

# Electrochemistry for environmental remediation: laboratory experiments

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## Resumen

Muchos contaminantes pueden convertirse en especies menos peligrosas mediante una transferencia de electrones. Estas transferencias pueden llevarse a cabo en interfases electrificadas (electrodos), ser directas o indirectas, oxidaciones o reducciones, usarse para tratar líquidos, gases, suelos, etc. En este artículo discutimos algunas aplicaciones y experimentos.

## Abstract

**Key words:** *electrochemistry, environment, oxidations, disinfectants, experiments*

Electron transfer can transform a plethora of pollutants into much less dangerous species. This transfer can often be performed at electrified interfaces (electrodes), be direct or indirect, produce reductions or oxidations, be used for the treatment of liquids, gases and soils, etc. In this paper we discuss several applications and experiments.

## Fundamentals

The degree of toxicity of a wide range of pollutants can be substantially decreased by oxidation or reduction processes. A large number of such processes can be performed by electron transfer at electrodic surfaces. Electrochemical techniques offer advantages in specific cases relative to other technologies for different environmental remediation schemes. Such advantages include environmental compatibility, versatility, energy efficiency, selectivity, amenability to automation, and cost effectiveness (Rajeshwar, 1997; Rajeshwar, 1994; Ibanez, 2004a). We have developed a series of laboratory experiments aimed at demonstrating some of the applications of electrochemical techniques to the remediation of hazardous wastes, dye wastewaters, textile dyeing wastes, contaminated soils, gaseous pollutants, and the electrochemical production of oxidizers-disinfectants.

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The main electrochemical strategies discussed in the present paper and used for environmental remediation involve the following.

## Direct Electrolysis

Pollutants capable of undergoing direct electrochemical oxidation or reduction at an electrode can in principle be transformed and/or removed from water streams or reservoirs by the application of appropriate potentials in electrochemical reactors. Here, oxidation or reduction processes occur directly on inert electrodes without the involvement of other substances (e.g. electron mediators, biocide species). Direct Electrolysis methods include: 1. Anodic Processes. 2. Cathodic Processes.

### Experiment 1. Metal ion recovery

(Note: For all the experiments in the present paper, a 9-V battery or an AC to DC converter set at approximately 9-12 V can be used as the power source).

Place enough 0.1 M  $\text{CuSO}_4$  solution as to cover the bottom of a small, shallow Petri dish. With a Cu wire, make a ring (2 or 3 cm in diameter) at one end and bend it at a 90-degree angle. See Figure 1. Place a piece of filter paper (not shown) on top of the ring. Secure the whole entity in such a way that the ring barely touches the surface of the solution. Place a

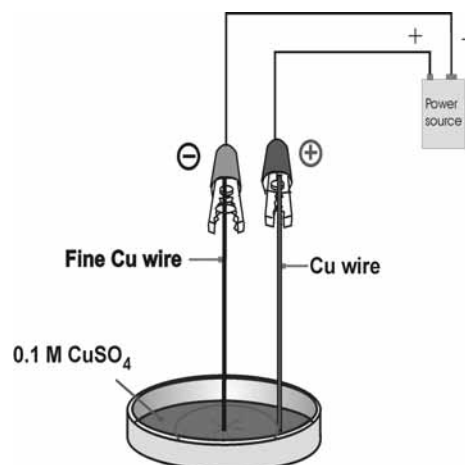


Figure 1. Electrodeposition of Cu.

straight Cu wire at the center of the ring in the same way (barely touching the paper). Connect the two Cu wires to the positive and negative terminals, respectively, of a 9 V battery. A Cu fractal is formed in a few minutes due to the recovery (by radial deposition) of Cu. One could even calculate its fractal dimension if desired (Fruen, 2006; Rybicki, 2006; Stanley, 2006; Talanquer, 1993).

### Indirect Electrolysis

Direct processes are often limited by diffusion, and thus low current densities need to be used if high efficiencies are desired. In addition, the high overpotentials required often necessitate noble metals or similarly expensive electrode materials to operate. Alternatively, homogeneous or heterogeneous, cathodic or anodic redox-mediated processes have been envisaged to overcome such difficulties, usually at ambient temperatures and pressures. The idea here is to use an electrochemically-generated redox reagent as a chemical reactant (or catalyst) to convert pollutants to less harmful products. The redox reagent then acts as an intermediary for shuttling electrons between the target pollutant and the electrode. These indirect processes can be performed as: 1. Reversible Processes. 2. Irreversible Processes.

#### Experiment 2. Electrocoagulation of a dye solution

Prepare approximately 7 mL of a 0.1 M solution of  $\text{Na}_2\text{SO}_4$  in a 10-mL beaker. Add two drops of methyl red indicator and three drops of bromocresol green. Adjust the pH of the resulting solution to about 3-4 (the solution should be slightly violet). Take two mL of this solution and set them aside in a separate container as a blank for comparison. Insert two iron paper clips on the sides of the beaker, and connect them to the terminals of the power source. Insert a micro stirring bar, but do not stir until the solution has turned red. See Figure 2. Then, stir suddenly and vigorously until the solution turns green. Stop stirring and allow the solution to become red again, and then stir vigorously again until it becomes green. This is called a *traffic-light effect* (Santoyo, 2006). Repeat the cycle until the solution is noticeably brownish as a result of the dissolution of the anode (that forms Fe(II) and Fe(III) species), and the production of  $\text{OH}^-$  at the cathode. These combined products yield precipitated iron oxyhydroxides. Then, discontinue the reaction and filter the resulting mixture with a very fine filter (e.g., a 0.45 micrometer membrane). Adjust the pH to the initial value of the

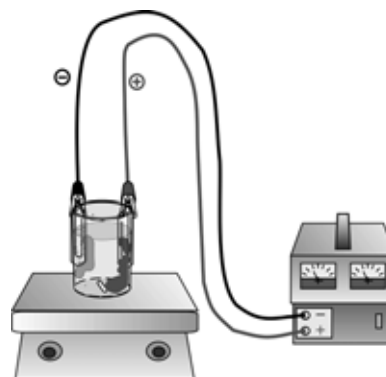


Figure 2. Electrocoagulation of simulated wastewater.

blank and compare their colors. The treated solution should be much clearer than the initial one (Ibanez, 1995; Ibanez, 1998a).

#### Experiment 3. The indirect oxidation of a surrogate organic pollutant by the Co(II)/Co(III) system.

In a 10-mL beaker prepare 5 mL of a 0.1 M  $\text{CoSO}_4$  solution in 2 M  $\text{H}_2\text{SO}_4$ . Add a drop of a dilute solution of glycerin (prepared for example by adding one drop of pure glycerin to 50 drops of water). Suction 3 mL of this mixture into a 4-mL Beral pipet. Insert at the top of the pipet bulb a 5-cm rod of graphite (cathode) and a 5-cm wire or a  $0.5 \times 5$  cm Pb stripe or a Pb wire. See Figure 3. Seal the electrode entrances into the pipet with silicon. Place this electrochemical cell (i.e., pipet) in a water bath at 40-50°C. Insert the stem of the pipet into a saturated

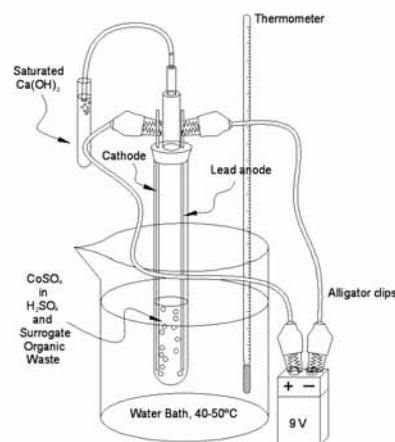


Figure 3. Indirect destruction of organic wastes (adapted from Ibanez, 1997).

lime solution (i.e., CaO) to collect any  $\text{CO}_2$  produced (see Figure 3); this should form insoluble  $\text{CaCO}_3$  as electrolysis proceeds due to the oxidation of the surrogate organic pollutant (glycerin in this case) by the Co(III) produced at the anode. Connect the electrodes to the power source and allow electrolysis to proceed until the pink Co(II) solution turns gray-bluish. This signals the end of the oxidation of the organic compound. The resulting Co(III) solution can then be expelled out of the pipet, and a drop of pure glycerin added to it to reverse the color back to pink (Ibanez, 1997).

### Electrokinetic Remediation of Soils

Electric fields as well as electron transfer processes have been used for the decontamination of soils and underground water containing unwanted organic or inorganic substances. The main phenomena involved here include electroosmosis, electrophoresis, and electromigration. When suitable anodes and cathodes are strategically buried in the ground or placed in contact with a slurry, and an electric field from a DC source is applied, one or more of these phenomena occur and the resulting effect is used for the removal of polluting substances. The technique is also called electroreclamation, electroosmotic purging, electroremediation, electrorestoration and electrokinetic processing.

*Experiment 4. Electrokinetics: a) ion migration, b) the creation of an acidic and a basic front during electrokinetic remediation, and c) the drying of a soil by electroosmosis.*

Take six microscope slides (preferably with their edges unsharpened by sanding). Make a thick, non-

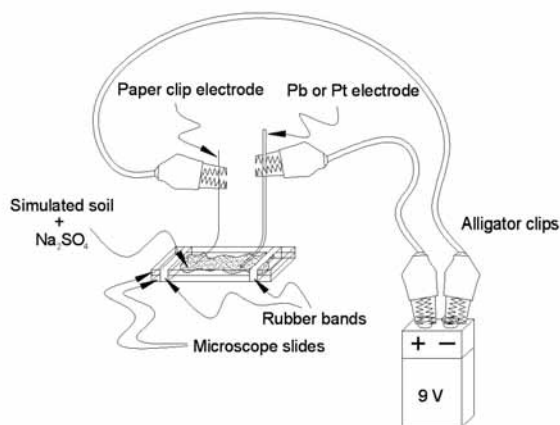


Figure 4. Electrokinetic remediation of soils.

flowing paste with kaolin and 0.1 M sodium sulfate. Use platinum or stainless steel electrodes (e.g., dental wire). Add indicators as specified below, and sandwich the two plates with a small amount of paste in between, as in Figure 4 (Ibanez, 1998b). Apply a potential with the power source (e.g., 9-12 V).

- Mix a solution 0.1 M in  $\text{CuSO}_4$  and 0.01 M in  $\text{K}_2\text{Cr}_2\text{O}_7$  with the kaolin and sodium sulfate as to see copper ions migrating towards the cathode and chromate ions towards the anode. **Caution: due to the carcinogenicity of chromate, this part a) must be performed as a demonstration by the instructor, using protective gloves.**
- Add a drop or two of an indicator (e.g., bromothymol blue or thymol blue) to a small amount of fresh paste and proceed as described above. The creation and movement of an acid and a basic front should be obvious within a few minutes.
- Add two drops of phenolphthalein indicator to a small amount of fresh paste, and proceed as above. After a few seconds, the indicator makes obvious the generation of base around the cathode and the electroosmotic flow of water from the anode towards the cathode, observed as an increase in humidity on the cathodic side and a drying near the anode.

### Electroremediation of Gases

Polluting gases generally need to be transferred to the liquid phase (normally aqueous media) by absorption or reaction before they can undergo electrochemical oxidation or reduction (Ibanez, 2001). This conversion can be effected in two absorption modes: a) the gas is directly absorbed in an electrochemical cell for treatment (i.e., inner-cell process), or b) the gas is absorbed in a separate reservoir and then transferred to the electrochemical cell (i.e., outer-cell process).

*Experiment 5. The conversion of a gaseous pollutant ( $\text{H}_2\text{S}$ ) into its clean and useful constituent elements ( $\text{H}_2 + \text{S}$ ).*

Prepare  $\text{H}_2\text{S}$  in a 30-mL syringe using Mattson's method (Mattson, 2005), consisting in the reaction of a metal sulfide (e.g.,  $\text{ZnS}$ ) with 6 M  $\text{H}_2\text{SO}_4$  inside a syringe barrel closed at the bottom (for example, with a Luer lock). The piston will slide upwards as the gas is produced inside. Pour out the remaining

reaction mixture, and push the plunger to direct the gas towards a 10-mL beaker containing a solution 0.25 M in KI, 0.05 M in  $I_2$ , and 0.05 M in HCl. The sulfide from the gas will be oxidized to yellow elemental sulfur by the brown-violet triiodide ions. Once the color has changed, filter the solution with fine filter paper, and apply a voltage with the power source to the resulting clear solution. Use preferably Pt as the anode, and graphite as cathode (see Figure 5). The triiodide ions are then regenerated at the anode, and hydrogen is released at the cathode. The end result is that a poisonous gas is converted into its constituent elements in a high-purity form. The triiodide solution can be reused many times for sulfide oxidation.

### Electrochemical Disinfection of Water

Potent disinfecting agents are produced electrochemically and then added to water to kill unwanted microorganisms. A key advantage of this approach involves the possibility of producing them in situ. Some of them produce fewer disinfection by-products than chlorine.

### Experiment 6. Production of ferrate ions

Fill a small U-tube to 80% of its capacity with concentrated NaOH (e.g., 10M). **Caution: Concentrated NaOH is highly corrosive, avoid contact with the skin and eyes and handle this reaction on a surface that can be easily cleaned afterwards.** Insert one iron nail (preferably rusted) in each side and connect them to the terminals of the power source (see Figure 6). Within minutes, a purplish color develops near the anode due to the formation of the powerful oxidizing  $FeO_4^{2-}$  ions. Test

for their presence by performing a spectrophotometric scan. A peak in the vicinity of 505 nm should appear (Ibanez, 2004b). A more appealing test from the environmental perspective is to add a few drops of an alcohol to the ferrate side of the U-tube and observe the interface of the two liquids for  $CO_2$  bubbles resulting from the mineralization of the organic. After a few minutes, the spent ferrate becomes orange-brownish as a result of the reduction of Fe(VI) to Fe(III), which is amenable for use in chemical coagulation processes.

### Experiment 7. Production of ozone

Prepare a Beral pipet exactly in the same way as described for the indirect method discussed above (which uses cobalt salts). See Figure 7. Add to it 3 mL of 5 M  $H_2SO_4$ . Place this electrochemical cell in an ice bath, connect the electrodes to a power source (the Pb electrode to the positive) and allow electrolysis to proceed. Collect the exiting gases in a 10-mL beaker containing 5 mL of a 0.1 M KI + a few drops of a recently-prepared starch indicator solution. The development of a blue-blackish color is indicative of the presence of ozone. Other tests for ozone can be performed as well.

### Conclusions

Electrochemistry provides a wealth of weapons in the war against pollution. Many of these are suitable for undergraduate (or even high school) demonstrations and experiments.

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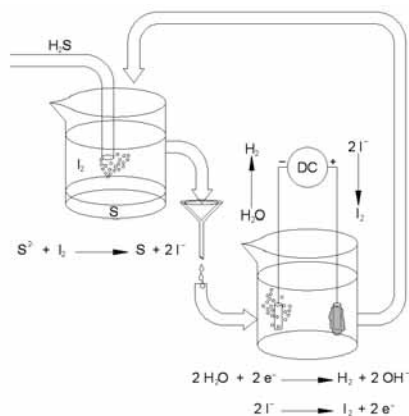


Figure 5. Electroremediation of  $H_2S$ .

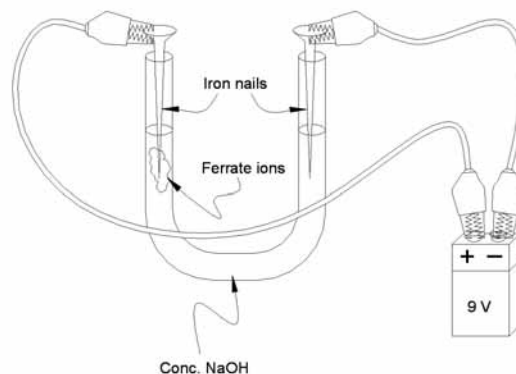
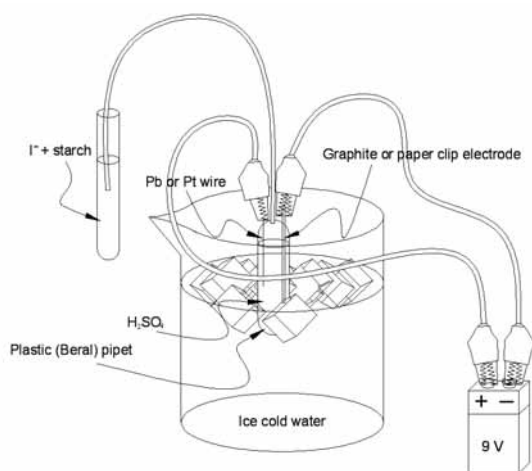


Figure 6. Electrochemical production of ferrate ions.



**Figure 7.** Electrochemical production of ozone (adapted from Ibanez, 2005).

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