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Laboratory Experiments on the Electrochemical Remediation of the Environment



Part 8: Microscale Simultaneous Photocatalysis

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Light with supraband gap energy absorbed by a semi-conducting particle (e.g., TiO_2) can excite an electron from its valence band to the conduction band. This process also creates a positive hole in the valence band that may react with adjacent oxygenated species to produce $\cdot\text{OH}$ radicals (1). These are well-known powerful oxidants capable of degrading a wide variety of organic and inorganic pollutants and even of destroying bacteria (2, 3). At the same time the excited electron is capable of directly or indirectly reducing species in contact with the semiconductor. It has been shown in the literature that such phenomena are electrochemical in nature (3, 4) and are under intense study for application in the environmental remediation arena where they are globally called *photocatalysis*. Chemical educators have thoroughly discussed the corresponding theory and designed several experimental routes in this *Journal* to help students learn and understand the photocatalytic oxidation processes (5–9). In this article we extend this experimental approach to show the simultaneous oxidation of an organic species as well as the reduction of a metal ion.

Photocatalysis with TiO_2 has been used mainly to mineralize toxic organic pollutants in air, water, or soil matrices by converting them into small, nontoxic inorganic molecules such as CO_2 , H_2O , HCl (10, 11), and in some cases it has been used for the reduction and removal of metal ions from aqueous solutions, for example, $\text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}^+ - \text{TiO}_2(\text{s})$ (12–14). This last approach has also been visualized for the production of supported catalysts by photodeposition of dissolved metal ions, for example, $\text{Pt}^{4+}(\text{aq}) \rightarrow \text{Pt} - \text{TiO}_2(\text{s})$ (15). In a few cases, both the anodic and cathodic reactions have been advantageously utilized (16). Key thermodynamic and kinetic aspects of photocatalysis are discussed elsewhere (4, 17, 18). A summary of the advantages (2–4, 11, 19, 20), challenges (11, 21, 22), and proposed solutions (5, 21, 23–25) in TiO_2 photocatalysis is given in the Supplemental Material.^W

As with their electrochemical counterparts, photocatalytic processes have almost always focused on one side of the phenomenon (typically the anodic component) and have essentially wasted the energy spent on the complementary reaction. A few cases have been reported in which both sides are used for pollutant treatment (19). In this article we describe a microscale experiment in which the simultaneous oxidation of an organic compound and the reduction of a metal ion are photocatalytically performed in an aqueous slurry containing TiO_2 irradiated with UV light. This experiment

allows students to gain a better comprehension of the different phenomena involved in a typical photocatalytic process.

Experimental Procedure

A TiO_2 suspension containing a metal ion, Cu^{2+} , and a surrogate organic pollutant, citric acid, will be irradiated with UV light to produce electrons (capable of reducing the metal ions) and holes (capable of oxidizing the organic molecule). With distilled or deionized water, prepare the following: (i) an aqueous slurry of 100 mg of TiO_2 (Degussa P25) in 50 mL of water, (ii) a 0.33 M solution of citric acid, and (iii) a 0.04 M solution of CuSO_4 . Arrange a setup consisting of a miniature UV-quartz pencil lamp (Spectroline model 11SC-1, Spectronics Corp.) introduced into a quartz test tube (Ace Glass, 13-mm o.d., 100-mm long quartz tube without lip). Surround this tube with six other labeled quartz tubes and secure them with two rubber bands. Place the bundle inside a 100-mL beaker on top of a magnetic stirrer (Figure 1). Add

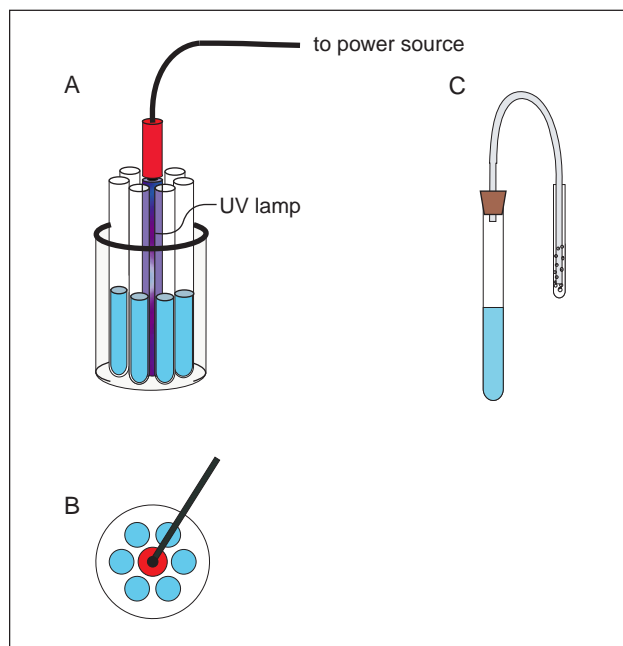


Figure 1. Experimental setup: (A) side view, (B) top view, and (C) collection tube containing barium hydroxide solution.

a stirring bar to each of the six labeled test tubes (triangular bars of the type used with conical-bottom vials work well). Add 2.5 mL of the TiO_2 suspension, 1 mL of the citric acid solution, and 2.5 mL of the CuSO_4 solution to each tube. Bubble nitrogen gas from a nitrogen tank into each of the resulting solutions for ~ 3 min and seal each tube with parafilm. If a test for the production of CO_2 is desired, instead of using parafilm, cap each quartz tube with a one-hole rubber stopper connected by a glass capillary U-tube to a small (5-cm long, 5-mm i.d.) test tube half-filled with a saturated Ba(OH)_2 solution as a CO_2 trap (Figure 1C). Before initiating the UV illumination, make sure that all six stirring rods are agitating each solution up to its highest point, and that you have a thick cardboard box or another suitable protective covering between the UV lamp and people to prevent any possible UV exposure. For added protection, cover the whole setup with a polyethylene bag.

Turn the UV light on and wait 10 min. Then turn it off and remove test tube 1. Cover the setup again and turn the UV light on once more. Move out of the reaction area, open tube 1, quickly filter its contents with a fine filter (we use a $0.45\text{-}\mu\text{m}$ syringe filter), and analyze for the removal of Cu(II) with the aid of a colorimeter or spectrophotometer set at 810 nm. (Note that the Cu(II) as well as the Cu(II) –citric acid absorbance spectra have their absorption maxima essentially at this same wavelength). Repeat the same procedure with the remaining five test tubes, after irradiating for 10 min every time. To show that light is required for this process to occur, a sample may be prepared and wrapped with Al foil, subject to the same conditions as the others, and then analyzed after a given period of time as to compare it with an irradiated one. Other articles in this *Journal* have addressed this effect more quantitatively (5, 7).

Hazards

UV light is dangerous so avoid exposure of any part of the body (particularly the eyes). Copper(II) sulfate is a strong irritant to skin and mucous membranes. BaCO_3 and Ba(OH)_2 are poisonous. Overexposure to TiO_2 may cause slight lung fibrosis, and it is a potential occupational carcinogen.

Results and Discussion

Cu(II) ions are removed from solution by photocatalysis. The Cu(II) absorbance decreases as a function of time, which reveals the extent of removal (Figure 2). This is the result of a photocatalytic-adsorption combined effect, which can be tested separately if desired as described in ref 5. Interestingly, the reduction of Cu(II) to Cu(I) yields a reversible, insoluble purple complex with TiO_2 (12). A very small quantity of elemental copper is sometimes observed as a thin-layer deposit on the walls of some quartz tubes, or even on the TiO_2 surface, which is further proof of its reduction. In addition, the production of a white precipitate in the collection tubes confirms the production of CO_2 as a result of the photocatalytic oxidation of the organic molecule. Once the experiment is finished, students can bubble oxygen from a tank into the purple suspension and observe in a few minutes the color change back to light blue as a result of re-oxidation

and dissolution of the Cu^+ in $\text{Cu}^+ \text{--} \text{TiO}_2(\text{s})$ that reverts to $\text{Cu}^{2+}(\text{aq})$. Air can also be used, instead of oxygen, but with less spectacular results. If desired, the photocatalyst may then be recovered by filtration with a $0.45\text{-}\mu\text{m}$ filter. This photo-redox cycling has been proposed as an environmentally friendly metal removal or concentration cycle (12). This is why the filtration step described above must be done quickly as to avoid metal re-dissolution, and this is also the reason for removing air by bubbling nitrogen at the beginning of the experiment. In addition, oxygen competes as an electron acceptor with Cu(II) . If desired, the whole experiment can be attempted without the deaeration step, in which case no observable results are obtained.

Conclusions

The simultaneous reduction of a metal ion and the concomitant oxidation of a surrogate organic pollutant by photocatalysis with UV-illuminated TiO_2 can be performed in a lab session with simple chemicals and equipment.

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Supplemental Material

A summary of the advantages, challenges, and proposed solutions in TiO_2 photocatalysis, instructions for the students, an additional student problem, and suggested mini-projects are available in this issue of *JCE Online*.

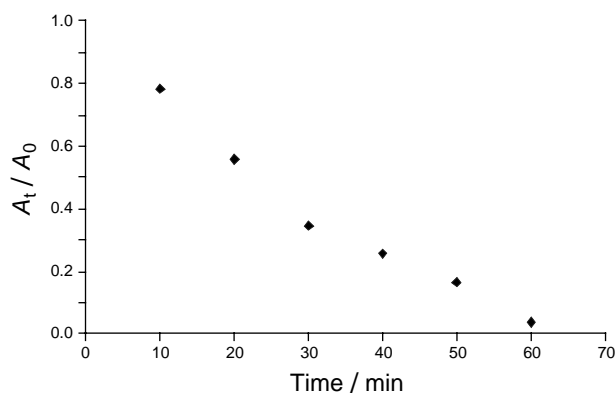


Figure 2. Cu(II) removal by photocatalysis. A_t is the absorbance at a given time and A_0 is the initial absorbance.

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