United States
Environmental Protection
Agency

SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Emerging Technology Summary

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

Photocatalytic oxidation offers a means of remediating low concentrations of organics in aqueous and air streams. Commercial development of this technology is limited by relatively low rates of oxidation of organics in aqueous systems and by fouling of the catalyst by other components of the waste stream. Results from this project indicate that applying an appropriate electric field across the photocatalyst extends the range of applications for this technology. The resulting "biased" photoelectrocatalytic reactor demonstrates ca. 40-60% higher rates of degradation of the test organic (25 ppm (as C) formic acid) than are observed in the corresponding non-biased reactor. However, the overall rate of reaction is still slow even when biased (a half-life of ca. 1 hour). This biased photoreactor successfully treated a waste containing both formic acid and dissolved copper. In addition, the biased photoreactor was not adversely affected by use in either relatively saline media or in media containing no dissolved oxygen. Non-biased photoreactors do not function under these conditions. Earlier studies of biased photoreactors employed photocatalysts coated on conductive glass. Because such photoelectrodes may not be commercially viable, photoelectrodes that were stable during repeated use were prepared for this project by coating the photocatalyst on a metallic substrate.

Introduction

Many remediation technologies treat relatively high concentrations of contaminants. Numerous laboratory studies suggest that photocatalytic oxidation (PCO) effectively treats low concentrations of organic contaminants (ca <100 ppm, either by weight in water or by volume in air) [1-3]. This emerging technology utilizes visible or near-UV light to activate a photocatalyst that then reacts with chemical species at or near the catalyst surface. Specifically, the photocatalyst must absorb a photon with enough energy to excite an electron from the occupied valence band of the material to its unoccupied conduction band (i.e., radiation with energy greater than the band gap energy of the material). Electron promotion also produces a positive hole. If this photogenerated electron-hole pair recombines, heat is produced. However, if they reach the surface of the material before recombining, either with themselves or other photogenerated electrons and holes, they can then react with species in the surrounding medium.

In most PCO studies, the photogenerated holes combine with water to form highly reactive hydroxyl radicals that then oxidize organic contaminants. Under appropriate reaction conditions, the organic contaminants are completely oxidized to CO_2, water, and halide ions with minimal, if any, generation of undesired byproducts [2,3]. However, several constraints on this process have limited commercialization of this technology for purifying water.

This project addresses three specific constraints. 1) Low apparent efficiencies of photon utilization (ca. 1-2% at best), where efficiency refers to the number of molecules degraded per incident photon. Relatively low rates of oxidation result, caused in part by electron-hole recombination within the photocatalyst. 2) Need to remove photogenerated electrons from the catalyst. Dissolved oxygen is generally employed for this purpose, but its concentration in water is low (ca. 8 ppm for room temperature water equilibrated with air). The resulting low rate of electron removal by this small amount of dissolved oxygen may limit the rate of oxidation that is observed in aqueous systems. 3) Catalyst deactivation. Many materials present in natural or waste waters can deposit on photocatalysts, deactivating them. Dissolved metal ions are a major concern because many metal ions (e.g., copper, silver) react with photogenerated electrons to form zero-valent metals that deposit (or electroplate) on the catalyst.

Applying an electric potential across a thin film of the catalyst, to produce a "biased photoreactor", can minimize these constraints. Such reactors employ separate electrodes: a working electrode coated with photocatalyst where holes oxidize organic contaminants (the photoanode) and a counter electrode where electrons reduce other species (the cathode). Applying a positive potential across the photoanode pulls photogenerated electrons to the cathode, thus minimizing electron-hole recombination within the catalyst and increasing the rate of oxidation of the organics. By separating the electrodes at which oxidation and reduction occur, concerns about deactivation of the photocatalyst are alleviated. Because the electron-accepting (reduction) reactions occur on a separate electrode, several species in the test solution can act as electron acceptors, possibly increasing the overall rate of reaction. One might even 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 suggested 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 even if no oxygen was 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.

Most of these early studies utilized electrodes in which the photocatalyst was deposited on conductive glass, a formulation that may not be suitable for commercial water purification systems. In this research project we fabricated photoelectrodes by coating the catalyst on a thin piece of conductive metal. Initial studies focused on selecting a substrate for the photoanodes from copper, aluminum, stainless steel, and titanium. Then a method was developed for fabricating effective and stable photoanodes on the selected substrate. Finally, a bench-scale, flow-through biased photoreactor containing an appropriate photoelectrode formulation was constructed and tested to elucidate its operating characteristics.

All studies were performed with titania-based photocatalysts synthesized using sol-gel processing techniques. Thin films (<1 micron thick) of these materials were coated on various substrates and then heated to sinter the film to the substrate and to obtain the desired crystal structure in the film [4]. Although the small amount of catalyst present in these thin films may limit the rate of oxidation, titania strongly absorbs the near-UV radiation required to activate these photocatalysts. As a result, a film of titania only a few microns thick will absorb all of the incident UV radiation [5]. Therefore, the loss in photocatalytic activity associated with using titania films <1 micron thick is not as great as initially expected.

At present, it appears that biased photoreactors are best used with aqueous wastes that contain semivolatile organic contaminants (e.g., pesticides). Aqueous wastes containing low levels of organic compounds that are easily stripped from water are probably better treated by air stripping and passing the resulting contaminated air through a gas-phase PCO reactor.

Procedure

Synthesis of Photocatalysts

All photocatalysts were synthesized as stable suspensions of nanoparticles (diameters <10 nm) in either water or t-amyl alcohol via the controlled hydrolysis of the appropriate metal-alkoxide precursor [4]. All alkoxides and alcohols were used as obtained from Aldrich Chemical.

Preparation of Photoelectrodes

All tests conducted to select an effective metallic support and to determine appropriate fabrication conditions employed 5x10 cm plates of the metals with a thickness of 0.5 mm. All metals were initially cleaned for 5 h in an ultrasonic bath containing acetone with the bath cycled on and off for 15-min periods. Stainless steel plates (but no other metals) were then heated in air at 450°C to generate an oxide film that improved the adherence of the photocatalyst.

After cleaning, all metal plates were dip coated one time with the alcoholic suspension of titania using a withdrawal speed of 1.5 cm/min, air dried, and heated in air at 450°C for 1 h. Following pretreatment, the plates were dip coated with aqueous suspensions of either titania or mixed zirconia-titania. Other processing variables tested were number of coatings, firing temperature, and withdrawal speed. For multiple coatings, the plates were air dried and fired at the desired temperature after each coating. X-ray diffraction analysis of the coated titanium plates indicated that the coatings contained the anatase form of titania.

Preliminary experiments indicated that titanium was the most appropriate support for use in the flow-through reactor, as it was the only support material that did not visibly degrade during testing, either by pitting or causing the test solution to change color [4]. Based on results of these tests, a piece of pretreated titanium foil (20x14 cm, 0.05 mm thick) was dip coated two times with the aqueous suspension of titania using a withdrawal speed of 21.6 cm/min and fired in air at 300°C for 5 h after each coating to obtain the photoelectrode used in the flow-through photoreactor [6,7].

Testing of Photoelectrodes

Preliminary experiments to select a suitable metallic support and appropriate processing conditions for preparing photoelectrodes involved measuring the catalytic activity of individual photoelectrodes in a batch reactor. This

reactor consisted of a rectangular borosilicate glass vessel placed on a magnetic stirrer and set 10 cm from two parallel 15-W fluorescent UV bulbs (F15T8-BLB with a broad emission over 300-400 nm centered at ca. 365 nm). The irradiance at the photoelectrode was 1.35 mW/cm^2 based on a single measurement with a photometer. (Note, however, that the irradiance from the bulb decreases with increased time of operation. In general, this loss of irradiance is an inherent property of fluorescent bulbs; however, for these experiments this loss of UV output was accompanied by a decrease in the rate of the desired reaction over the same time period.)

Electrical potentials were controlled by a potentiostat operated in either a two- or three-electrode configuration using the photoelectrode (photoanode), a platinum mesh (2x5 cm) counter electrode (cathode), and a saturated calomel electrode (SCE) as a reference when needed, as shown in Figure 1**.** In this project, all voltages are measured with respect to an SCE (indicated as (vs SCE)), with the exception of the test of the flow-through photoreactor using a mixed waste.

Catalytic activities of photoelectrodes were determined by monitoring changes in the concentration of total organic carbon (TOC, but not including volatiles) in 70 mL of an aqueous solution of formic acid (25 ppm (as C)) in 0.01 M NaCl through which oxygen was bubbled continuously. Formic acid was selected because it is chemically unreactive in both electrochemical (expect for applied voltages > +2.75 V vs SCE) and direct photochemical (except for incident radiation with wavelengths < 260 nm) applications and is relatively nontoxic when diluted. Initial tests confirmed that there was limited, if any, adsorption of formic acid on these photoelectrodes and no loss of formic acid through volatilization. TOC measurements were employed because no long-lived intermediates were expected to form and our interest was in monitoring carbon removal rather than in quantifying any intermediates produced. Specifically, catalytic activities were evaluated by monitoring the change in TOC concentration in the test solution after exposure of the photoelectrode to UV radiation for 3 h.

Fabrication of Flow-through Photoreactor

The flow-through photoreactor was fabricated concentrically around an 8-W fluorescent UV bulb (F8T5BL). A 26-cm long Pyrex glass tube (22-mm OD) placed around the bulb served as the transparent inner wall of the reactor. The outside wall was a 26-cm long Pyrex tube (45-mm OD), providing a total reactor volume of ca. 200 mL. The photoelectrode was rolled into a cylindrical tube and fitted inside the outer glass wall. The irradiance at the photoelectrode was ca. 5 mW/cm^2. The cathodes were 15-cm long, 5-mm diameter, reticulated vitreous carbon (RVC) rods that contained 500 pores per inch. Platinum wires attached to the rods provided electrical contact. (Platinum wire or mesh also act as effective cathodes but were not used because of their expense. Smooth graphite sheets were tested but released carbon into the test solution. RVC rods are not the optimum choice because they are relatively weak.) Three cathodes were employed to obtain a relatively uniform electrical field throughout the reactor. Teflon end caps held the feed lines and cathodes. This reactor design was difficult to assemble without leaks, so the reactor was disassembled only after performing several tests once a leak-tight seal was obtained [7].

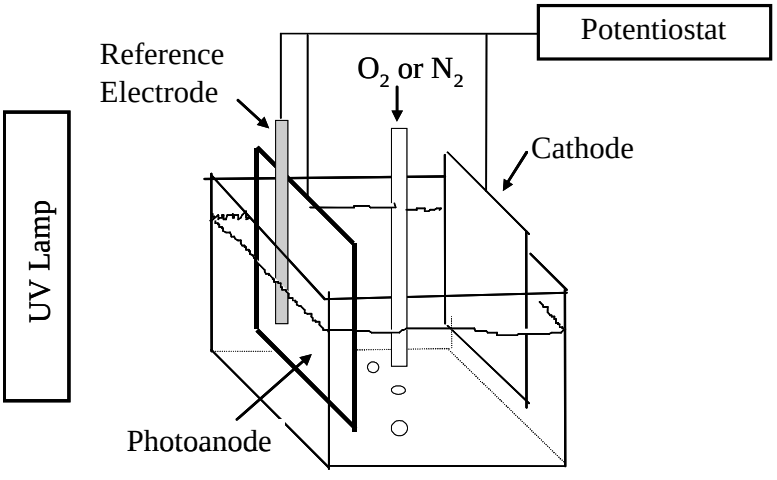

Figure 1. Schematic diagram (not to scale) of batch reactor system employed to test activities of photoelectrodes (photoanodes).

Testing of Flow-through Photoreactor

This photoreactor was evaluated by recirculating a test solution from a 500-mL reservoir. Initial tests and a study with a surrogate mixed waste (25 ppm (as C) formic acid and 50 ppm Cu(II) (from cupric nitrate) in 0.01 M NaCl) were conducted at flow rates from 4 to 27 mL/min even though mass transfer limitations were present (i.e., formic acid degraded faster at higher flow rates). In tests with the mixed waste, it typically required ca. 7 h to degrade 80-90% of the TOC and to remove ca. 50% of the dissolved copper at 12 mL/min and potentials up to +2.75 V. Clearly, this system can treat this waste, although these results cannot be used to estimate treatment rates in scaled-up units. Later tests employed only formic acid and showed a constant rate of removal at flow rates between 63 and 127 mL/min. Most tests were performed at 90 mL/min, typically requiring 3 h to remove 80-90% of the TOC.

The atmosphere in the test system was controlled by continuously bubbling either oxygen or nitrogen into the test solution after cleaning and humidifying the gas stream by passing it through deionized water. When necessary, pH and/or reaction temperature were measured in the solution in the reservoir. All samples were obtained from the reservoir.

Several characterization tests were performed with the solution used for the batch tests, 25 ppm (as C) formic acid in 0.01 M NaCl. To determine a kinetic expression relating the rate of reaction to the concentration of formic acid, formic acid concentrations between 4 and 70 ppm (as C) were utilized. For the mixed waste test, we did not verify the assumption that formic acid and cupric nitrate did not react.

For all tests of the flow-through reactor, the rate of removal of the contaminant of interest was observed by measuring the amount of contaminant remaining in the test solution at a minimum of seven different times, ideally with at least two measurements obtained after 50% removal of the contaminant. Throughout this project, measured concentrations of two samples obtained at a given time were averaged to obtain individual data points (i.e., measurements).

Results and Discussion

Initial tests were performed to develop an appropriate method for fabricating active photoelectrodes that provide reasonable reproducible performance. Results of these tests are reported in references 4 and 6. However, representatives of the U.S. Environmental Protection Agency (EPA) have not assessed the quality of the data underlying these reported results. These papers should be read with this caveat in mind. Results presented in the following sections are based on data that have been verified by the EPA. Some of the results presented herein are discussed further in reference 7.

Ability to Treat a Surrogate Mixed Waste

In initial tests of the flow-through photoreactor at flow rates of 4-27 mL/min (i.e., residence times of 8-50 min in the reactor per pass), higher activities were observed as the flow rate increased, indicating the presence of mass transfer limitations. Consequently, several tests were repeated at a flow rate that was high enough (ca. 90 mL/min with a residence time of some 2 min) to avoid these limitations. Results of tests conducted at 90 mL/min are discussed later.

One key test conducted at a low flow rate (12 mL/min) evaluated the ability to treat a mixed waste solution [formic acid + Cu(II)] at different operating conditions. Copper metal was observed to deposit on the three cathodes while formic acid was oxidized on the photoanode. For just this specific test, the applied potentials were measured directly between the photoanode and the RVC cathodes (i.e., a two-electrode configuration) instead of utilizing a saturated calomel reference electrode (i.e., a three-electrode configuration). This approach was taken in part to mimic the expected operation of a biased photoreactor in field applications, where a two-electrode configuration would likely be employed. However, because of this difference in operation, the values of applied potential reported in this section (not vs SCE) may not correspond directly to the values of applied potential reported elsewhere (vs SCE) in this project summary.

Given the difficulty in obtaining a leak-tight seal with the reactor design employed in these tests, the reactor was not disassembled after each test and copper was not cleaned off of the cathodes. As a result, recirculating the acidic test solution (pH > 3) through the reactor before turning it on caused some deposited copper to dissolve, leading to somewhat different initial concentrations of dissolved copper in each test. In spite of this confounding factor, the rates of removal of copper and carbon appeared to follow first-order kinetics. Up to 60% of the dissolved copper and over 80% of the carbon were removed in an 8-h period at applied potentials between +1.0 and +2.75 V. Direct comparisons of rates of removal of these contaminants are not feasible because of changes in irradiance in the reactor during the ca. 60 h of operation required to perform this set of experiments.

In addition, these rate constants are affected by the mass transfer limitations in the reactor. However, the presence of such limitations should not change the conclusion that a surrogate mixed waste can be treated with this configuration of a biased photoreactor.

The remaining tests were performed with just the formic acid test solution at a flow rate (ca. 80-90 mL/min) high enough to minimize these concerns. Increasing the flow rate to either 85 or 125 mL/min resulted in oxidation of ca. 80% of the formic acid in a 3-h period rather than 5 to 6 h as required at a 12 mL/min flow rate. In addition, because a given set of experiments could be completed in 10-15 h, changes in irradiance from the bulb were minimized. Tests with the mixed waste were not repeated at 90 mL/min because of time constraints.

Kinetic Expression for TOC Removal (at Constant pH)

Eventual scale-up of this system requires understanding the kinetics of photodegradation in this reactor, so the effect of varying the concentration of formic acid on its rate of oxidation was determined. These experiments were performed in oxygen with a potential of +1.0 V (vs SCE) applied across the photoelectrode. Although the mixed waste experiments were modeled assuming pseudo-first-order kinetics at a constant initial concentration of contaminant, these experiments required a more complex kinetic expression for a reasonable fit. The following Langmuir-Hinshelwood-Hougen-Watson expression proved suitable:

$$dC_F / dt = - (k K_F C_F) / \{S (1 + [K_F /S] C_F)\}$$

where k is a rate constant, K_F is a constant representing the adsorption of formic acid on the titania photocatalyst, S is a constant incorporating oxygen adsorption on the photocatalyst and the dissolved oxygen concentration in the test solution, and C_F is the concentration of formic acid (as represented by TOC) at time t.

Integrating this equation gives an expression for the half-life ($t_{1/2}$, the time required to oxidize half of the formic acid) of the reaction as a function of initial concentration of formic acid, C_{F0}:

$$t_{1/2} = S \ln 2 / (k K_F) + C_{F0} / (2 k).$$

A plot of $t_{1/2}$ vs C_{F0} is linear ($r^2 = 0.9957$) and yields the following values: k = 0.0206 ± 0.0025 mmol min^{-1} L^{-1} (equivalent to 0.247 ± 0.030 ppm min^{-1}) and K_F/S = 1.284 ± 0.488 L/$mmol^{-1}$ (equivalent to 0.107 ± 0.041 ppm^{-1}). However, this analysis is only valid when the pH of the formic acid test solution remains near 3.2 during photoelectrooxidation. Changes in pH during the reaction affect both the rate of oxidation of formic acid and the adsorption constant K_F. These values are also expected to change if one treats a mixed waste rather than pure formic acid.

Effect of Applied Potential on the Photodegradation of Formic Acid

An advantage of operating at a higher flow rate was that it allowed comparisons of the rates of removal of formic acid (monitored by TOC) as a function of applied potential. Rates of oxidation of TOC were compared with the reactor operated as a purely photocatalytic reactor (i.e., no applied potential, which is not the same as an applied potential of 0.0 V) and at applied potentials of 0.0, +1.0, and +2.0 V (vs. SCE). As shown in Figure 2, rates of oxidation increased as the applied potential increased.

Close inspection of Figure 2 indicates that little reaction occurred during the first few minutes of operation. Therefore, rate constants for the comparisons discussed below were calculated without including the data points at the start of the tests. In addition, the last two data points for the NAP test were excluded, as the reaction essentially ceased after 150 min of operation with a corresponding increase in the pH of the test solution to above 5.

Table 1 presents the rate constants, error estimates for those rate constants to within a 95% confidence interval, and the coefficients of determination (i.e., r^2 values) for the fit of each set of data to a first-order rate expression for each of the conditions shown in Figure 2. Based on the results of a least significant difference multiple comparison procedure, it appears that, to within a 95% confidence interval, the rates of degradation for the pure photocatalytic reaction and any photoelectrocatalytic reaction with an applied potential of 0.0 V or higher are different. On the other hand, in comparing photoelectrocatalytic reactions at differ-

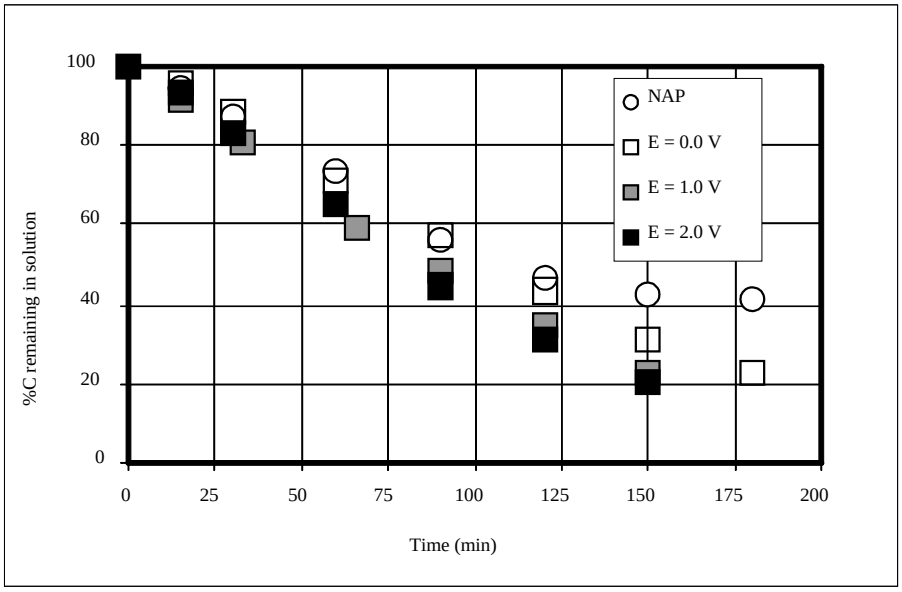

Figure 2. Effect of applied potential on the photodegradation of an oxygenated formic acid test solution (25 ppm as C in 0.01 M NaCl). (NAP = No Applied Potential)

ent applied potentials, there is no statistical difference at a 95% confidence level in the rates of degradation at +1.0 V and +2.0 V. No other comparisons were made at this time. (The value of the rate constant for an applied potential of +2.0 V corresponds to a half-life of about 1 h for 25 ppm as C formic acid. Because half-life is directly proportional to the initial concentration of contaminant in this system, this reactor is more effective for treating wastes with low concentrations of organics.)

Effect of Operating Conditions on pH in the Biased Photoreactor

Colloid chemists have observed that the properties of oxides such as titania are strongly affected by pH when in contact with water. The variations in oxidation rate noted above correlate with the pH of the test solution, which reached 3.2 after recirculation through the non-operating reactor. In the biased photoreactor, the pH of the test solution remained constant (at 0.0 V) or decreased slightly (to 2.9 at +2.0 V) during the test. Thus, the fastest degradation of formic acid was observed at the lowest pH at applied potentials $\geq$+1.0 V, which also indicates that hydrogen ions were generated in the biased photoreactor because formic acid was continually degraded during the experiment. However, when the reactor was operated in a purely photocatalytic mode, the pH of the test solution continually increased, reaching 4.3 after 100 min and 5.4 after 150 min, when degradation essentially ceased.

When only the 0.01 M NaCl background electrolyte was recirculated through the reactor with no illumination and no applied potential, the pH of this solution increased from 6.4 to 9.0, most likely caused by an ion exchange reaction in which the photocatalyst adsorbs chloride ions and releases hydroxide ions. When the salt solution was illuminated without applying a potential or when a potential was applied without illumination, the pH remained near 9.0. However, under both UV illumination and an applied potential, the pH dropped dramatically over 30 min, to 4.2 at 0.0 V and to 3.5 at +2.0 V. Photogenerated holes can reach the surface of the titania catalyst readily in a biased reactor. Apparently these holes react with surface hydroxyl groups and/or adsorbed water molecules to release hydrogen ions to the solution, as suggested above.

The pH changes described above were not observed when saline solutions of formic acid were tested because the for-

Table 1. Effect of applied potential on the pseudo-first-order rate constants, errors in these rate constants at a 95% confidence interval, and coefficients of determination (r^2) for the kinetic analysis of each data set shown in Figure 1.

Applied Voltage (V)	Rate Constant (min^{-1})	Error in Rate Constant (min^{-1})	Coefficient of Determination
None (NAP)	6.92×10^{-3}	1.07×10^{-3}	0.9930
0.0	8.70×10^{-3}	1.00×10^{-3}	0.9902
1.0	10.03×10^{-3}	1.41×10^{-3}	0.9899
2.0	11.18×10^{-3}	1.48×10^{-3}	0.9910

mic acid buffers the test solution, although the processes discussed above should still occur. These processes have two specific implications for useful operation of a biased photoreactor. 1) Because there appears to be ion exchange between anions in the test solution and the catalyst surface, the composition of the test solution may affect the performance of the reactor. In particular, phosphate ions, which bind strongly to most oxides, may inhibit reactions. 2) This biased reactor was tested with acidic waste streams. Because acid is generated in the biased reactor during operation, it may be possible to treat non-acidic wastes in such a reactor. However, this possibility may only apply to oxygenated solutions. A reasonable potential cannot be applied to the reactor when only the deoxygenated supporting electrolyte is present. On the other hand, the formic acid test solution can be oxidized in the biased photoreactor whether or not oxygen is present. Apparently hydrogen ions are reduced at the cathode when no oxygen is present, thus allowing the biased reactor to operate normally. If this assumption is correct, then treatment of non-acidic organic species in biased photoreactors under anaerobic conditions may require the addition of acid from a separate source.

Conclusions and Recommendations

Several conclusions result from this study.

1. Photoelectrocatalytic (biased) reactors can be employed to treat aqueous mixed-waste solutions.
2. Stable photoelectrodes can be prepared by coating titania on titanium supports.
3. Such photoelectrodes can be used in saline solutions. These photoelectrodes were tested in 0.01 M NaCl for this project. Further testing at higher salt concentrations is needed.
4. Reticulated vitreous carbon rods serve as effective cathodes in biased photoreactors. Platinum can also be employed but is more expensive.
5. Because biased photoreactors generate acid during operation, only a small amount of additional acid may have to be added to a non-acidic waste to obtain reasonable treatment rates.
6. Biased photoreactors are relatively unaffected by operation under anaerobic conditions, at least for the systems tested in this project.
7. The kinetics of degradation in biased reactors is modeled better by a Langmuir-Hinshelwood-Hougen-Watson expression than by a simpler first-order rate expression.
8. Rates of reaction in this biased photoreactor are relatively slow with half-lives for reaction on the order of 1 hour. Applications for this technology will remain limited unless reaction rates can be increased by at least an order of magnitude over the rates observed in this project for photoelectrocatalysis.

This investigation generated several observations and questions concerning the operation of biased photoreactors that lead to the following recommendations.

1. Because of the relatively slow rates of reaction in biased reactors, they are probably best considered for treating wastes that contain relatively low levels of contaminants (<100 ppm might be a reasonable cutoff).
2. It is not clear that simply scaling up the reactor will provide the desired improvement in performance for this reactor. One option is to replace the 15-W UV light source used in this reactor with a 40-W bulb. This change would lengthen the reactor but would also require using larger cathodes. Another option is to test different cathodes and cathode geometries. A third possibility is to employ a photocatalyst that contains a small amount of a dopant (e.g., 1 wt% niobium) that increases the photoconductivity of the catalyst.
3. The underlying processes that control the behavior of biased photoreactors are rather complex and require further elucidation, preferably by research groups with a background in both electrochemistry and the colloid chemistry of the interactions between metal oxides and aqueous solutions.
4. Bench-scale tests of biased photoreactors with actual waste streams would be appropriate. Given the apparent interactions of chloride ions with the surface of the titania photocatalyst, the ability of biased photoreactors to treat waste streams containing other anions should be evaluated. Of particular interest are anions that bind to metal oxides more strongly than chloride (e.g., phosphate).
5. Alternative designs for biased photoreactors should be evaluated. Such alternatives include designs that increase the turbulence of the flow through the reactor and that place an externally illuminated photoanode around a cathode sitting at the center of the reactor.
6. One consideration that was not studied in this project is to replace the simple DC bias that we employed with a modulated AC bias in an attempt to partially disrupt the water layer around the electrodes.

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