

ELECTROCHEMICAL REDUCTION

CEE 597T

Electrochemical Water and Wastewater Treatment

Electrochemical reduction (ER)

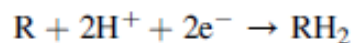
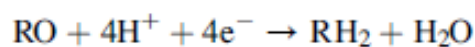
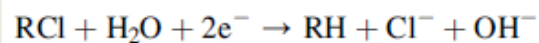
- is a chemical reaction, involving the gain of one or more electrons by an atom or a molecule at the cathode surface during the passage of direct electric current through the electrochemical system (anode, cathode, and an electrolyte solution).
- ER can be used
 - *for organic compounds that are refractory to oxidation or
 - *for heavy metal ions such as Pb(II), Sn(II), Hg(II), Cu(II), As(III), and Cr(VI).
- Deposited at the cathode, metals can be further recovered.

Electroreduction of Organics

- ER of different organic compounds in wastewater is expedient when
 - *the direct anodic oxidation of these compounds either does not occur or
 - *require high electric power consumption, and
 - *if products formed during the cathodic reduction of organic compounds are nontoxic (or of low toxicity) or
 - *relatively readily undergo further oxidative degradation.

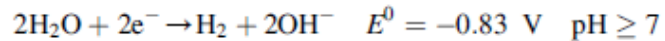
Mechanism

- Increased toxicity of organic substances is explained by the presence of the halogen atoms, aldehyde, amino, nitro, and nitroso groups in their molecule structure. Thus, loss of the halogen atom or reduction of aldehydes and ketones, for example, will lead to the formation of alcohols and hydrocarbons, which are less toxic.
- The mechanism of direct ER of organic compounds can be shown through the following reactions:

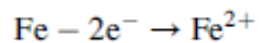


- Similar to EO, ER can occur either directly through the direct accepting of electrons by molecules and ions or indirectly through the mediated reactions with electrochemically generated species at the cathode and anode such as H₂ and iron, respectively.

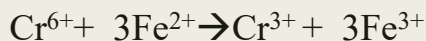
At cathode:



At anode:



- Mediated reactions of anodic material dissolution (mostly iron and aluminum) followed by reduction of different compounds such as Cr(VI) according to the reaction

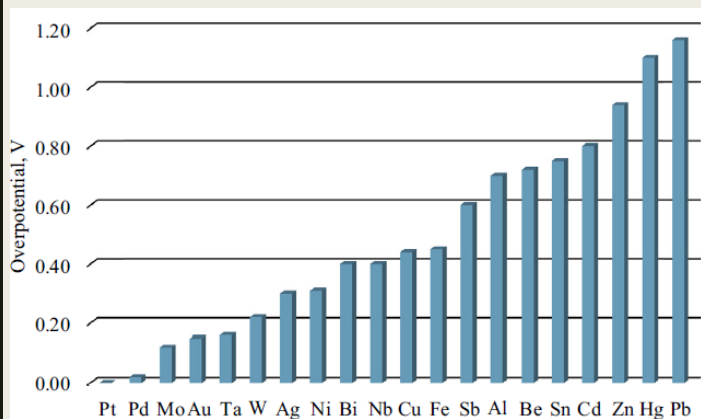


- An example of direct mechanism is a reduction of metals ions at the cathode surface according to the following reaction:



- Cathodes with high overpotential toward hydrogen evolution are more efficient in reduction of pollutants.
- Overpotential toward hydrogen evolution for different metals
 - *decreasing with ambient temperature increase,
 - *decrease of current density, and
 - *increase of the electrode surface roughness, which is directly related to the catalytic surface area increase.

The values of different cathodic overpotentials toward hydrogen evolution reactions

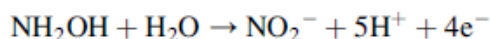
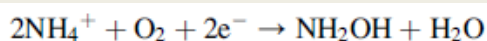


Overpotential of different cathode materials toward hydrogen evolution reactions.

- Electrodeposition of strongly electronegative species can be conducted while using Hg electrodes due to their high overpotential toward hydrogen evolution.
- ER of highly electronegative species could theoretically be conducted using Pb cathode because of their high overpotential characteristics.
- However, Pb electrodes interact easily with acids.

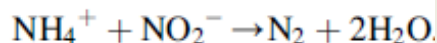
Electrochemical Reduction of Inorganic Nitrogen Compounds

- Inorganic nitrogen in natural waters originates from ammonification process of organic nitrogen compounds contained in dead plants and animals. Moreover, some bacteria can catch the atmospheric nitrogen and reduce it to NH_4^+ forms in accordance with the following eq.

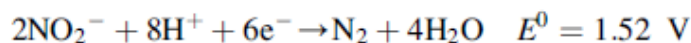
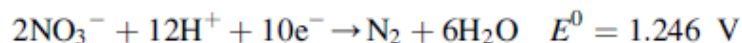


- Increased agricultural and industrial activities contribute to additional wastewater and natural water pollution by nitrogen species, which cause eutrophication of water bodies and suppression of water quality and natural growth of water biota, acidify the surface water, increase the content of atmospheric ozone, etc.

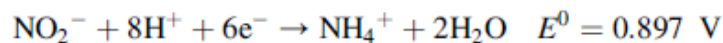
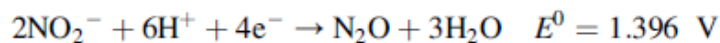
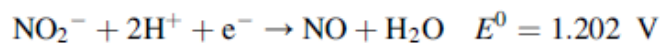
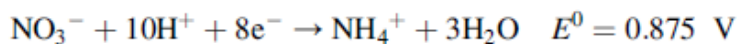
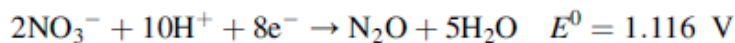
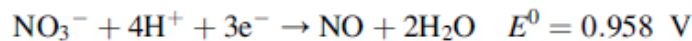
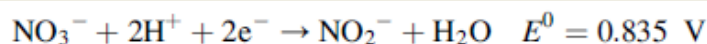
- The main goal of ER of inorganic nitrogen is to conduct denitrification of N-species with the formation of nontoxic N_2 gas, which is in nature conducted by anammox bacteria through the following transformations:



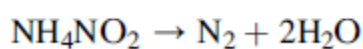
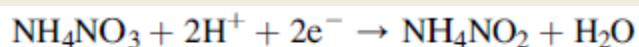
- However, in practice, ER of nitrogen compound is difficult to conduct because of a wide variety of stable nitrogen species such as NO_3^- ; N_2O_4 ; NO_2^- ; NO ; $N_2O_2^{2-}$; N_2O ; N_2 ; NH_3 ; NH_3OH^+ ; $N_2H_5^+$ and N_4^+ with oxidation states varying from 3 to +5.
- In this regard, the use of electrocatalytic material is required to enhance the process of denitrification.
- The most favorable reaction of nitrates and nitrites is reduction to N_2 gas, which is described as follows:



In practice, nitrates and nitrites are usually reduced to other more thermodynamically favorable compounds, such as NO , NO_2 , N_2O , etc., in accordance with the following reactions:



- One of the most selective catalysts toward N₂ generation from nitrates is platinum copper electrode. So far, there is no efficient catalyst for complete conversion of nitrates and nitrites to N₂ gas. Most reduction mechanisms lead to the formation of intermediate NO gas. Therefore, there is an approach trying to find effective catalytic materials for ER of NO.
- Ammonia nitrate can be reduced at graphite electrode to ammonium nitrite, which decomposes on heating to nitrogen gas.



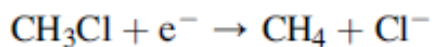
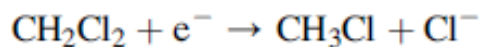
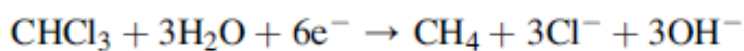
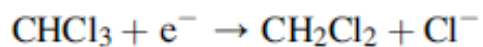
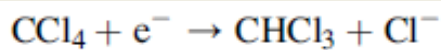
Electrochemical Reduction of Organic Nitrogen Compounds

- ER of organic nitrogen-containing compounds such as nitrobenzene and trinitrotoluene is conducted using lead, zinc, copper, and stainless steel cathodes in two-compartment electrolyzers where anodic and cathodic chambers are separated by a membrane.
- At first nitrobenzene and trinitrotoluene undergo cathodic reduction with formation of amines, which is further electrochemically oxidized in anodic compartment to nontoxic compounds.
- Moreover, amines are valuable intermediates for dyes and drugs production and therefore can be recycled.

Electrochemical Reduction of Chlorinated Hydrocarbons

- Chlorinated hydrocarbons such as polychlorinated biphenyls, dichlorodiphenyl trichloroethane, trichloroethylene, chlorinated benzenes, and others are highly toxic compounds able to cause cancer and threaten the environment biota.
- ER allows reducing the toxicity of chlorinated hydrocarbons through a step reduction process with a gradual abstraction of chlorine atoms.

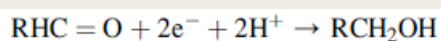
- As an example of electrochemical dechlorination, the mechanisms of carbon tetrachloride cathodic reduction are shown in the following equations



Electrochemical Reduction of Aldehydes and Ketones

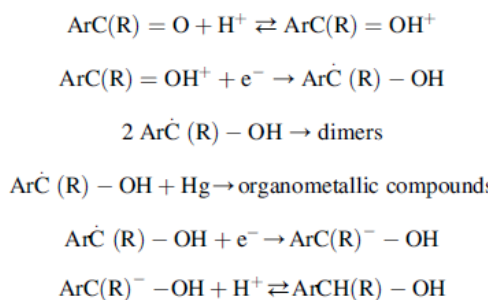
- Aldehydes and ketones are organic compounds containing carbonyl group $>C=O$ in the molecule structure. Carbonyl carbon of aldehydes is connected to hydrogen atom and an organic group R (general formula, $RHC=O$), and carbonyl carbon of ketones is connected with two organic groups (general formula, $R_2C=O$).
- Both groups are toxic compounds having irritating and neurotoxic effects. Some of these compounds can have mutagenic and carcinogenic properties.
- Mechanism of reduction of carbonyl compounds consists of multi stages such as hydration, dehydration, keto-enol equilibria, interactions with radical anions, etc., resulting in either formation of alcohols through a two-electron transfer process or formation of picanols as a result of one electron transfer process.

- General mechanism of ER of aliphatic aldehydes is represented as follows.

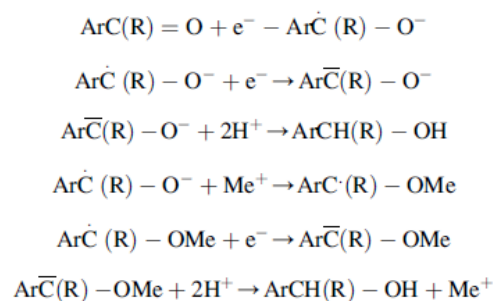


- The mechanism of benzaldehyde reduction is more complex depending on pH of the medium and includes reaction of mediated radical formation.

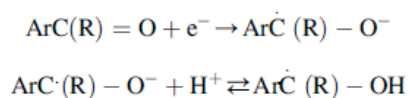
Acidic media:



Alkaline media:



Neutral media:

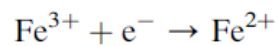
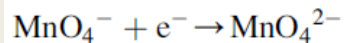
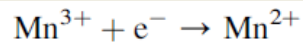


Electrochemical Reduction of Metals

- Electrochemical deposition of metals from wastewater finds more applications nowadays because of the possibility of further recovery of valuable products.
- Moreover, there is no need for addition of chemicals usually, process is selective and operation costs are low.
- Along with recovery of metals, water can undergo disinfection by the formed electroactive species.
- ER has a disadvantage: Process efficiency is sensitive to wastewater composition and interfered easily by side reactions of hydrogen generation and oxygen reduction.

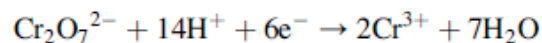
- The value of overpotential strongly depends on the nature of metal needed to be discharged. Depending on the overpotential value metals can be conditionally divided into three categories.
- The first group consists of metals of very low overpotential not more than a thousands of a volt. They are Cd, Pb, Ag, and Hg.
- Second group consists of Zn, Bi, and Cu with overpotential lying in the range of a hundreds of a volt and
- The third group includes Co, Ni and, Fe having overpotential in the order of several tenths of a volt. The value of overpotential is also influenced by the nature of salt anion.

- Usually overpotential increases for different anions in the following order:
- $\text{J}^- > \text{Br}^- > \text{Cl}^- > \text{ClO}_4^- > \text{NO}_3^- > \text{PO}_4^{3-}$.
- Alkalinity of solution also affects overpotential. High alkalinity can cause additional deposition of metal hydroxides on the surface of electrodes along with metal deposition.
- Moreover, a number of strongly electronegative metals cannot be deposited from aqueous solutions.
- Also some metals, such as manganese, can undergo ER by changing only the valence electrons without the formation of solid products.

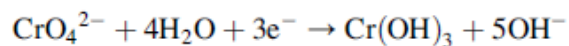


- Direct ER methods using insoluble anodes are particularly effective for the neutralization of chromium-containing wastewater with high concentration of Cr(VI) usually above 2 g/L and allow reduction of Cr(VI) content approximately by three orders of magnitude.
- An optimal media for Cr(VI) reduction is considered to be acidic with pH of 2 and applied current density between 2 and 20 mA/cm². Reduction of Cr(VI) depending on the media conditions can be represented via the following reactions:

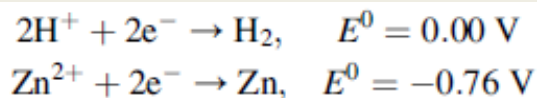
Acidic media:



Slightly alkaline media:



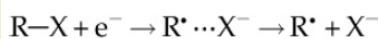
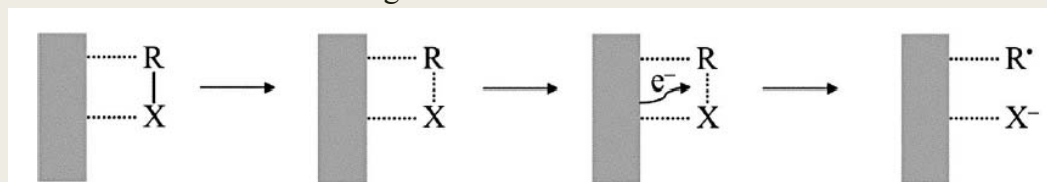
- ER of zinc at a cathode occurs with simultaneous allocation of hydrogen and deposition of zinc according to the following reactions:



- As it is seen from reduction potentials, ER of zinc should not allocate only H₂ gas; however, because of the high value of overpotential, Zn can be successfully recovered from solutions with current efficiency (CE) of 80%-90%.
- It is known that different electrochemical reactions occur at a particular electrode potential; therefore, when there is a mixture of different compounds in solution, reaction having more positive reduction potential thermodynamically are more favorable, thus suppressing reactions with more negative electrode potential reducing its CE and purity of deposit. In this regard, if there is a necessity to recover a metal of high purity from a solution, then solution should not contain impurities at concentrations above the maximum allowable levels.

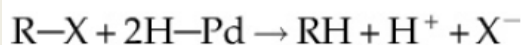
Electrode Materials

- Silver**
- Silver was reported to have a strong electrocatalytic behavior toward dehalogenation of organic compounds.
- Silver has been used to dehalogenate a huge number of very different organic compounds, ranging from aliphatic long and short linear-chain molecules to aromatic rings.



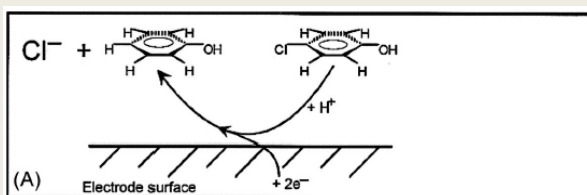
■ Palladium

- The treatment of toxic organic halides in water using palladized iron leads to rapid non-electrochemical dechlorination.
- In a Pd/Fe bimetallic system, the zero valent iron can be oxidized in water to Fe^{2+} accompanied by production of molecular hydrogen, which in turn can be absorbed into Pd, thus forming the active chemical species PdH, which likely acts as a source of atomic hydrogen.
- The hydrodehalogenation reaction is:

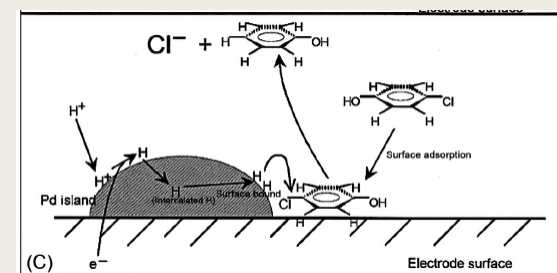
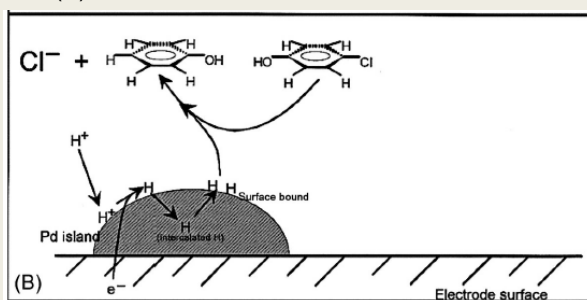


- The rate of reaction is mainly a function of the surface area of metallic iron (consumed during the reaction) and palladium (not consumed during the reaction), the Pd/Fe ratio at the iron surface, and pH.

Proposed mechanisms for the hydrodehalogenation of 4-chlorophenol to phenol



(A) Direct reduction at electrode surface



(C) Adsorption of 4-chlorophenol at electrode substrate followed by hydrogenation at palladium island/electrode surface.

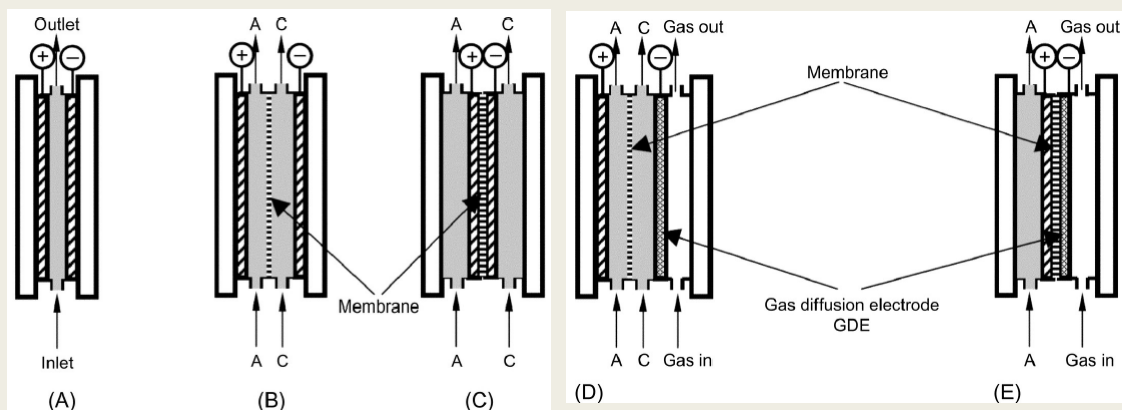
(B) Hydrogenation at palladium catalyst surface

Copper

- Copper has been largely investigated as a possible low cost substitute for silver in the electroreductive dehalogenation processes.
- Cu is reported to be a good electrocatalytic metal, which leads to a complete dechlorination of polychloromethanes, even if it is less active than Ag.
- In addition, Cu is about 100 times cheaper than Ag, largely cheaper than Pd and very abundant.
- Thus, bimetallic cathodes Ag/Cu or Pd/Cu have been prepared and studied for electrochemical dehalogenation of different organic halides

Reactors

- The very popular plate-and-frame is used for a large variety of applications



A) undivided cell; (B) 2-compartment membrane or separator cell; (C) solid polymer electrolyte reactor (SPE); (D) 2-compartment membrane cell with GDE; (E) SPE-GDE reactor.

*Liquid compartments are denoted in gray.

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