ANL/ES/CP--85670
Conf-950241--2

Use of Cysteine-Modified TiO_2 Photocatalyst for Treatment of
Combined Organic/Inorganic Wastewaters

by

Robert W. Peters¹, Jiann-Min Wu¹, Natalia Meshkov¹,
Marion C. Thurnauer² and Agnes E. Ostafin²

¹Energy Systems Division

²Chemistry Division

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

submitted to

The 5th International Symposium on

"Chemical Oxidation: Technology for the Nineties"

Nashville, Tennessee

February 15-17, 1995

The submitted manuscript has been authored
by a contractor of the U. S. Government
under contract No. W-31-109-ENG-38.
Accordingly, the U. S. Government retains a
nonexclusive, royalty-free license to publish
or reproduce the published form of this
contribution, or allow others to do so, for
U. S. Government purposes.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Use of Cysteine-Modified TiO₂ Photocatalyst for Treatment of Combined Organic/Inorganic Wastewaters

by

Robert W. Peters¹, Jiann-Min Wu¹, Natalia Meshkov¹,
Marion C. Thurnauer² and Agnes E. Ostafin²

¹Energy Systems Division

²Chemistry Division

Argonne National Laboratory

9700 South Cass Avenue

Argonne, Illinois 60439

Introduction:

The utilization of semiconductor-based photocatalysts, such as titanium dioxide (TiO₂), for carrying out photochemical reactions to treat water contaminated with organic and inorganic compounds has received considerable attention in recent years. Semiconductor particles can act as short-circuited microelectrodes and directly oxidize and reduce the adsorbed substrates, or they can serve as mediators for the charge transfer between two adsorbed molecules, thereby enhancing the efficiency of the photocatalytic reaction in the process. The development of this process in order to achieve complete mineralization of individual organic or inorganic pollutants has been widely tested for a large variety of chemical compounds (Abdullah et al., 1990; Low et al., 1991; Matthews, 1987; Prairie et al., 1993; Kormann et al., 1991; Foster et al., 1988). Nevertheless, it remains surprising that only a few researchers have investigated the application of the process to simultaneously eliminate organic and inorganic compounds present in the same stream. In this process, the toxic organic compounds present in the solution are oxidized to their less hazardous or non-hazardous forms, while the inorganic contaminants are simultaneously reduced to their metallic forms and can be removed/recovered.

Oxidative degradation of pollutants by photocatalysis using semiconductor particles such as TiO₂ has been the subject of numerous recent studies. The principle behind semiconductor-assisted photocatalysis in the aqueous phase containing organic pollutants and semiconductor particles involves the photoexcitation of the semiconductor particles by ultraviolet (UV) light. This causes the energy state of trapped electrons to change from the valence band of the solid to the conducting band, resulting in the formation of electrons and holes at the surface of the semiconductor particle, which can either recombine, producing thermal energy, or interact with other molecules. The radicals generated can either oxidize organic pollutants or reduce heavy metals at the solid/liquid surface.

Numerous reports of organic pollutant degradation with mineralization to inorganic products have been reported; degradation has involved the following types of compounds: aliphatic acids, alkanes, aromatic compounds, chlorinated and brominated aliphatic compounds, chlorophenols, colored organic compounds, cyanide, DDT, fluorinated aromatic compounds,

methyl vinyl ketone, nitroaromatics and amines, organophosphorus compounds, PCP, polychlorinated dioxins, polychlorinated biphenols, gas-phase pollutants, pesticides, herbicides, solvents, surfactants, and urea (Venkatadri and Peters, 1993). The rate of degradation of organics by TiO_2 -assisted photocatalytic oxidation is influenced by the solution pH, TiO_2 concentration, temperature, dissolved oxygen concentration, light intensity, contact time, and dissolved anions and cations.

Although photocatalytic degradation can be conducted with several semiconductors, e.g., zinc oxide and cadmium sulfate, TiO_2 has been widely studied at concentrations ranging from 1 to 5 g/L and is known to be the most efficient catalyst (Barbeni et al., 1985; Pelizzetti et al., 1988). TiO_2 is also more stable, insoluble, nontoxic, and inexpensive compared to the other catalysts (Sclafani et al., 1990).

TiO_2 -assisted photocatalysis may also be useful for removal of certain heavy metals, including mercury and silver, via their reduction followed by deposition at the catalyst surface (Prairie et al., 1992; Domenech and Andres, 1987; Serpone et al., 1987). The catalytic activity of TiO_2 can be improved by loading such metals as silver or platinum on the catalyst surface (Kondo and Jardim, 1991; Harada et al., 1990; Rose and Nanjundiah, 1985; Hisanaga et al., 1990). Mercury and methylmercury salts at concentrations of 100 mg/L could be removed from solution by photoreduction in less than 30 min (Serpone et al., 1987). A laboratory-scale TiO_2 -catalyzed process was used to remove and concentrate copper ions in aqueous solution (Foster et al., 1993).

Most laboratory studies involving TiO_2 -assisted photocatalysis have been conducted with reaction volumes ranging from 20 mL to 5.5 L. The primary focus to date has been on the destruction of organic pollutants in solution using photocatalytic oxidation, with little attention devoted to recovery of heavy metals. A recent study involving the use of TiO_2 to treat water contaminated with both heavy metals and organic chemicals (Prairie et al., 1993) concluded that both oxidation and reduction processes must be taken into account in photocatalytic water treatment. Our current study seeks to enhance the performance of TiO_2 -assisted photocatalysts to sequester and recover heavy metal ions in their metallic form while simultaneously destroying organic compounds, potentially in a single step.

Our strategy for optimizing the process of photocatalytic reduction of heavy metals on TiO_2 colloids involves modifying the colloid surface. The issue of enhancing passive sorption of the heavy metal ions is being addressed by using materials that have high affinity for specific metal ions. These materials promote rapid transfer of the electron generated by photo-excitation of TiO_2 to the bound metal ion to ensure efficient reduction of the adsorbed metal ion. Additionally, surface modification can also increase the reducing power of the TiO_2 colloid, thereby making the process accessible to different metal ions. Finally, the immobilized reduced metals can be removed from the modified TiO_2 colloids by acid treatment. This last step allows the metallic species to be recovered and the photocatalysts to be recycled for repeated metal ion removal.

Specific project objectives included: (1) identification and development of potential biomimetic photocatalysts for simultaneous heavy metal recovery and organic destruction; (2)

identification of treatment conditions that minimize the residual metal concentration(s) contained in the effluent, even in the presence of complexants and interferences, and development of appropriate scale-up criteria; and (3) determination of system performance, including an economic analysis for comparison with conventional technologies (such as pump-and-treat using metal hydroxide precipitation or ion exchange).

The research project consists of two major tasks: (1) development and design of catalysts, and (2) their application to contaminated waste streams. The development and design work focuses on determining the mechanism of the photocatalytic process in order to design catalysts that are specific and efficient, while the application task involves batch, bench-scale studies involving parametric testing. The research work addresses three separate processes of a metal treatment/recovery scheme: passive sorption, photochemical reduction of the adsorbed metals, and catalyst recycling.

Experimental Section:

All of the chemicals used in the studies were reagent grade (obtained from Fisher Scientific) and were used as received. Lead acetate ($\text{Pb}[\text{C}_2\text{H}_3\text{O}_2]_2$) and naphthalene (C_{10}H_8) were selected as the representative target contaminants to be treated. The sample solutions were prepared freshly before conducting the experiment using laboratory deionized water. All of the experiments were conducted using a quartz reactor with a total capacity of 250 mL. The photochemical reactor (Rayonet Model RMR-600, Branford, CT) used in the studies had a reactor chamber 10" in diameter and 10½" high, equipped with eight UV light sources surrounding the chamber. The eight UV light sources provided a maximum of 32 watts (four watts for each UV lamp) of UV energy at a wavelength of 254 nm to the reactor. During a typical experiment, a 50-mL sample solution containing a known amount of contaminant(s) and photocatalyst were placed in the center of the reactor chamber and irradiated for a desired period of time with the UV lights. The irradiated solutions were well stirred throughout the experiment. After irradiation, the photocatalyst and elemental metals were separated from the solution by filtration. The organic compound was analyzed using a gas chromatograph (HP 5890 series II, Hewlett Packard, Wilmington, DE) equipped with a FID detector; the lead concentration in the solution was analyzed using an atomic absorption (AA) spectrophotometer (model 200 A, Buck Scientific, East Norwalk, CT). The sample solutions were preserved in a 1% nitric acid solution ($\text{pH} < 2$) before being analyzed.

Adsorption studies for the target contaminants were carried out in the laboratory using a shaker table (Eberbach Co., Ann Arbor, MI) to provide sufficient mixing of the sample solutions.

A 30-mL vial sealed with a Teflon™ cap was used for each sample solution. During the experiments, the sample solutions and the vials were covered with aluminum foil to avoid any exposure to light. The experimental contact time for adsorption isotherm experiment was 72 h.

Results and Discussion:

Adsorption of Contaminants:

Adsorption is the first reaction that occurs when the photocatalyst is contacted with contaminants. This process is reversible, does not require light, and is very sensitive to the pH. Figure 1 shows the adsorption isotherm for the two applied photocatalysts for residual lead concentration in the range of 20 mg/L to 100 mg/L. The adsorption capacities of the two photocatalysts appear to be linearly proportional to the lead concentrations in the liquid phase. The adsorption capacity of the treated TiO_2 photocatalyst is higher than that of the untreated photocatalyst. The cysteine behaves as an active site for capturing the dissolved metal ions in solution.

The pH of the solutions was about 4. Changing the pH value of the solution changes the surface charge of TiO_2 , as well as the extent of hydrolysis and species distribution of the metal ions and, as a result, changes the adsorption capacity of the photocatalysts to metal ions. It has been reported that there was no adsorption of Pb^{+2} ions on TiO_2 photocatalyst semiconductor particles in the dark and at pH 1.4. If there is another chemical compound such as naphthalene in the irradiated solution, the lead ions will compete with the chemical compound for the adsorption sites on the photocatalyst. The adsorption capacity for each compound may be lower than that with only one compound in the solution, depending on the selectivity of the photocatalyst for the compounds involved.

The adsorption rate and adsorption capacity may have significant effects on the reaction rates of the photo-induced REDOX reactions. During a typical irradiation with a photocatalyst in the solution, the electrons (e^-) and holes (h^+) formed on the surface of the photocatalyst would preferentially recombine on the surface sites in the absence of surface-adsorbed lead ions or other electron acceptors. If this happens, the lead ions have to diffuse from the bulk solution to the interface where the REDOX reaction occurs. The diffusion rate, in this case, may become a significant factor in the REDOX efficiency. The adsorption kinetic results of lead in solution during the first 60 min of adsorption are shown in Figure 2. The initial lead concentration in solution was about 91 mg/L. After mixing with the photocatalysts, the concentration decreased to about 60 mg/L and 15 mg/L within 60 min of adsorption for the two cases (untreated TiO_2 and cysteine-modified TiO_2 , respectively). Adsorption rates of the lead ions in the system using treated TiO_2 photocatalyst were about three times faster than those using untreated TiO_2 photocatalyst. The adsorption rates of TiO_2 photocatalysts (either treated or untreated) remained constant within this lead concentration range.

Photocatalytic REDOX Reaction:

UV-irradiation of organic and inorganic compounds in the aqueous solution results in the oxidation/degradation of organic compounds and reduction of the inorganic compounds. The mechanism of using TiO_2 -induced photocatalytic reaction for simultaneous oxidation of organic compounds and reduction of inorganic compounds in the irradiated aqueous solution is complicated and involves a series of chemical chain reactions. In general, the first step is absorbance by TiO_2 photocatalyst of UV irradiation more energetic than the band-gap (wavelength < 400 nm), resulting in transition of electrons from the valence to the conduction band and generation of trapped electrons (e^-) and holes (h^+):

The organic compounds present in the irradiated solution, therefore, can be oxidized by the excited TiO_2 photocatalyst or directly decomposed by adsorption of the UV light:

The dissolved metal ions present in the irradiation solution serve as accepting species in the electron-transfer reaction, and as a result, they are reduced to their metallic forms:

If the metal ions were not present, molecular oxygen would serve as the electron-accepting species in the system. Addition of the metal ions in the system would increase the amount of electron-accepting species, resulting in the increasing of the photocatalytic oxidation of organic compounds.

The decrease of the introduced lead ion and naphthalene concentrations in the irradiated aqueous solution is represented in Figures 3 and 4, respectively. With the initial concentration of about 120 mg/L, lead ion concentration slowly dropped down to about 30 mg/L with 60 min of irradiation using the untreated TiO_2 photocatalyst. In other experiments, the use of treated TiO_2 photocatalyst significantly enhanced the concentration-decreasing rate, down to about 5 mg/L with 25 min of irradiation; greater than 95% of dissolved lead ions was removed from the irradiated solution. The removal rate of lead ions in the system using treated TiO_2 photocatalysts was about two to three times faster than that using untreated TiO_2 photocatalysts. The removal of lead ion in the solution was verified from the residual lead analysis (using AA) of the irradiated solution along with the observation of black particulates (which is believed to be metallic lead) generated in the solution. The lead ions were first adsorbed by the TiO_2 photocatalyst and then reduced to elemental lead. However, it is uncertain how many lead ions were removed from the solution through photo-reduction to their metallic form and how many were removed by only adsorption on the TiO_2 photocatalysts.

As shown in Figure 4, the naphthalene concentration decreased with increasing irradiation time. Concentrations of less than 2 mg/L of naphthalene (initial naphthalene concentration was about 11 mg/L) were obtained within 30 min of irradiation in both cases. The difference in the degradation rate between the use of treated and untreated TiO_2 photocatalysts was satisfactorily insignificant. The introduced naphthalene may be degraded through direct adsorption of UV energy or by the excited TiO_2 photocatalysts or by the photocatalysts themselves.

Simultaneous Removal of Naphthalene and Lead:

Experiments were performed in which naphthalene and lead ions were simultaneously treated with the UV- TiO_2 photocatalyst. Theoretically, the lead ions would provide additional

electron-acceptors, resulting in the increase of the naphthalene removal/degradation rate. However, probably due to the low naphthalene concentration in the solution, the experimental results (as shown in Figure 5) showed that the presence of lead ions had little effect on the removal/degradation of naphthalene from solution. Figure 6 shows the residual lead ion concentration versus irradiation time for combined naphthalene-lead removal. The presence of naphthalene resulted in a "lag-time" effect on the photoreduction of lead from solution. In both cases (lead and naphthalene), the cysteine-modified TiO_2 photocatalysts resulted in removal rates that were faster and more effective than those for the untreated TiO_2 system.

Summary and Conclusions:

The experimental results indicate that simultaneous removal of organic compounds (such as naphthalene) and inorganic compounds (such as lead ions) in aqueous solution can be achieved using a TiO_2 photocatalyst system with UV light. The removal rates of organic and inorganic compounds can be enhanced through surface modification of the TiO_2 photocatalyst using an organic substance such as cysteine. The cysteine-modified TiO_2 photocatalyst enhanced the oxidation rates of organics as well as the reduction rates of heavy metals in the irradiated solution, resulting in improved treatment efficiencies for combined organic/inorganic wastestreams.

Acknowledgement:

The authors want to thank John Taylor and Laura Skubal for their atomic absorption spectroscopy measurements for determination of the lead concentrations. We appreciate useful discussions with Tijana Rajh and David M. Tiede. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-Eng-38.

References:

- Abdullah, M.; Low, G. K-C.; Matthews, R. W., *Environ. Sci. Technol.*, 1990, 94(17), 6820-6825.
- Barbeni, M., Pramauro, E., Pelizzetti, E., Borgarello, E., and Serpone, N., "Photodegradation of Pentachlorophenol Catalyzed by Semiconductor Particles," *Chemosphere*, 1985, 14(2): 195-208.
- Carey, J. H., Lawrence, J., and Tosine, H. M., "Photodechlorination of PCBs in the Presence of Titanium Dioxide in Aqueous Suspensions," *Bull. Environ. Contam. Toxicol.*, 1976, 16(6):697-701.
- Doménach, J. and Andrés, M., "Photocatalytic Reduction of Mercury (II) Ions in Aqueous Suspensions of Titanium Dioxide and Tungsten Dioxide," *Gazzetta Chimica Italiana*, 1987, 117:495-498.
- Foster, N. S., Noble, R. D., and Koval, C. A., "Reversible Photoreductive Deposition and Oxidative Dissolution of Copper Ions in Titanium Dioxide Suspensions," *Environ. Sci. Technol.*, 1993, 27(2):350-356.
- Harada, K., Hisanaga, T., and Tanaka, K., "Research Note: Photocatalytic Degradation of Organophosphorus Insecticides in Aqueous Semiconductor Suspensions," 1990, *Water Res.*, 24(11):1415-1417.
- Hisanaga, T., Harada, K., and Tanaka, K., "Photocatalytic Degradation of Organochlorine Compounds in Suspended TiO_2 ," *J. Photochem. Photobiol. A: Chem.*, 1990, 54:113-118.
- Kondo, M. M., and Jardim, W. F., "Photodegradation of Chloroform and Urea Using Ag-Loading Titanium Dioxide as Catalyst," *Water Res.*, 1991, 25(7):823-827.
- Kormann, C., Bahnemann, D. W., and Hoffmann, M. R., *Environ. Sci. Technol.*, 1991, 25(3), 494-500.
- Low, G. K-C.; McEvoy, S. R.; Matthews, R. W., *Environ. Sci. Technol.*, 1991, 25(3), 460-467.
- Matthews, R. W., *J. Phys. Chem.*, 1987, 91, 3328-3333.
- Matthews, R. W., "Photooxidative Degradation of Colloid Organics in Water Using Supported Catalysts TiO_2 on Sand," *Water Res.*, 1991, 25(10):1169-1176.
- Pelizzetti, E., Borgarello, M., Minero, C., Parmauro, E., Borgarello, E., and Serpone, N., "Photocatalytic Degradation of Polychlorinated Dioxins and Polychlorinated Biphenyls in Aqueous Suspensions of Semiconductors Irradiated with Simulated Solar Light," *Chemosphere*, 1988, 17(3):449-510.
- Prairie, M. R., Evans, L. R., Stange, B. M., and Martinez, S. L., *Environ. Sci. Technol.*, 1993, 27(9), 1776-1782.

Prairie, M. R., Pacheco, J., and Evans, L. R., "Solar Detoxification of Water Containing Chlorinated Solvents and Heavy Metals via TiO_2 Photocatalysis," prepared for the 1992 ASME International Solar Energy Conference, April, SAND91-1285C, Sandia National Laboratory, Albuquerque, N.M.

Rose, T. L., and Nanjundiah, C., "Rate Enhancement of Photooxidation of CN^- with TiO_2 Particles," J. Phys. Chem., 1985, 89:3766-3771.

Sclafani, A., Palmisano, L., and Schiavello, M., "Influence of the Preparation Methods of TiO_2 on the Photocatalytic Degradation of Phenol on Aqueous Dispersion," J. Phys. Chem., 1990, 94:829-832.

Serpone, N., Ah-Yu, Y. K., Harris, R., Hidaka, H., Pelizzetti, E., and Tran, T. P., "AM1 Simulated Sunlight Photoreduction and Elimination of Hg(II) and $\text{CH}_3\text{Hg(II)}$ Chloride Salts from Aqueous Suspensions of Titanium Dioxide," Solar Energy, 1987, 36(6):491-498.

Venkatadri, R., and Peters, R. W., "Chemical Oxidation Technologies: Ultraviolet Light/Hydrogen Peroxide, Fenton's Reagent, and Titanium Dioxide-Assisted Photocatalysis," Haz. Waste & Haz. Mater., 1993, 10(2):107-149.

Figure 1. Adsorption Isotherm - Lead Only

Figure 2. Adsorption Kinetics

Figure 3. Effect of Irradiation Time - Lead Only

Figure 4. Effect of Irradiation Time - Naphthalene Only

Figure 5. Combined Naphthalene-Lead System - Naphthalene Concentration

Figure 6. Combined Naphthalene-Lead System - Lead Concentration