

REDOX CHEMISTRY AND THE AQUATIC ENVIRONMENT EXAMPLES AND MICROSCALE EXPERIMENTS.

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Redox phenomena are common in the aqueous environment. We present here experiments addressing processes that require *light* as well as *dark* processes. Also, examples of pollutant-treatment schemes employing redox techniques are given.

Nitrate photolysis

Nitrate ions are photoreactive and produce the highly oxidizing $\bullet\text{OH}$ radicals (1,2). We devised a simple set up for undergraduate-level experimentation that uses a Hg-lamp to irradiate NO_3^- solutions contained in quartz test tubes. Oxidation of an added probe, Fe(II) to Fe(III) in the absence of air is ascribed to the production of $\bullet\text{OH}$ radicals. The Fe(III) thus produced is monitored at 450 nm. The (linear) results are shown in Figure 1.

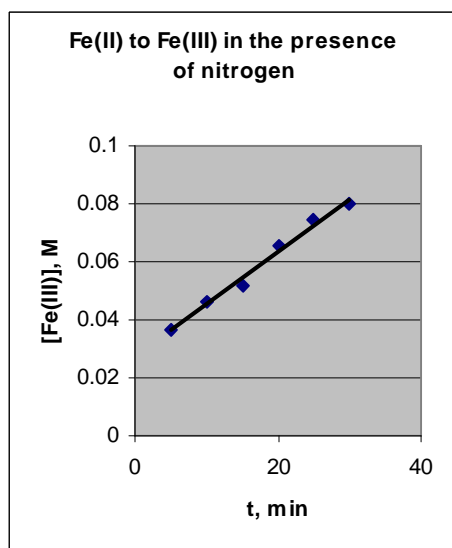
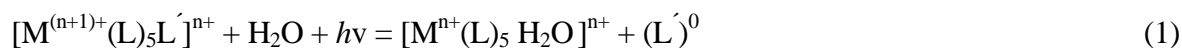


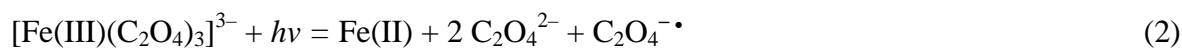
Figure 1. Fe(III) production from the photolysis of nitrates in the presence of Fe(II).

Photoreduction of a metal complex

The photochemistry of metal complexes often involves charge-transfer transitions, in which the excited state undergoes the transfer of electronic charge from an occupied orbital in the ligand to an unoccupied orbital in the central metal ion, reducing it to a lower oxidation state. This is depicted in the following reaction:



A typical example is the photolysis of iron carboxylato complexes (i.e., complexes with oxalate, aminopolycarboxylates, citrate, humic and fulvic acids), which can occur with high quantum yields. A simplified reaction mechanism is (using oxalate as the ligand) (3,4):



Note that C in the $C_2O_4^{-\bullet}$ ligand has an average oxidation state of +7/2, whereas in $C_2O_4^{2-}$ it is +3. Then, it underwent oxidation in order to reduce Fe(III). We designed an experiment in which an [Fe(III)EDTA] complex is exposed to light (either natural or artificial) and decomposed to produce Fe(II), which reacts with $K_3[Fe(CN)_6]$ as indicator, yielding a highly colored (blue) solution (5).

Photodissolution

Many solid iron compounds are photoreactive. We have worked on the photodissolution in the Fe(III)oxide-oxalato as a function of pH. We analyzed the oxalato speciation and found that the highest amount of Fe(II) produced (as measured by the standard colorimetric method with *o*-phenanthroline) corresponds to the pH region where the hydrogen oxalate anion predominates.

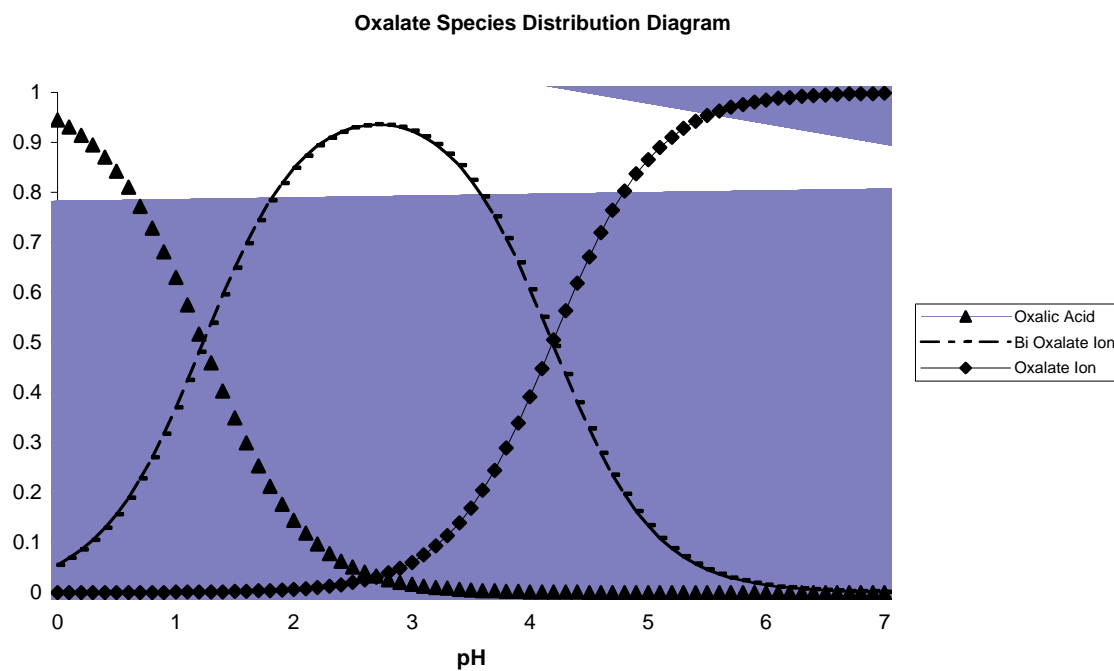


Figure 2. Distribution diagram for oxalate species (6).

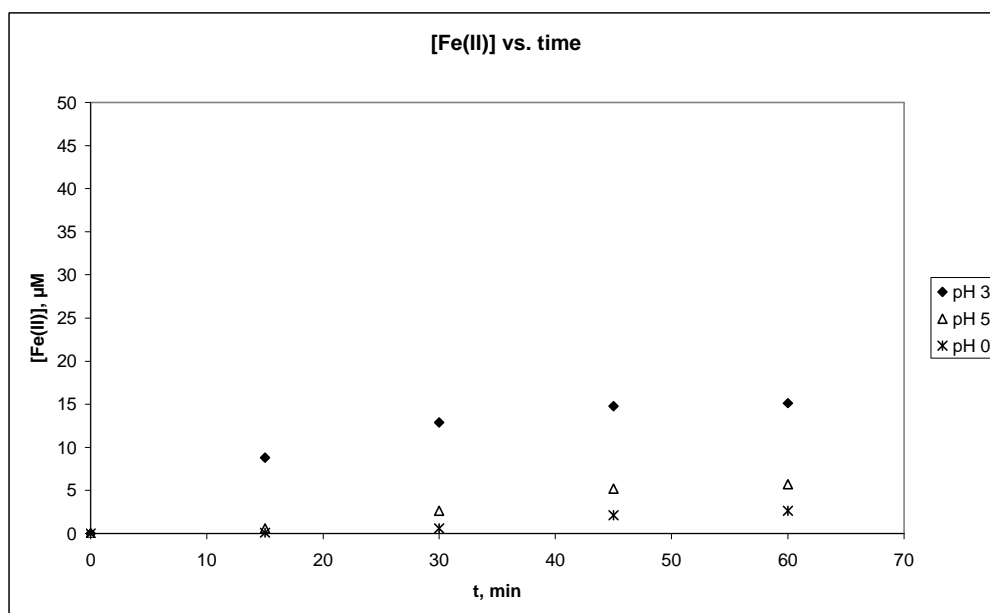


Figure 3. Photoproduction of Fe(II) as a function of pH and time.

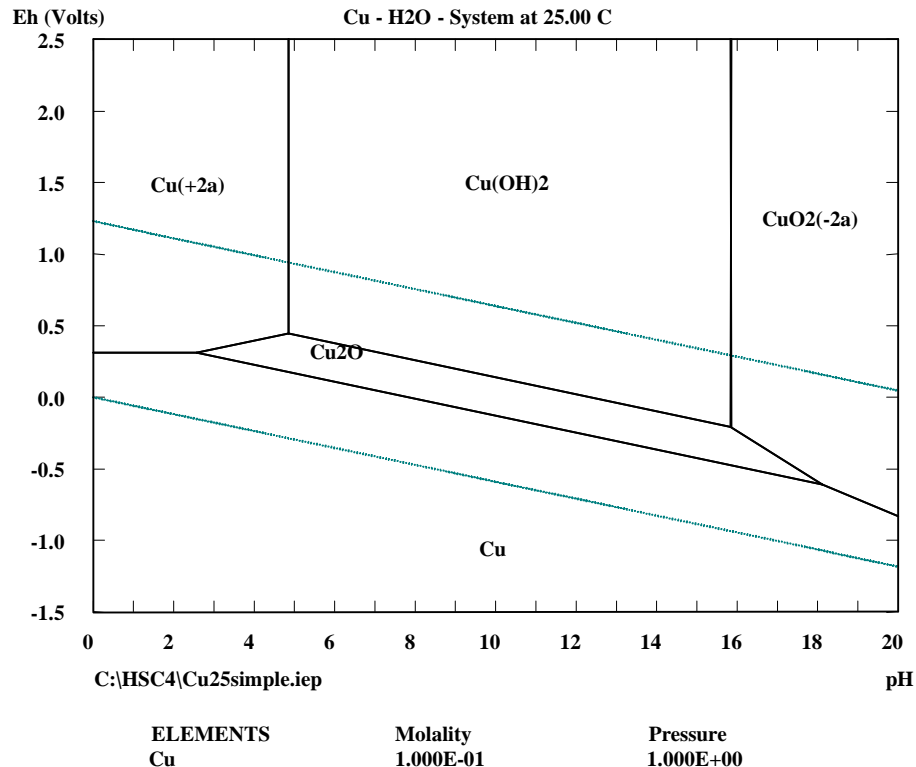


Figure 4. Pourbaix diagram of Cu species in water (8).

Pourbaix diagrams

Potential-pH diagrams are of paramount importance in Environmental studies. We have devised an experiment in which students perform five chemical and five electrochemical transitions in the Cu-Pourbaix diagram (Figure 4).

POLLUTANT-TREATMENT SCHEMES BASED ON REDOX REACTIONS

Fenton reaction

Organic pollutants and hazardous wastes can be mineralized upon oxidation by powerful oxidizing agents like hydrogen peroxide, which is capable of self-decomposing to produce a powerful oxidizer intermediate: the hydroxyl radical ($\cdot\text{OH}$). The reaction we use is



We demonstrate the effect of adding H_2O_2 to a surrogate pollutant, i.e., an acidified 0.003% solution of rhodamine B (sodium salt of 4-[(4-Dimethylamino)phenyl]-azo]benzene-sulfonic acid) under different conditions. The qualitative results obtained are shown in Table 1. We have also reported quantitative results elsewhere (9).

Table 1. Qualitative results from Fenton Chemistry.

Reaction vial	Effect	Major discoloration	Bubbling	BaCO ₃ precipitate
A	Blank	No	No	No
B	Fe ²⁺ alone	No	No	No
C	H ₂ O ₂ alone	No	No	No
D	H ₂ O ₂ + Mn ²⁺	No	Yes	No
E	H ₂ O ₂ + Fe ²⁺	Yes	Yes	Yes
F	Sunlight alone	No	No	No
G	H ₂ O ₂ + Sunlight	Yes	Yes	Yes

Photocatalysis

The simultaneous oxidation of an organic compound (ethanol) and the reduction of a metal ion (Cu²⁺) are photocatalytically performed in an aqueous slurry containing TiO₂ irradiated with UV light. This produces electrons (to reduce the metal ions) and holes (to oxidize the organic molecule). The experimental conditions are varied in such a way that only one of the qualitative tests (tube #5, see Table 2) gives a color change, indicative of the formation of a violet Cu⁺-TiO₂ complex. We have reported a quantitative procedure elsewhere (10).

Table 2. Experimental design for simultaneous photocatalysis.

Tube #	TiO ₂	Cu(II)	ethanol	N ₂	hν
1	✓		✓	✓	✓
2	✓	✓		✓	✓
3	✓	✓	✓		✓
4	✓	✓	✓	✓	
5	✓	✓	✓	✓	✓
6		✓	✓	✓	✓

Chemical oxidation: preparation of oxidants/disinfectants

a) Chlorine dioxide

Water treatment normally involves the use of oxidizing/disinfecting agents. A greener chlorine-based alternative to chlorine itself is chlorine dioxide, ClO₂ (also called chlorine peroxide). We produce chlorine dioxide mainly through the chemical and electrochemical reduction of Cl(V) or the oxidation of Cl(III). See ref. (11).

b) Ozone

We produce it electrochemically in the undergraduate laboratory with simple equipment and under very mild conditions. We designed tests to characterize it, observe its action in simulated environmental applications, and measure its rate of production (see 12).

c) Ferrate

Ferrate, a powerful oxidizing/disinfecting agent, is synthesized chemically and electrochemically in the undergraduate laboratory with simple equipment and under very mild conditions. We designed tests to characterize it and to observe its action in simulated environmental applications (see 13).

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