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Emerging Technology Bulletin

Photoelectrocatalytic Degradation and Removal of Organic and Inorganic Contaminants in Ground Waters

Study Performed at the University of Wisconsin – Madison Water Chemistry Program

Technology Description: The University of Wisconsin – Madison (UW-Madison) is developing a photocatalytic technology that uses titanium dioxide (TiO_2) suspensions to coat various supports used in aqueous treatment applications. Photocatalysis involves the use of UV light to illuminate the surface of a catalyst such as TiO_2 . As the photocatalyst absorbs near-UV light, electrons in the valence band are excited into the conduction band and produce highly reactive electrons and holes that promote oxidation of organic compounds. In this project researchers sought to overcome some of the challenges of photocatalysis by developing a “biased” photoreactor. A metallic substrate was coated with TiO_2 to prepare a photoelectrode which was then combined with a cathode to form an electrolytic cell. UV light illuminates the TiO_2 coating on the electrode and allows the electrolytic cell to serve as a biased photoreactor, which was the subject of this study. A design for a biased photoreactor in an annular configuration is shown below. A similar system was employed for this project.

In this approach, coating a conductive substrate (metal foils in this project) with a thin film of TiO_2 (< 1 micron thick) allows a positive potential to be applied across the catalyst, producing a photoanode. Electrons produced when the catalyst is illuminated flow preferentially to a separate cathode. This approach provides several advantages over the conventional photocatalytic oxidation (PCO) process.

- 1) By forcing photogenerated electrons and holes to move to separate electrodes, electron-hole recombination within the catalyst is minimized, thus increasing the rate of oxidation of organic contaminants.
- 2) In conventional PCO, photogenerated holes oxidize dissolved organics in the waste stream. However, another species, typically dissolved oxygen, is required to remove photogenerated electrons or else the process will shut down. In a biased photoreactor, the electron-accepting (reduction) reactions occur on a separate electrode (the cathode). Consequently, several species in the test solution can act as electron acceptors, possibly increasing the overall rate of reaction.

- 3) In conventional PCO, many materials present in natural or wastewaters can deposit on photocatalysts, deactivating them. Specifically, dissolved metal ions such as copper and silver react with photogenerated electrons to form zero-valent metals that deposit (or electroplate) on the catalyst. In a biased photoreactor, these reduction reactions occur on one electrode whereas organic oxidation occurs on a separate electrode, thus minimizing catalyst deactivation. One might employ biased photoreactors to treat mixed wastes containing both organic contaminants and dissolved heavy metals (and/or reducible oxyanions such as nitrate or perchlorate) and then reclaim the metals after they deposit on the cathode.

Early studies of biased photoreactors suggest two further advantages of this approach as compared with conventional PCO.

- 1) Solutions containing only a dissolved organic contaminant could be treated in biased photoreactors with no oxygen present, whereas conventional PCO requires dissolved oxygen.
- 2) Solutions containing relatively high concentrations of dissolved salts (specifically NaCl) could be treated in biased photoreactors, whereas saline solutions inhibit conventional PCO. This phenomenon might extend to ions such

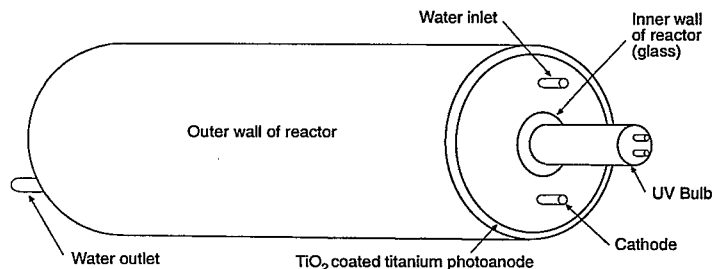


Figure 1. Biased photoreactor design employing a TiO_2 -coated photoelectrode in which a sheet of titanium is coated with TiO_2 , rolled into a cylinder, and placed inside the outer wall of the reactor.



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as bicarbonate that are known to be problematic in the UV/TiO₂ treatment of contaminated groundwater.

In addition, the use of thin-film TiO₂ photocatalyst coatings on supports allows one to distribute the activating UV radiation relatively uniformly throughout the reactor. This technology does not require the addition of oxidants such as ozone or hydrogen peroxide to achieve complete oxidation of organic contaminants. Because the catalyst adheres to a support, there is no need for an additional unit to separate and recover the catalyst from the purified water after the reaction is complete.

Waste Applicability: This technology is designed to treat groundwater and dilute aqueous waste streams contaminated with semivolatile organics, some dissolved metal ions, and possibly some oxyanions. Organics are completely oxidized to carbon dioxide, water, and halide ions. Dissolved metals that plate out on the cathode can be stripped and subsequently recovered. Oxyanions may be reduced to lower oxidation states (e.g., perchlorate to chloride).

Status: The UW-Madison photoelectrocatalytic technology was accepted into the SITE Emerging Technology Program in 1995. The overall objectives of this study are to develop an effective photoelectrode and to refine the reactor design to allow the unit to treat dissolved metals as well as organic contaminants. Material development difficulties limited this project to laboratory studies at a bench-scale level. Most studies were performed with a surrogate waste consisting of a solution of formic acid (usually 25 ppm as C) in 0.01 M NaCl.

Stable photoelectrodes with reproducible behavior were prepared by coating TiO₂ on titanium supports. Coated copper, aluminum, and stainless steel supports could not withstand the treatment conditions. Tests employing a bench-scale, flow-through biased photoreactor with both electrodes placed in one compartment indicated that the rate of oxidation of formic acid increased 50% by applying potentials of +1 to +2 V across the

photoelectrode as compared with operating with no applied potential. Under these applied potentials, 500 mL of waste were treated by recirculation at 90 mL/min with a half-life of ca. 1 hour. Because the half-life of this reaction was directly proportional to the initial concentration of the organic contaminant, this technology appears to be best applied to aqueous solutions containing low concentrations of organic contaminants. Rates of reaction were similar when either oxygen or nitrogen was bubbled through the solution. In one test in which copper (II) nitrate was added to the surrogate waste, both copper and formic acid were removed from the waste.

In early 2001 the EPA will publish an Emerging Technology summary that describes the results in greater detail.

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