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# Laboratory Experiments on Electrochemical Remediation of the Environment. Part 2: Microscale Indirect Electrolytic Destruction of Organic Wastes

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Several electrochemical processes can be used for the prevention and or remediation of environmental problems (1-11). We have described in this *Journal* the electrocoagulation of an oil-water emulsion (12).

The objective of the experiment described below is to destroy, at the microscale level, a sample of surrogate organic waste by generating a powerful oxidizer at the anode of an electrochemical cell. This in turn will oxidize the waste to harmless products. The oxidizer can then be regenerated and recycled.

## Indirect Electrolysis

The electrolytic production of an intermediate species for the oxidation/reduction of another substance is known as *indirect electrolysis*. Many polluting species can be oxidized directly at an electrode; however, this process is often limited by diffusion or by electrode kinetics. Potentials much higher than the standard oxidation potential of a given species (overpotentials) are frequently required to attain reasonable rates of oxidation, necessitating more energy and the use of corrosion resistant electrodes such as noble metals. Alternatively, homogeneous or heterogeneous redox-mediated processes can generate redox species electrochemically as mediators for transferring electrons from the electrode surface to the pollutant. These processes are reversible or irreversible, depending on whether the mediator can or can not be electrochemically regenerated and recycled in the process. The equations that describe the reversible case (for an oxidation reaction) are:



where C is the redox mediator, R is the pollutant species,  $Ox^+$  is its oxidized product, and  $E_1^\circ$  and  $E_2^\circ$  are the corresponding standard potentials for reactions 1 and 2 (here,  $E_1^\circ > E_2^\circ$ ). This type of process has also been termed *mediated electrochemical oxidation*, or MEO (13-15). In addition to the reduction or oxidation of the target pollutant, other reactions can compete. The most likely cathodic parasitic reactions (reductions) in the presence of oxygen in aqueous solutions are proton reduction (to form  $H_2$ ) or oxygen reduc-

tion (to form  $OH^-$ ), whereas the most common competing anodic reaction (oxidation) is the oxidation of water (to form  $O_2 + H^+$ ).

In the following experiment, a microscale version of this technique utilizes a redox mediator with a high standard potential (viz., the Co(III/II) couple,  $E^\circ = 1.82$  V) to destroy a surrogate organic waste (e.g., glycerin or acetic acid) by converting it into  $CO_2$  and water. This process has been shown to successfully destroy some chlorinated and nonchlorinated organics (13, 14). Students can observe the evolution of  $CO_2$ , which precipitates  $CaCO_3$  from a  $Ca(OH)_2$  solution, as well as the end of the reaction, which is signaled by a color change of the electrolytic medium (from pink to gray-light purple). Similar systems have been used with other redox mediators, mainly Ag(II/I), Fe(III/II), and Ce(IV/III) (13-16).

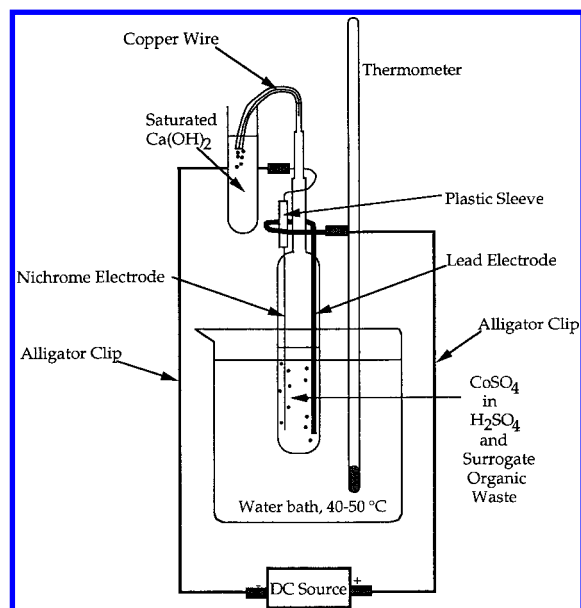


Figure 1. Microelectrochemical cell for the indirect electrolytic destruction of organic wastes.

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## Experimental Procedure

Obtain a disposable plastic transfer pipet (Beral pipet) of approximately 5–6 mL capacity for use as a microelectrochemical cell. Cut 6–7 cm (approx. 2.5 in.) of Pb wire (alternatively, a small piece of thin Pb foil can be “rolled” so as to make a wire replacement) to act as the anode and a similar length of either nichrome wire or a paper clip (normally made of steel) to serve as the cathode. Pt wire can also be used as the anode. Insert the electrodes in opposite sides of the upper portion of the Beral pipet so they do not touch each other, as shown in Figure 1. Prepare a clear saturated solution of  $\text{Ca}(\text{OH})_2$  by stirring approximately 0.2 g of  $\text{Ca}(\text{OH})_2$  in 10 mL of deionized water followed by filtration. The mediator is prepared as a stock solution of 0.05–0.1 M  $\text{CoSO}_4$  in 2 M  $\text{H}_2\text{SO}_4$ . Place 2–3 mL of this solution in a small container. In a separate vessel, prepare a solution of a nonvolatile surrogate organic waste—for example, by adding 1 drop of glycerin to 40 drops of water. Add one drop of this solution to the cobalt–sulfuric acid solution. If acetic acid (or vinegar) is used, add 4 drops of a 6 M acetic acid solution directly to the cobalt–sulfuric acid solution. Shake to dissolve. Then, either draw this pink solution into the Beral pipet through its stem or introduce it with a disposable Pasteur pipet or a small syringe through one of the holes punctured by the wires (then, reinsert the wire that was removed). To prevent any gas leaks (see below), a silicone-type sealant or melted wax may be applied at the electrode insertion points. Next, place the saturated  $\text{Ca}(\text{OH})_2$  solution in a small collection tube. Introduce the tip of the stem of the pipet into this solution so that the gases exiting from the pipet bubble through it. A piece of Cu wire may be inserted to facilitate its bending (see Fig. 1). Place the bulb of the pipet in a hot (40–50 °C) water bath. Connect the wires with alligator clips to the positive (Pb wire) and negative (nichrome wire or paper clip) ends of a DC power source that has a potential of at least 3 V (e.g. a 9-V battery, an AC/DC adapter or an adjustable dc power source). A voltage fall below this value would not have enough driving force to carry out the desired reaction.

## Results and Discussion

Once the power source is turned on, bubbles are observed at both electrodes. Water is being reduced to hydrogen at the cathode, whereas at the anode water is being oxidized to oxygen gas and  $\text{Co}^{2+}$  is being oxidized to  $\text{Co}^{3+}$ , which in turn oxidizes the organic compound to the  $\text{CO}_2$  that forms insoluble  $\text{CaCO}_3$  when it comes in contact with the freshly prepared  $\text{Ca}(\text{OH})_2$  solution. When all the organic compound has been destroyed (after 10 to 30 min, depending on the amount of organic compound added, the number of carbons in it, and the applied voltage), the solution turns gray–light purple because  $\text{Co}^{3+}$  ions continue to form but are no longer

used up to oxidize the waste. This color change indicates the end of the reaction. (The  $\text{Co}^{3+}$  can also oxidize water, although this reaction is considerably slower.) At this point, the liquid can be squeezed from the pipet into a small beaker and while it is still hot, some more surrogate organic waste (e.g., one drop of glycerin or ethanol) can be added to it to be oxidized. An immediate change in color to the initial pink is then observed. To test the presence of  $\text{CaCO}_3$  in the collection tube, add to it a few drops of dil  $\text{H}_2\text{SO}_4$  or dil  $\text{CH}_3\text{COOH}$ , which dissolves the precipitate producing  $\text{CO}_2$ .

The  $\text{Co}(\text{II})$  solution and Pb electrodes can be reused. Because a small amount of Pb may be present in this electrolyte owing to the anodic process, reuse of this solution will be more environmentally sound.

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