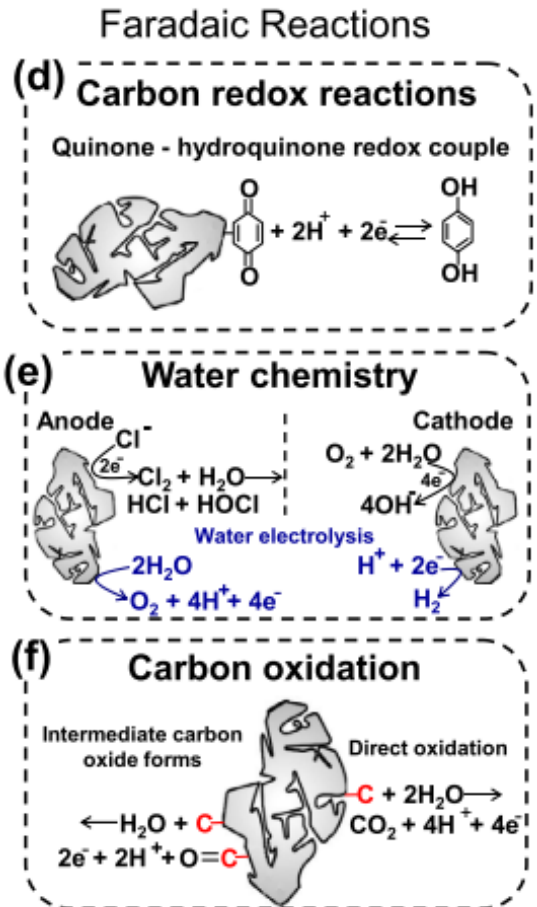
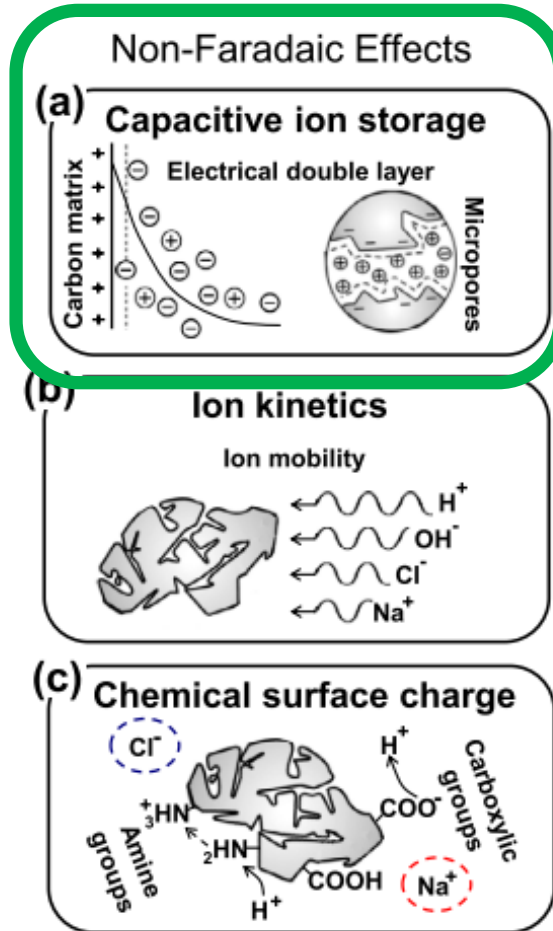
As a result, desalinated water is produced.



Mechanism

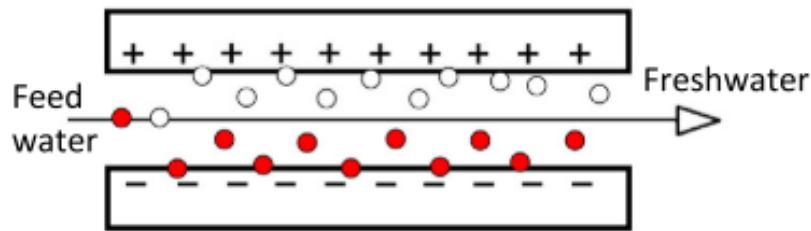
Capacitive ion storage is the phenomenon of the formation of an electrical double layer (EDL), where upon applying a charge, ions are captured electrostatically and stored capacitively in the diffuse layer formed next to the carbon interface.

The formation of the capacitive EDL is the heart of the CDI process.

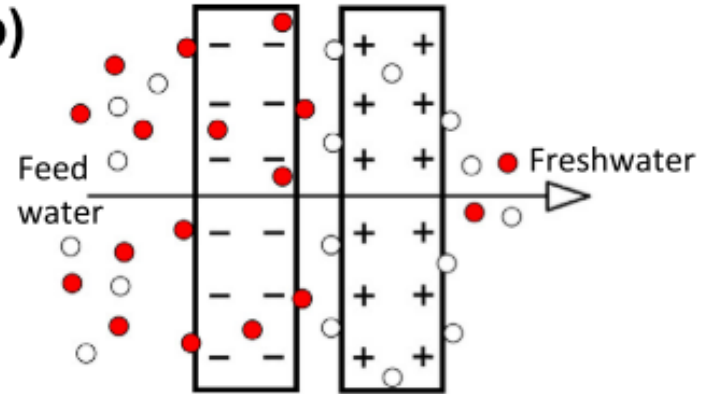


Types of reactors

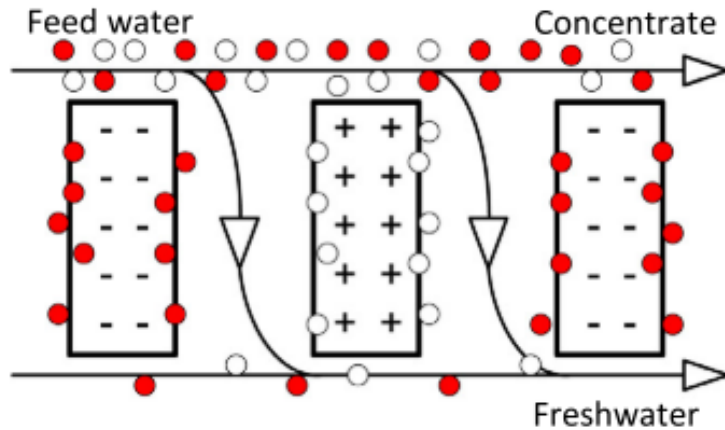
(a)



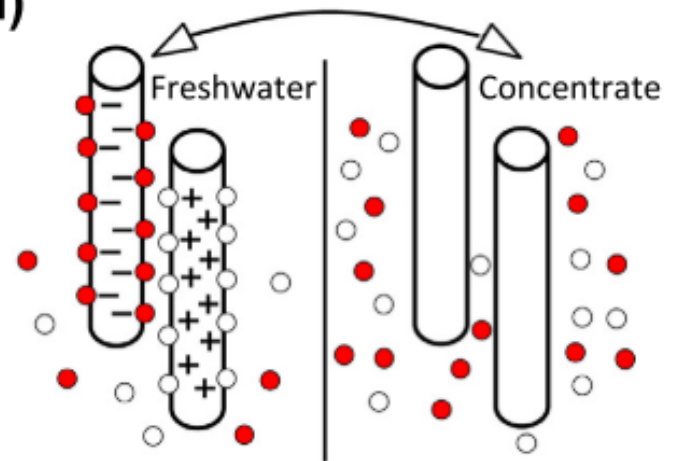
(b)



(c)



(d)



References

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