A Photocatalytic Membrane Reactor for Enhanced Destruction of Chloro-Organics in Aqueous Media

Richard J. Higgins (higgins@ceramem.com; 781-899-4495 x 23)
Bruce A. Bishop (bishop@ceramem.com; 781-899-4495 x 30)
Robert L. Goldsmith (goldsmith@ceramem.com; 781-899-4495 x 24)
CeraMem Corporation
12 Clematis Avenue
Waltham, MA 02453

Introduction

Remediation of contaminated soil at DOE sites often encompasses the *ex-situ* treatment of contaminated groundwater (pump and treat operations). While air stripping is generally the lowest-cost method for groundwater treatment and has the attributes of simplicity and flexibility, it cannot cost-effectively attain extremely high removal of many commonly encountered contaminants. This is problematic in that regulatory standards have become increasingly stringent (e.g., the maximum allowable contaminant level for trichloroethylene (TCE) is 0.005 mg/l or 5 wppb). "Polishing" techniques, employed alone or in parallel with air stripping, are typically required to attain high contaminant removal rates. Absorption using granulated activated carbon (GAC) is a feasible polishing method for low-polarity hydrocarbons, but does not work well for halogenated hydrocarbons, which constitute a significant fraction of contaminants in the U.S. water system. Hence, there has been much recent research and development activity in the area of advanced oxidation processes (AOP's) that provide very high levels of destruction for all hydrocarbons, including halogenates.[1]

Among the various types of AOP's, *heterogeneous photocatalytic techniques* have been the subject of appreciable research efforts for these applications, due to their capabilities for complete destruction of common but poorly absorbing contaminants and/or highly hazardous contaminants (explosive compounds) and completeness of degradation to innocuous products. Heterogeneous photocatalysis employs wide band-gap semiconductors such as TiO_2 (titania) that are contacted with the contaminant molecules while subjected to UV illumination. As a result of illumination, electron holes are generated on the TiO_2 surface to initiate an oxidation reaction which ultimately mineralizes organics to CO_2 and, if chlorine atoms are present, HCl. Although TiO_2, as a wide band-gap semiconductor (E_g = 3.1 to 3.3 eV), absorbs near-UV and shorter wavelengths of the electromagnetic spectrum, TiO_2 has been favored in this regard because it is abundant, inexpensive, and resists photo-corrosion. The presumed solid and interfacial reaction processes leading to organic destruction (using TCE as an example) can be summarized as follows:

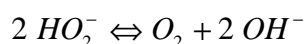"Bulk" Reactions

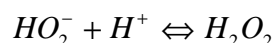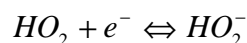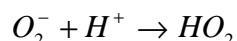$$hv \rightarrow e^- + h^+ \qquad \text{Light Absorption}$$

---

[1] Rajeshwar, Krishnan and Jorge G. Ibanez, Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement, Academic Press, New York, 1997.
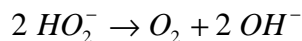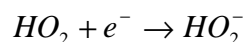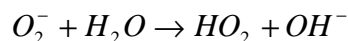
$$e^- + h^+ \rightarrow heat \qquad \text{Recombination}$$

Surface Electron Transfer Reaction

$$h^+ + OH^- \rightarrow OH\bullet \qquad \text{Hole Conversion}$$

$$e^- + O_2 \rightarrow O_2^- \qquad \text{Electron Conversion}$$

Surface Reactions (Acid Conditions)

$$O_2^- + H^+ \rightarrow HO_2$$

$$HO_2 + e^- \Leftrightarrow HO_2^-$$

$$HO_2^- + H^+ \Leftrightarrow H_2O_2$$

$$2\,HO_2^- \Leftrightarrow O_2 + 2\,OH^-$$

Surface Reactions (Basic Conditions)

$$O_2^- + H_2O \rightarrow HO_2 + OH^-$$

$$HO_2 + e^- \rightarrow HO_2^-$$

$$2\,HO_2^- \rightarrow O_2 + 2\,OH^-$$

Mineralization

$$C_2HCl_3 + 4\,OH\bullet \rightarrow 2\,CO_2 + 3\,H^+ + 3\,Cl^- + H_2$$

In this scheme, there are typically two related kinetically limiting parameters. First, the rate of electron/hole recombination to produce (waste) heat increases as a function of UV illumination intensity. Second, molecular oxygen typically acts as an electron acceptor to "drain" electrons away from trapped holes, thereby sustaining the mineralization process. However, in aqueous phase photocatalysis, due partly to the low solubility of oxygen in water, low quantities of adsorbed oxygen exacerbate the tendency for recombination to consume holes and prevent their use in the organic destruction process. High levels of recombination lead to low *quantum efficiency*, which is defined as the number of molecules destroyed per UV photon emitted. Achievement of high quantum efficiencies in heterogeneous photocatalytic processes is critical to attaining favorable economics, since a major portion of the operational costs of such processes is due to electrical energy for UV photon emission.

Aside from the process kinetic issues, significant mass transfer limitations are present in most heterogeneous photocatalytic reactor configurations that have been examined to date.[2] Photocatalytic reactor design presents unique challenges due to the requirement that a high-surface-area particulate catalyst, a UV illumination source, and contaminant species be kept in close proximity. Typical reactor designs fall into two general classes: (i) those that utilize an immobilized layer of photocatalyst in close proximity to a UV-emitting source, and (ii) those that use fluid-suspended or air-suspended photocatalyst that is periodically passed by the UV-

---

[2] Photocatalytic Purification and Treatment of Water and Air, D. Ollis and H. Al-Ekabi (Editors), Elsevier, New York, 1993.

emitting source by convective means. The former reactor types are typically subject to significant mass transfer limitations caused by the need for contaminants present at low concentration in the fluid phase to diffuse towards and into the immobilized photocatalyst layer. Reactors of the second class are also subject to similar mass transfer limitations in that the suspended photocatalyst tends to be present not as discrete fine nano-size particles but as micrometer-size agglomerates or flocs. In addition, suspended photocatalyst reactor designs are plagued by problems and inefficiencies related to collection, re-suspension, and fouling of the photocatalyst.

Because of these issues, practical application of heterogeneous photocatalysis is still in its infancy and has only been performed to some degree of success for gas-phase streams. Heterogeneous photocatalytic reactors for gas-phase contaminant destruction that have desired technical performance and reasonable economics have typically achieved quantum efficiencies in excess of 10%. In contrast, prototype photocatalytic reactors for aqueous media have generally not exhibited quantum efficiencies greater than ca. 1%. Substantially higher quantum efficiencies are required if aqueous-phase photocatalysis is to achieve favorable costs vis-à-vis alternative polishing technologies.

Objectives

The overall objective of this program, a Phase II project funded by USDOE's Small Business Innovation Research Program, is development of a novel photocatalytic reactor that focuses on minimization of critical process kinetic and mass transfer limitations for aqueous-phase heterogeneous photocatalysis. The reactor design incorporates a "photoanode" that serves to significantly increase the conversion of UV radiation to reactive hydroxyl species on the photocatalyst, thereby significantly increasing contaminant destruction rates. The novel configuration of the reactor serves to minimize or effectively eliminate the most critical mass transfer limitations found in alternative photocatalytic reactors. These improvements are expected to lead to significant lowering of projected capital and operating costs for the photocatalytic process. Specific technical objectives of the program include demonstration of the following:

1. A mineralization efficiency of greater than 99.9% for remediation of 5 ppm trichloroethylene in simulated wastewater at a reaction rate that is deemed economically viable by Zentox Corporation, an industrial partner that is commercially active in development of photocatalytic decontamination technology. This level is sufficient to meet EPA drinking water guidelines.

2. A quantum efficiency (moles of organic destroyed per mole of photons emitted in the reactor as measured by actinometry) of at least 5% at an economically viable light intensity level.

3. Significant photodestruction of chloro-organic contaminated wastewater (>95%) in a field test for more than 200 hours.

4. A projected catalyst lifetime of at least 3 years based on field test results.

Technical Approach

General Process Concept

The overall reactor concept currently under development is shown in Figure 1. The process is based on use of electrochemically enhanced, heterogeneous photocatalysis combined synergistically with homogeneous photo-oxidation. The reactor design consists of a cathode flow cell and a photoanode flow reactor. Contaminated wastewater to be treated is initially adjusted to pH 4.5 to 6 and dosed with hydrogen peroxide, which provides a means for parallel homogeneous photo-oxidation reactions (as detailed below). The dosed wastewater flows into the cathode flow cell, which is essentially a high-surface-area platinum-plated wire mesh and serves to supply electrons that have been extracted from the photoanode cell as described below. Transfer of the electrons from the cathode to the wastewater promote the following electron-scavenging reactions:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \text{and}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
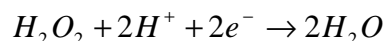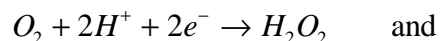
This pre-conditioned wastewater flows into the photoanode flow reactor, which contains the key innovative features of the overall reactor.

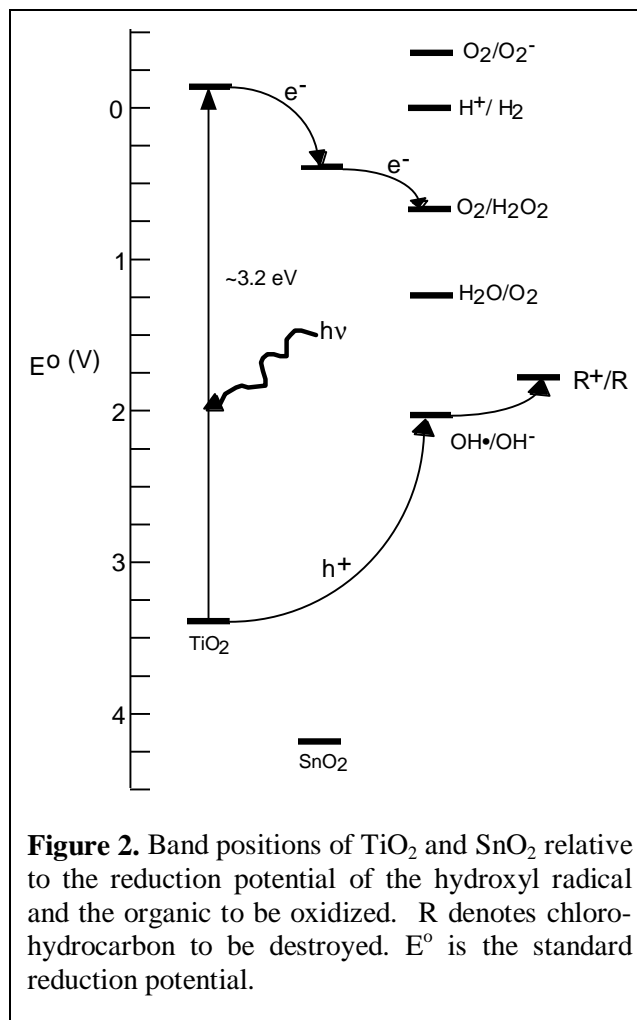**Figure 1.** Schematic of Electrochemical Photocatalytic System
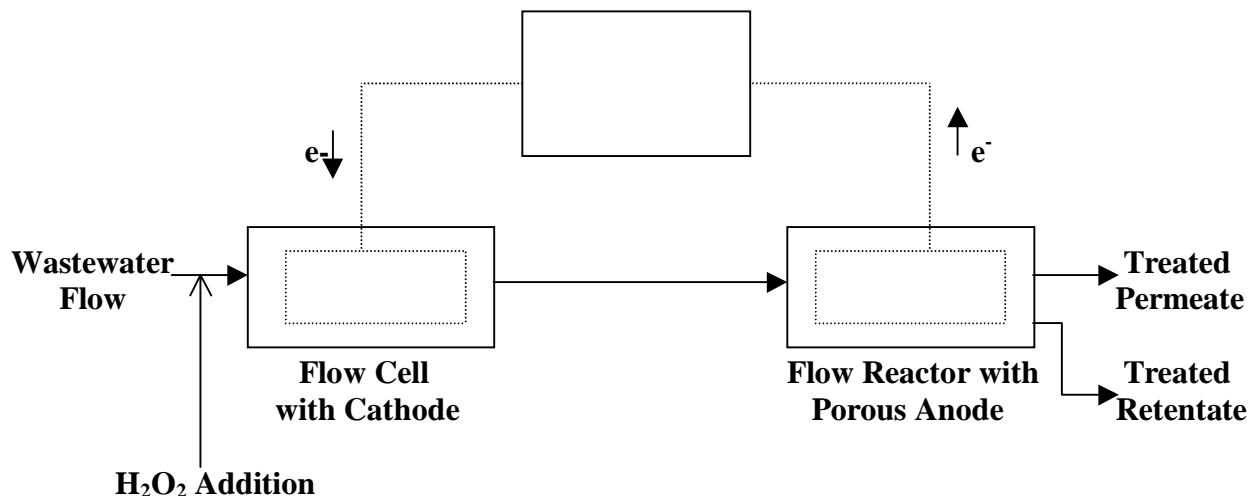
Photoanode Concept and Construction

One method that has been demonstrated previously to retard the rate of electron-hole recombination in heterogeneous photocatalysis is application of the catalyst upon an electrode with supply of a positive (anodic) bias to act as a sink for photogenerated electrodes. Anderson

and co-workers[3] first utilized this concept using a UV-illuminated porous TiO_2 electrode for destruction of formic acid. Their results indicated a consistent improvement in the amount of organic contaminant destroyed (roughly by 30%) in the presence of O_2 and almost a factor of 3 improvement when O_2 was displaced by N_2. The full potential of the process was not realized due primarily to the high resistance path (hopping or tunneling through titania particle grain boundaries) present for electron conduction.

This approach was further refined by Vinodgopal and Kamat,[4] who investigated photoanodes as part of an electrochemical cell. Comparing photoanodes comprised of TiO_2 and TiO_2/SnO_2 nanocomposites, and a 0.6 V (SHE) potential, they achieved an eight-fold increase in oxidation efficiency of an azo dye using a TiO_2/SnO_2 electrode in comparison to a pure TiO_2 electrode. They attributed the outcome to the close association of TiO_2 and SnO_2, as well as to the fact that SnO_2 ($E^o = 0.5$ V vs SHE) has a conduction band lower (more positive) than that of TiO_2 ($E^o = -0.12$ V vs SHE), resulting in a charge separation with

Figure 2. Band positions of TiO_2 and SnO_2 relative to the reduction potential of the hydroxyl radical and the organic to be oxidized. R denotes chlorohydrocarbon to be destroyed. E^o is the standard reduction potential.

photogenerated electrons leaving the TiO_2 for the SnO_2 while the holes remain in the TiO_2. Charge separation slows down the recombination process and allows holes to react with surface adsorbed hydroxyl ions to form hydroxyl radicals to be used in the subsequent organic destruction process. The basic concept is illustrated schematically in Figure 2. For reduction to be thermodynamically favored, the reduction potential of the reducing agent must be more negative than that of the oxidizing agent. Therefore, electrons cascade down to more positive values while holes cascade up to more negative values. Electrons are extracted to an O_2-saturated cathode by applying a positive potential, because the conduction band potential of SnO_2 lies more positive than the $O_2|O_2^-$ couple. In this way electrons can be pumped uphill from a positive potential of SnO_2 ($E(SnO_2) = 0.1$ V at pH 5) to the negative reduction potential required for the reduction of oxygen $E(O_2|O_2^-) = -0.33$ V.

By employing the electrochemical photocell concept, Vinodgopal and Kamat demonstrated that, with a TiO_2/SnO_2 photoactive layer, the photocatalytic oxidation destruction process can be made substantially more efficient. Further, the need for surface-adsorbed molecular O_2 on TiO_2

[3] D. Kim and M. Anderson, *Environ. Sci. Technol.*, **28**, 479 (1994).
[4] K. Vinodgopal and P. Kamat, *Chemtech*, 18-22, April 1996.

completely disappears. Because they used an applied electromagnetic field (EMF), any necessary over-potentials could easily be overcome at the cathode for O_2 to be reduced by the platinum cathode. Consequently, any pH constraint on the process becomes moot.

CeraMem Corporation has developed a further improvement upon such constructs that mitigates mass transfer limitations on the overall process that are associated with diffusion of the organic contaminants to the surfaces of activated photocatalyst particles. CeraMem utilizes a *porous photoanode*, as shown schematically in Figure 3, that is in close proximity to a UV light source. The photoanode contains a mixed TiO_2-SnO_2 particulate layer, applied directly over a second layer of larger conductive particles, which is applied over a macroporous ceramic support. The UV light source is positioned in close proximity to the TiO_2-SnO_2 layer, the thickness and TiO_2 content of which can be optimized to absorb > 95% of impinging UV photons of appropriate energies. A positive electrical bias (up to about 1.0 V SHE) is applied to the conductive layer using a potentiostat to provide the driving force for electron draining from the photocatalyst layer, out of the photoanode and into the cathode. Most importantly, aqueous fluid flow is constrained so as to pass at relative high velocity perpendicular to the layers comprising the photoanode. This results in maximized mass transport of contaminants from the bulk liquid to the solid photocatalyst surface, as well as within the pore structure of the photocatalyst coating.

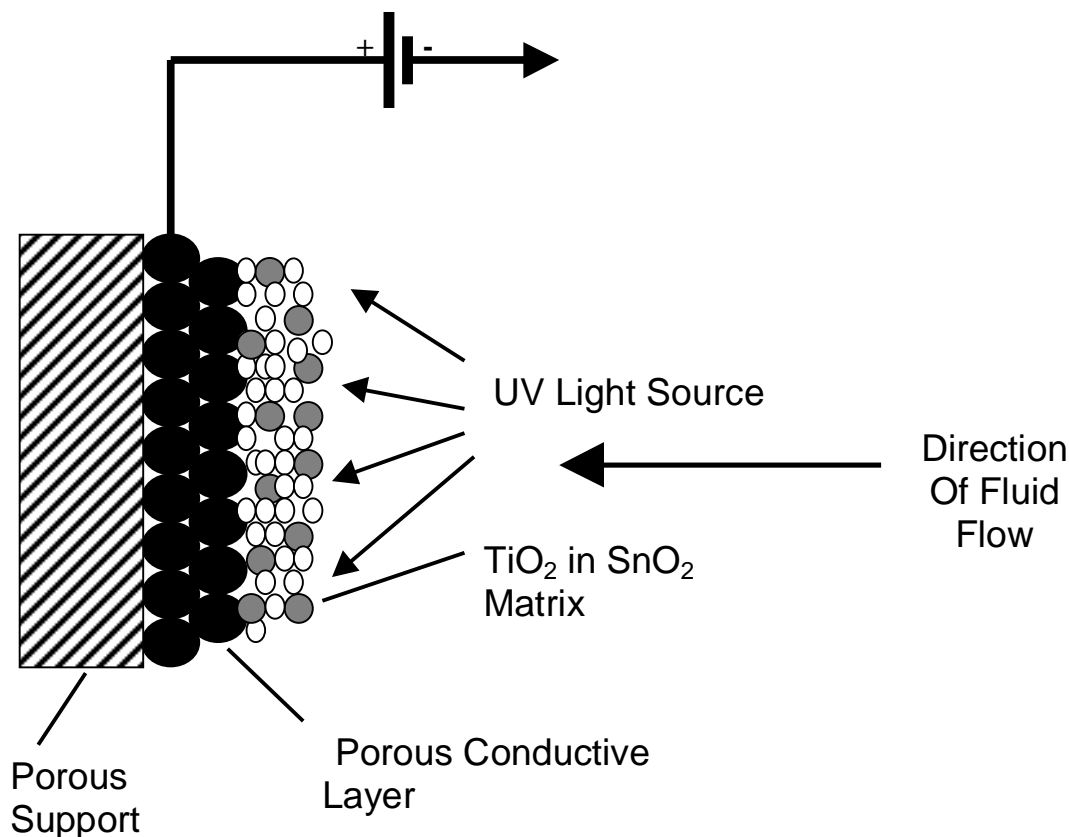**Figure 3.** Composite Porous Photoanode Structure

Figure 4 shows how such a photoanode could be incorporated within a tubular reactor of relatively simple design. Here, the photoanode is coated on a porous ceramic tube, which is sealed into a housing shell and has an electrode bonded to the downstream end. This element is housed such that feed wastewater that does not flow through the photocatalyst coating flows out the outlet end of the tube. The UV light source (e.g., a tubular lamp or "leaky" optical fiber) is inserted concentrically within the lumen of the tube.

Figure 4. Simplified Schematic of Proposed Flow Reactor Concept.
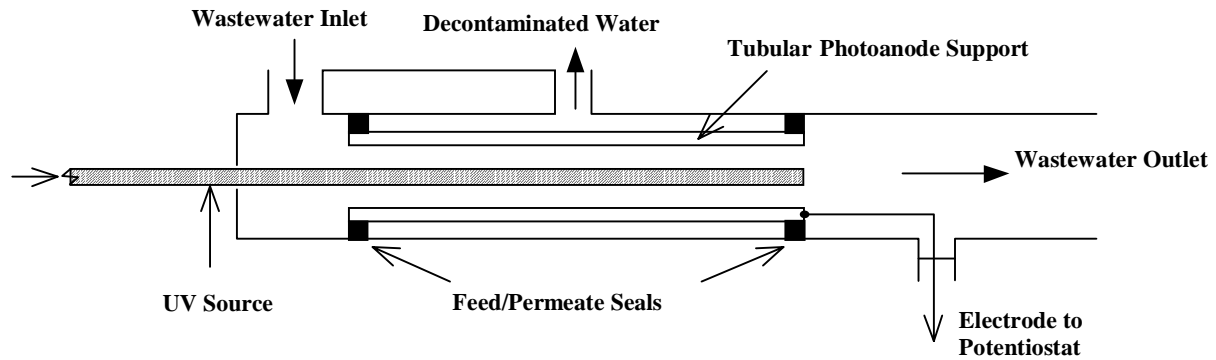

Deployment of the photoanode within a more compact reactor configuration, however, utilizes a multi-channel ceramic monolith as the porous support. Figure 5 shows a flow schematic of such a monolith, where the term "membrane" is used to designate the photoanode coating. For such a monolith, the internal surfaces of each individual passageway are coated with the photoanode composite structure and are provided with a UV-emitting source, as shown in Figure 6.

Figure 5. Schematic of Flow Distribution in a Multi-Channel Monolithic Photoanode Reactor
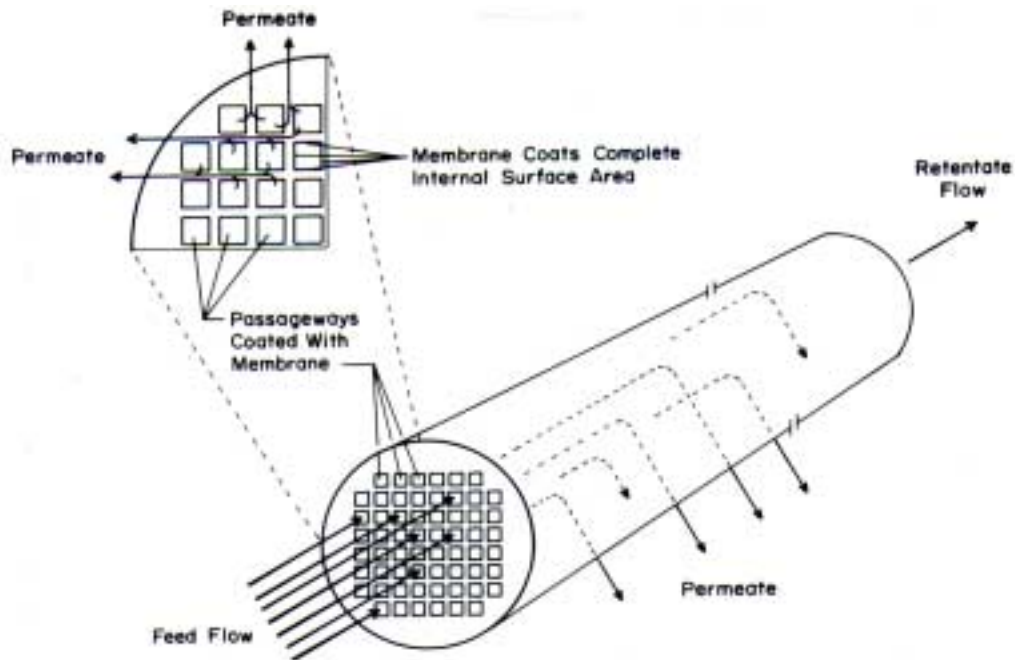
Figure 6. Cross-section of Monolith Segment Showing Applied Photoanode Structure
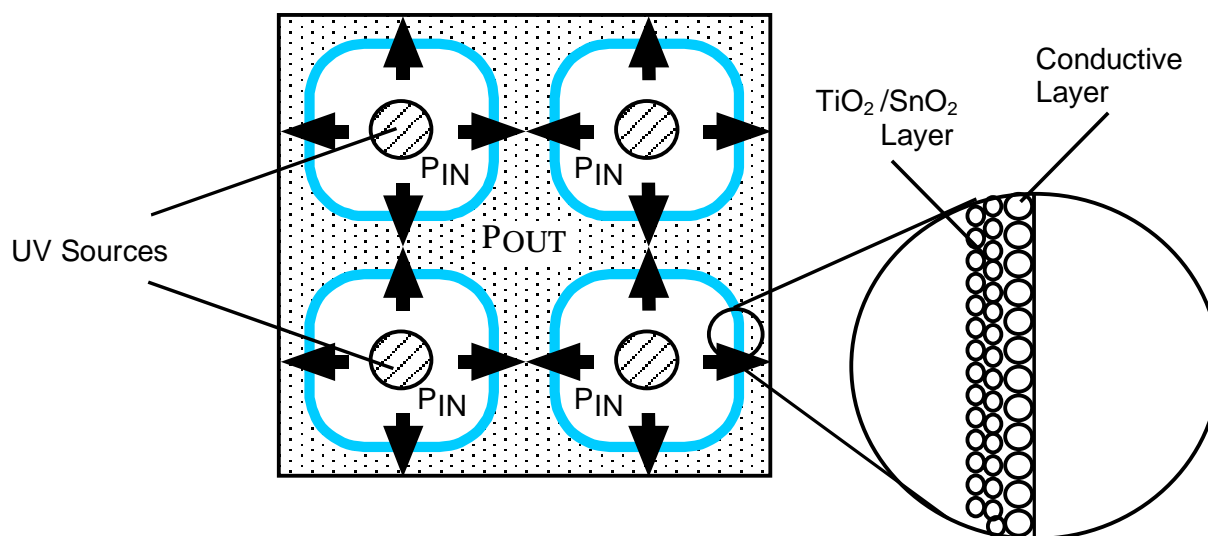
The monolithic flow reactor functions akin to a crossflow membrane device, whereby the fluid pressure within the channels (denoted as P_{IN} in Figure 6) is significantly greater than P_{OUT}, giving a significant driving force for wastewater flow through the porous photoanode structure. For such a reactor, permeate flow rates could be adjusted to provide complete decontamination in a single pass or, alternatively, permeate could be recycled for additional treatment in a batch or semi-batch process.

UV Light Delivery

Two different methods of UV light delivery to the photoanode structures are possible. The first, which can be best applied for channels of relatively small diameter (e.g., ca. 2 mm) involves use of an outside UV lamp, the output of which is collimated and transmitted down a bundle of optical fibers. Individual optical fibers from this bundle feed into individual passageways, and the fibers are stripped of cladding and provided with surface scattering sites along their sections that are adjacent to photoanode layers. With proper density of scattering sites, light will leak from the fibers at a controlled intensity level along the entire stripped length. The ends of the fibers are "silvered" to provide reflection of UV light that is not leaked radially. Such an approach has been used in at least two other reactor designs.[5] However, there are disadvantages associated with this approach associated with the complexity of the required system, photon losses due to scattering losses during focusing and collimation, and limited corrosion resistance of the stripped fibers.

For flow reactors with reasonably large channels (e.g., diameter of about 4 mm and larger), individual tubular UV lamps can be employed. In such a case, lamp intensity must be carefully selected to provide optimal quantum efficiencies. For use of either multiple lamps or optical fibers, the distances between the UV sources and photocatalyst layers must be carefully calibrated to minimize absorption by the interlaying aqueous phase. Lamps of interest include

---

[5] N. Peill and M. Hoffmann, *Environ. Sci. and Technol.*, **30**, 2806 (1996); B.L. Bischoff et al., U.S. Patent No. 5,862,449, issued Jan. 19, 1999.

both low-wattage and high-wattage Hg vapor lamps, expected to be most economical due to their long lifetimes and resulting reduced maintenance costs, or Hg arc lamps when fiber optic illumination is employed.

Use of Hydrogen Peroxide For Parallel Homogeneous Photo-Oxidation

In Figure 1, the use of continuous hydrogen peroxide addition to the cathode of the reactor is shown. A principal role of this inexpensive additive is electron scavenging, either directly or via conversion to oxygen as shown above (under mildly acidic to neutral pH conditions, H_2O_2 reacts directly about ten times more rapidly than oxygen for this purpose). In addition, absorption of higher-energy UV photons by hydrogen peroxide leads to direct production of hydroxyl radicals as follows:

$$H_2O_2 + h\nu \rightarrow 2OH\bullet$$
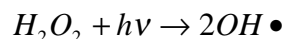
These hydroxyl radicals in turn will initiate separate free radical reaction pathways for destruction of organic contaminants, away from the titania photocatalyst surface. Such combined use of photocatalytic UV-H_2O_2 and UV-TiO_2, although requiring some degree of tuning and control to avoid undesirable side-effects (such as scavenging hydroxyl radicals), has been employed previously and demonstrated to provide significantly improved destruction rates as compared to use of UV-TiO_2 alone.[6]

Initial Results

This SBIR Phase II program consists of the following tasks:

>   Task 1. Develop Photoanode Fabrication Procedures and Characterize Photoelectro-chemical Behavior
>   Task 2. Develop Fabrication Processes for Photoanodes on Multi-Channel Monolith Supports
>   Task 3. Develop Improved Light Delivery System
>   Task 4. Design and Fabricate Bench Scale Reactor System
>   Task 5. Perform In-House Tests of Monolith-Based Photoreactor
>   Task 6. Conduct Field Tests
>   Task 7. Perform Engineering Cost Analysis

Work conducted to date has involved primarily the first two tasks with focus on development of porous photoanode composite structures on small flat porous disk supports and on small tubular and monolithic supports. Initial samples have used particulate gold as a conductive layer to facilitate photoelectrochemical testing, but indium-tin oxide (ITO) conductive layers are also being developed, as gold is too expensive for use with photoanodes having significant surface area. Figure 7 shows initial results for generated photocurrent as a function of applied electrical bias under UV illumination for two similar Al_2O_3 disk-supported composite photoanodes that employed a porous gold conductive layer. However, one sample utilized a porous mixed TiO_2-SnO_2 (20:80 volume ratio) layer while the other used only a porous TiO_2 photocatalyst layer, as denoted on the figure. These results clearly show the effectiveness of use of SnO_2 in the

---

[6] Lichtin et al., U.S. patent No. 4,861,484, issued Aug. 29, 1989.

photoanode, leading to a two orders of magnitude increase in the photocurrent extracted from the activated photocatalyst layer.

Figure 7. Photocurrent Measured From SnO_2-TiO_2 and TiO_2 Photoanode Structures as Function of Applied Bias (I = 40 mW/cm^2).
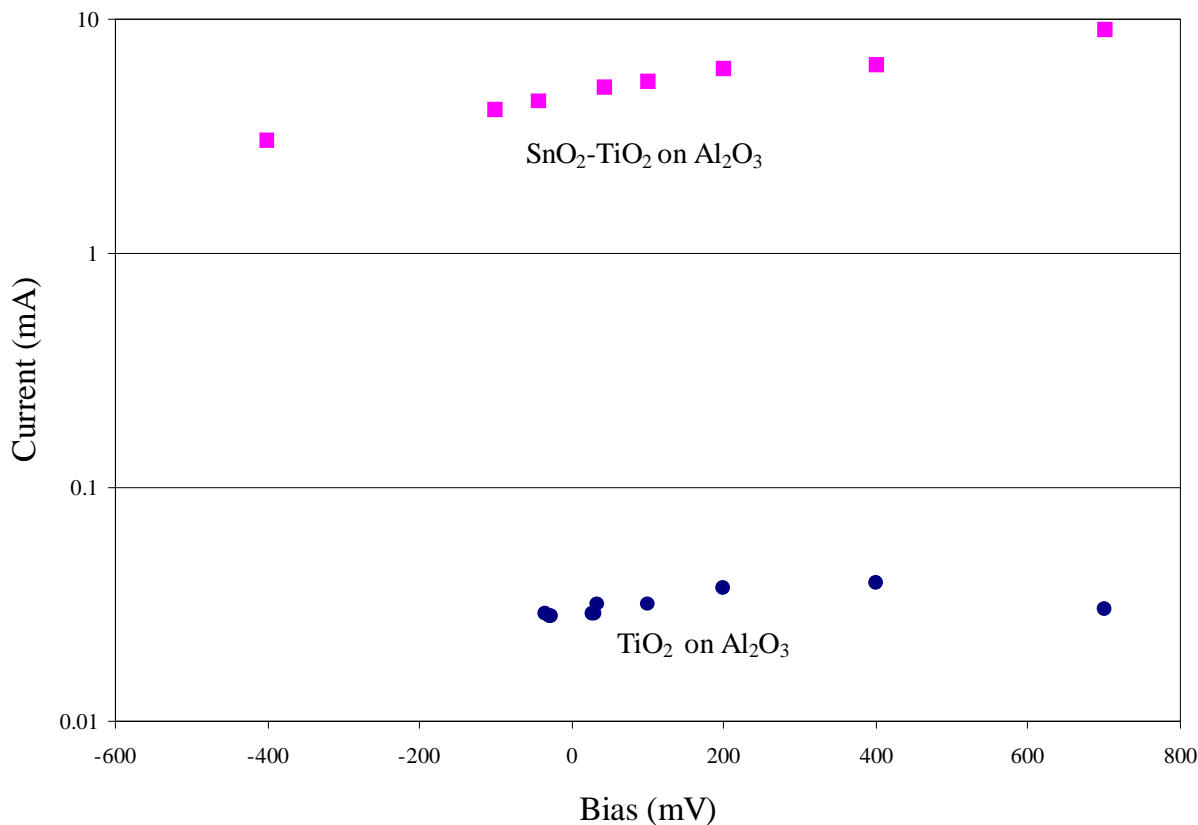
Ongoing work focuses on extension of these highly positive results to demonstration of ability to attain quantum efficiencies for destruction of TCE that are significantly in excess of 1%.

Future Work

During the immediately following few months, it is expected that preferred fabrication procedures for porous photoanode structures on disk, tubular and small multi-channel supports will be defined. The primary focus of experimental work will then shift to demonstration of the photocatalytic properties of the structures. Significant progress will be made in development of a preferred light delivery system for the bench scale reactor system and on assembly of the reactor system itself. Full completion of the program is scheduled to take another 18 to 24 months.