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Laboratory Experiments on Electrochemical Remediation of the Environment: Electrocoagulation of Oily Wastewater

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Oily wastewater is generated from many sources, such as, machining shops, refineries, off-shore platforms, automotive repair shops, and oil transportation, distribution, and storage facilities. The free or suspended oils can be readily separated from the aqueous phase in these wastes by simple physical processes (e.g., skimming). However, chemically stabilized oil–water emulsions present an environmental problem. The usual treatment is chemical deemulsification followed by a precipitation reaction (1). This method, however, generates a high water-content sludge with attendant dewatering and disposal problems (2).

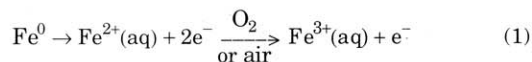
We describe below a simple laboratory experiment based on an electrolytic alternative for treating oily wastewater (2, 3). This experiment, which can be carried out within a 3-h laboratory period is designed to highlight an important environmental problem and to demonstrate how chemistry, specifically electrochemistry, can play a useful role in waste disposal and environmental restoration.

Electrocoagulation of an Oil–Water Emulsion

An oil–water emulsion is a colloidal dispersion in which oil constitutes the dispersed phase and water forms the continuous phase (4). A common example of an emulsion is milk, which contains fat dispersed in water. Emulsions are normally stabilized by the presence of an emulsifying agent, such as a surfactant (4). In milk, the (natural) emulsifying agent is casein, a protein that contains phosphate groups. The anionic head groups on the surfactant molecules prevent aggregation and coagulation of the oil droplets via electrostatic repulsion. (See Fig. 1a.)

Progressive Electrolysis

During electrolysis in an electrocoagulation procedure, the sacrificial iron anode is oxidized to Fe^{2+} , which in turn is further oxidized to Fe^{3+} ions (2).



With progressive electrolysis, the ionic strength of the medium increases. The electrogenerated cations with their high (+3) charge effectively “shield” or neutralize the surface charge on the surfactant molecules (Fig. 1b). Simultaneously, hydrogen is evolved at the cathode.



The pH of the medium rises as a result of this electrochemical process. The net result of the reactions of eqs 1

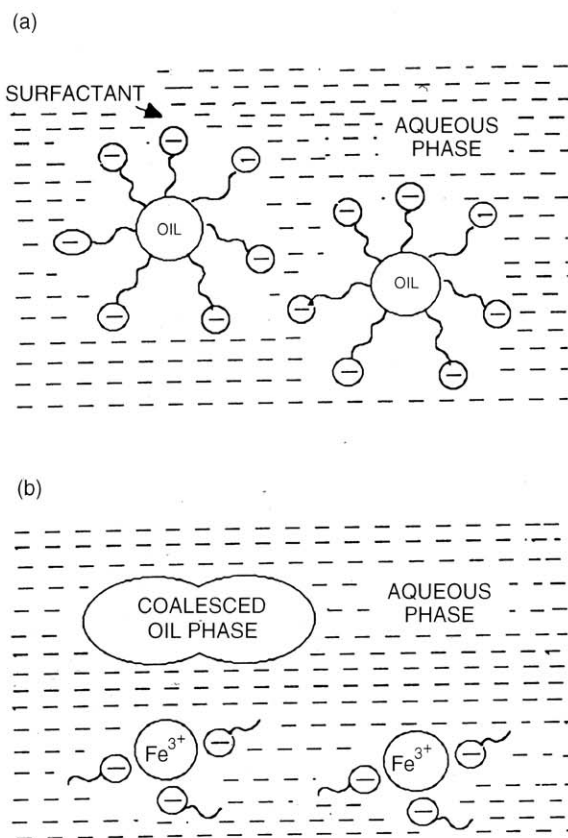


Figure 1. (a) The stabilization of an oil–water emulsion by a surfactant shown with a polar (e.g., anionic) head group and a nonpolar tail. (b) Early stages in the coalescence of oil droplets.

and 2 is that the emulsion is destabilized, and the colloidal oil particles begin to coalesce (Fig. 1b).

Formation of an Oil-Rich Sludge

Ultimately, the destabilized oil droplets sorb onto the highly dispersed ferric hydroxide colloid formed by the reaction between the electrogenerated Fe^{3+} and OH^- .



The oil-rich sludge floats to the top where it is easily removed by skimming.

The process is called electrocoagulation because coagulation of the oil is promoted by electrolytic means (2, 3). Electrolytic cells and electrochemical concepts are discussed in several textbooks (5). Figure 2 contains a schematic of the experimental set-up for electrocoagulation.

This paper was presented at the 205th ACS National Meeting in San Diego, CA, March, 1994.

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Experimental Procedure

- **Caution:** The stainless steel shaving blade used as the cathode has *sharp edges*. Use care in handling.

Cell

A 250-mL beaker can be used as the electrolytic cell. We have used a stainless steel shaving blade as the cathode. An iron plate of approximately the same dimensions serves as the anode. The reference electrode shown in Figure 2 is optional. We have used a SCE for monitoring the potential of the anode. A regulated dc power supply was used to apply 1.5 V between the anode and cathode as illustrated in Figure 2. A voltmeter and ammeter (Fig. 2) are optional for monitoring the anode potential and the current during electrolysis.

Procedure

A suitable emulsifier (e.g., 0.9 g of Tween 80 or Triton X-100) is added to 90 mL of a 0.1 M NaCl solution in the beaker. Then 10 g (about 11 mL) of sunflower-seed oil is added to this solution with vigorous stirring. After this emulsification step, the power supply is connected to the two electrodes as shown in Figure 2. (The polarities are important when making the connections). Air-bubbling is simultaneously provided (from a compressed air source) for several reasons:

- to promote the coalescence of the oil particles
- to detach the hydrogen gas bubbles from the cathode surface
- to induce the flotation of the oil layer

Analyses

One-milliliter samples are removed from the beaker every few minutes with a syringe. The oil is extracted in each sample with 1 mL of hexane followed by centrifugation. Sodium methoxide (1 drop of a 14% solution) must be added to the oil extract to esterify the fatty acids because they have high molecular weights and high boiling points; the corresponding methyl esters are low-boiling derivatives, and thus require only modestly high column and injection-port temperatures for their GC separation.

We have used a Hewlett-Packard (Model 5890 series II) equipped with a Model 5971 mass-selective detector or a Perkin-Elmer Sigma 300 fitted with a flame ionization detector for GC analyses. A typical set of analysis conditions is

- helium flow rate and pressure, 1 mL/min (5 psi)
- injection port temperature, 250 °C
- detector temperature, 280 °C
- column temperature program, 60 °C to 235 °C at 8 °C/min followed by a 13-min plateau at 235 °C
- column, Carbowax, 30-m long, 0.32-mm-inside diameter

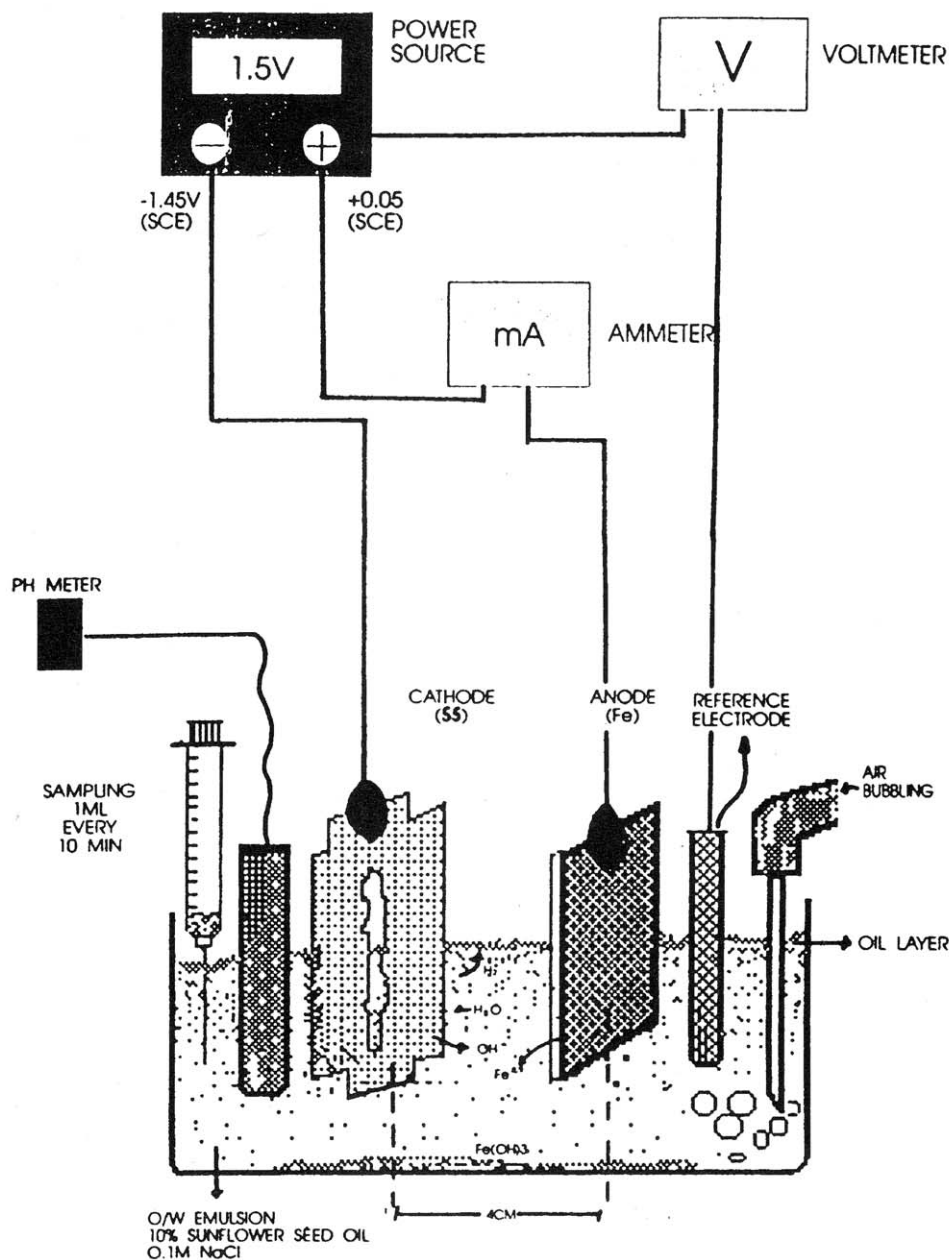


Figure 2. The set-up for electrocoagulation of an oil-water emulsion.

Aliquots (e.g., 1 μ L) of the derivatized samples were injected into the GC column for analyzing their oil content.

Under these conditions, excellent separation of the (methylated) main components of the oil (i.e., palmitate, oleate, and linoleate) was obtained; Figure 3 contains a representative set of gas chromatograms. The various components are identified from their retention times by injecting standard samples under the same conditions. Other measurements that can be carried out in this laboratory exercise include monitoring of the solution pH and the anode potential as a function of electrolysis time.

Results

After only a few minutes of electrolysis, an oil layer starts forming at the top of the solution in the beaker. Simultaneously, iron hydroxide begins to appear in the solution. After about half an hour, the solution becomes clear at the bottom, and the top oil layer can be skimmed off. The change in the oil content of the solution is shown in Figure

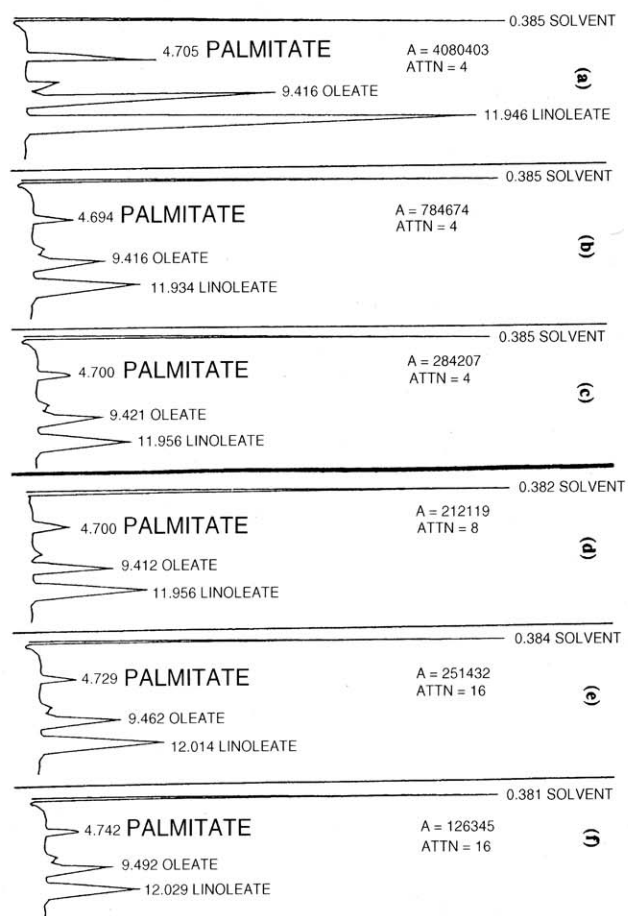


Figure 3. Gas chromatograms as a function of electrolysis time (in min); (a) 0.5, (b) 8, (c) 20, (d) 30, (e) 144, (f) 288. The peak amplitudes (in arbitrary units) are shown in each frame as well as the area (A) of the linoleate peak and the ordinate scale setting (ATTN). Note the increase in the ordinate sensitivity in d–f relative to a–c.

4a, and the pH change is illustrated in Figure 4b. The former was obtained from quantitative analyses (i.e., integration) of the GC peak corresponding to linoleate (see also Fig. 3). The region of relatively constant pH in Figure 4b signifies iron hydroxide formation.

Conclusions

This simple experiment provides an excellent opportunity for the instructor and the students to explore a variety of aspects including the following.

- Colloid chemistry and the principles of emulsion formation. The role of emulsifying agent may also be examined.
- The electrochemistry of iron corrosion. The change of the anode potential with time may provide useful clues, and the students can consult the literature (ref 6).
- The mechanistic aspects and the chemistry underpinning electrocoagulation. Again, the original literature (ref 2) may be consulted.
- The influence of variables, such as solution pH, the operating voltage, the anodic potential, and the salt content of the solution.
- The need for methylation of the fatty acids before GC analyses.
- The principles behind the GC separation of the oil components.

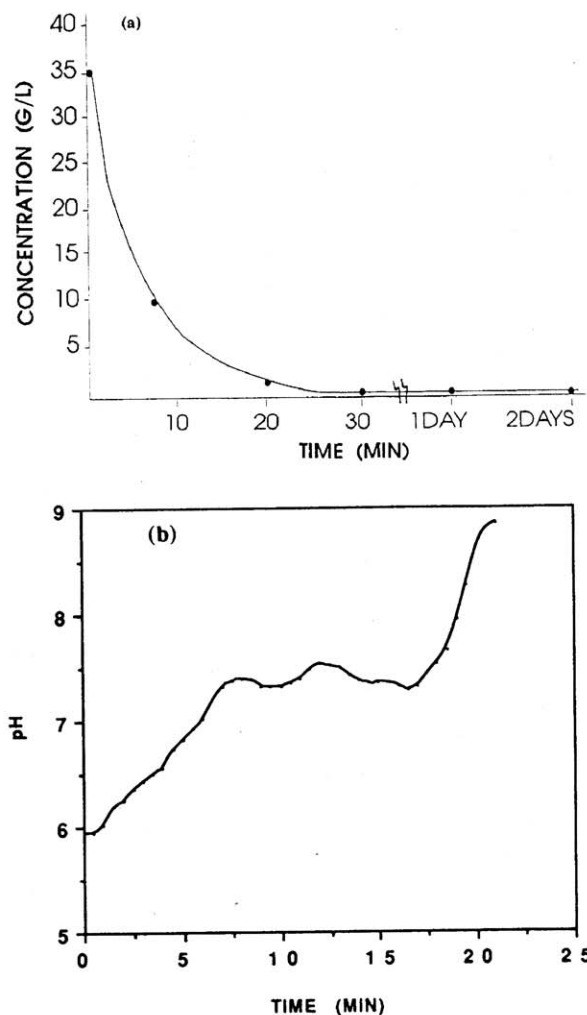


Figure 4. Variation of (a) the sunflower-seed oil concentration and (b) the solution pH with electrolysis time. The data in Figure 4a were obtained from GC analyses.

- Fundamental electrochemical concepts, for example, the distinction between voltage and (anode) potential.

The above topics could be discussed in a laboratory report of the experiment.

Acknowledgment

J. G. Ibanez thanks Arturo Fregoso and Samuel Macias at U. Iberoamericana (UIA) for helpful comments and discussions; and the Direccion General Adjunta and the Direccion General de Intercambio Academico of UIA and the Conacyt, Mexico for financial support. K. Rajeshwar wishes to thank Richard B. Timmons for access to the GC/MS instrumentation and Sebastian Vasquez for technical assistance.

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