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Combined Photooxidation/Photoreduction Using TiO_2 Photocatalysts to Treat
Organic/Inorganic Metal-Laden Wastewaters

by

Robert W. Peters¹, Jiann-Min Wu¹, Natalia Meshkov¹,
Marion C. Thurnauer², Agnes E. Ostafin², and Tijana Rajh²

¹Energy Systems Division

²Chemistry Division

Argonne National Laboratory

9700 South Cass Avenue

Argonne, Illinois 60439

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COMBINED PHOTOOXIDATION/PHOTOREDUCTION USING TiO_2 PHOTOCATALYSTS TO TREAT ORGANIC/INORGANIC METAL-LADEN WASTEWATERS

Robert W. Peters¹, Jiann-Min Wu¹, Natalia Meshkov¹,
Marion C. Thurnauer², Agnes E. Ostafin², and Tijana Rajh²

¹Energy Systems Division

²Chemistry Division

Argonne National Laboratory

9700 South Cass Avenue

Argonne, Illinois 60439

ABSTRACT

A technology has been developed that employs new photocatalysts that have the capacity of both sequestering and converting heavy metal ions from aqueous solution to their less toxic, readily recoverable metallic forms. The technology exploits a strategy to enhance the reactivity of semiconductor photocatalysts for selected toxic compounds by derivatization of the photocatalyst surface with metal-binding ligands. Titanium dioxide (TiO_2) colloids prepared from titanium chloride (TiCl_4) were used as photocatalysts in the experiments. Cysteine was selected as the model derivative for the surface modification of the TiO_2 nanoparticles. Testing of TiO_2 photocatalysts conducted in the absence of organic compounds demonstrated that adsorption of lead ions (Pb^{2+}) occurred in the system with either untreated (virgin) or treated (modified using cysteine) TiO_2 photocatalysts. Adsorption rates of the metal ions in the systems that used treated TiO_2 photocatalysts were about three times faster than those where untreated TiO_2 photocatalysts were used. Lead ion concentrations in the irradiated solutions decreased as the UV irradiation time increased; greater metal removals were achieved at longer irradiation times. The rate of decreasing lead ion concentrations in the system that used treated TiO_2 photocatalysts was about two to three times faster than that in the system using untreated TiO_2 photocatalysts.

Experiments were also performed in which organic compounds (naphthalene or phenol) and heavy metals (Pb^{2+}) were simultaneously treated with TiO_2 photocatalysts. The presence of lead ions did not interfere with the photo-degradation of the selected organic compounds from solution. The presence of phenol compound appeared not to affect the photoreduction of lead ions, while addition of naphthalene compound resulted in a "lag-time" effect on the photoreduction of lead ions from solution. All of the experimental results showed that the cysteine-modified TiO_2 resulted in faster and more effective removal than that for the untreated TiO_2 system. This technique has resulted in the simultaneous photocatalytic removal/recovery of organic and inorganic compounds in the system.

INTRODUCTION

Toxic organic and inorganic contaminants in waste streams generated by chemical, metallurgical, and other industries must be destroyed or removed before the waste streams are released to the environment. Waste streams containing toxic organics and heavy metals have also been generated by DOE activities. It has been estimated¹⁻³ that more than 200,000 m³ of aqueous

mixed waste, contaminated with both toxic organics and metals, will have to be treated at DOE sites over the next 20 years.

In the last ten years, extensive studies of photocatalytic methods for the removal of organic and inorganic contaminants from aqueous waste streams have been undertaken⁴⁻¹³. Such semiconductor particles as TiO_2 can act as microelectrodes that consist of cathodic and anodic parts. These materials are excellent light-harvesting materials and mediators for photochemical degradation of various environmental contaminants. The principle behind semiconductor-assisted photocatalysis involves the photoexcitation of the semiconductor with light energy greater than the semiconductor band gap, followed by generation of electron-hole pairs. The electrons and holes diffuse to the semiconductor particle surface and can be exploited for the various REDOX processes analogous to those of an electrochemical cell.

Application of semiconductor-assisted photocatalysis is primarily focused on TiO_2 , because it is cost-effective, non-toxic, insoluble under most conditions, and photostable. It is effective for oxidative destruction of the most resistant organic compounds, such as polychlorinated aromatics¹⁴ or polyaromatic hydrocarbons (such as those prevalent in oil spills)¹⁵, and for reduction of several heavy metals (Hg^{2+} , Pt^{4+} , Au^{4+} , Rh^{4+}). The principal advantage of these systems is the potential for accumulation of charges on the particle surface, resulting in simultaneous injection of multiple charges if a suitable scavenger of the opposite charge is present on the surface. However, the reduction of toxic heavy metal ions such as Pb^{2+} or Cd^{2+} with negative REDOX potentials of the first one-electron transfer process was not reported in aqueous suspensions of TiO_2 .

Because the charge carriers created on an illuminated semiconductor are trapped on the surface, and the REDOX reactions occur at the solid/solution interface, the surface of the particles plays an important role in electron/hole transfer reactions and can be engineered to improve both light-harvesting and/or REDOX characteristics of a semiconductor.

It has been recently shown¹⁶ that the modification of the particle surface of colloidal TiO_2 enhances the reduction properties of conduction band electrons and enables effective removal of lead and mercury ions from aqueous solutions. These surface-modified TiO_2 colloids form the basis of an engineering study whose objective is to develop an industrial process for selective heavy metal recovery and for simultaneous removal of organic and metal contaminants from aqueous waste streams.

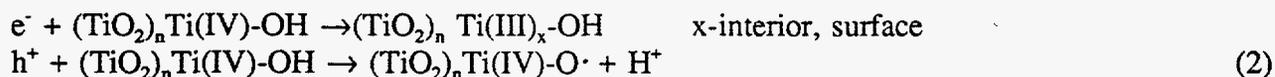
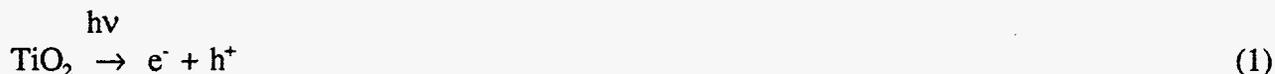
This paper briefly describes the mechanism of lead reduction initiated by colloidal TiO_2 photocatalyst, in which the particle surface has been modified by cysteine and presents the results of bench-scale engineering studies in which surface-modified TiO_2 colloids have been used as photocatalysts for the combined removal of organic compounds and lead from aqueous solutions.

UNDERLYING CHEMISTRY

Unmodified and Modified TiO_2 Catalysts

Electron-hole pairs generated during the illumination of TiO_2 particles (Eq. (1)) can be exploited

for various REDOX processes. Conduction-band electrons that have the potential of -0.3 V (vs. NHE) at pH 3¹⁷ are trapped on the particle surface in about 30 picoseconds, and valence-band holes with potential of +2.9 V at pH 3 are trapped in the hundred-nanosecond range¹⁸. As the energy levels of the surface traps lie within the band gap, the actual reduction and oxidation properties of photogenerated charges are reduced and are dependent on the REDOX potential of surface trapping sites. EPR investigations of surface trapping sites in colloidal TiO₂ suggests that electrons are trapped at metal centers (Ti³⁺), while the holes are trapped on the surface OH groups as a (TiO₂)_nTi(IV)O• radical intermediate.^{19, 20}



where (TiO₂)_n represents bulk material.

We have found that in the presence of the tridentate ligand cysteine, the characteristic oxygen radical signal in the EPR spectrum disappears, and an axially symmetrical, lattice-defect-type EPR signal with g=2.004 is observed²¹. These results suggest that cysteine is strongly bound to a colloid surface and passivates the surface states, which act as hole traps. Infrared spectroscopy results indicate that cysteine is bound to a surface Ti atom through the carboxyl group, with formation of the corresponding salt. As oxygen is covalently linked to the lattice, it can easily accept the photogenerated hole and transfer it to a cysteine molecule. Indeed, we found that at 200K, the electron transfer process occurs, the holes are transferred from the TiO₂ particle to a cysteine molecule, and a sulfur-centered radical is formed:

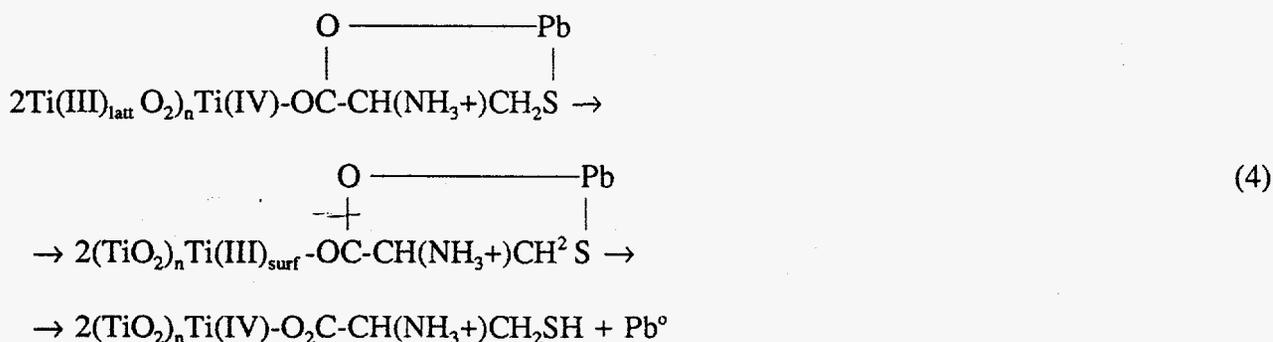


The EPR signal of the TiO₂ colloid itself at 200K was not observed²¹. The REDOX potential for the oxidation of cysteine into a sulfur radical intermediate requires the potential of the hole to be greater than +0.92 V vs. NHE²². The sulfur-centered cysteine radicals most probably undergo dimerization with free cysteine molecules and form the cystine radical (RSSR; E (RSSR•/2RS-) = +0.65 V vs. NHE)²³ at room temperature. Illumination of a cysteine-modified TiO₂ colloid thus results in oxidation of cysteine molecules into cystine and accumulation of trapped electrons.

Photodeposition of Lead

Upon addition of lead ions into solutions with surface-modified TiO₂ colloid, a new complex of cysteine with heavy metal was observed with IR spectroscopy. Lead ions bind with the cysteine molecule in a strong 1:1 complex (pK=11.6), in which cysteine acts as a tridentate ligand²⁴. IR spectroscopy of the cysteine-modified TiO₂ colloid containing lead ions also suggests that lead is chelated with cysteine ligand, with only the carboxyl and mercapto groups. The carboxyl group bridges Ti and Pb ions (Ti-O-C-O-Pb), and in this way Pb becomes covalently linked to

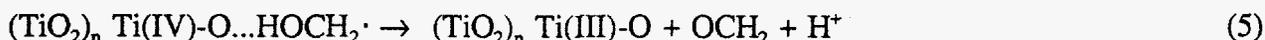
the particle surface as a continuation of the particle lattice. Illumination of this system did not result in the formation of a sulfur-centered radical at 200K, probably because the lone pair of electrons from sulfur that participate in oxidation are bound to the lead ion. However, upon increasing the temperature to room temperature for several minutes, all photogenerated electrons were scavenged by metal ions,



and the metal lead was observed to precipitate.

As the reduction of Pb^{2+} ions in TiO_2 aqueous suspensions was not observed previously^{25, 26}, our results suggest that surface modification of TiO_2 particles with cysteine molecules is responsible for lead reduction. There are four ways that cysteine can modify the system properties that would lead to the reduction of Pb^{2+} ions: (1) electron accumulation, (2) strong adsorption of lead ions, (3) modification of lead ion reduction potentials after complexation, and (4) the modification of the REDOX properties of TiO_2 itself. Our results indicate that all four factors are responsible for enhanced reduction properties of the TiO_2 colloid.

We have found that the yield of trapped electrons is further enhanced after addition of methanol, which is an effective hole scavenger ($E(\text{CH}_3\text{OH}/\cdot\text{CH}_2\text{OH}) = +1.2 \text{ V}$)²⁷. It has been shown previously that electrochemical oxidation of methanol results in formation of electron donating species ($E(\cdot\text{CH}_2\text{OH}/\text{CH}_2\text{O}) = -0.95 \text{ V}$)²³. The large negative potential of the methanol radical induces electron injection into colloidal TiO_2 with formation of surface trapped electrons:



The net effect is that from one photon, two electrons are formed, and consequently the yield of electrons is doubled. Trapped electrons in TiO_2 have enough potential to reduce lead ions in two electron reduction processes. It should be noted that direct reduction of Pb^{2+} ions was not observed in homogeneous solutions due to the negative potential of one-electron reduction of lead ions. Direct reduction of Pb^{2+} by $\cdot\text{CH}_2\text{OH}$ on colloidal TiO_2 was not observed.

EXPERIMENTAL SECTION

Lead acetate ($\text{Pb}[\text{C}_2\text{H}_3\text{O}_2]_2$) were selected as the representative inorganic contaminant to be tested while naphthalene and phenol were chosen as the target organic compounds to be treated. All of the chemicals used in the studies were reagent grade (obtained from Fisher Scientific) and were used as received. The sample solutions were prepared fresh before conducting the

experiments using laboratory deionized water. All of the experiments were conducted with a quartz reactor having a total capacity of 250 mL.

The photochemical reactor (Rayonet Model RMR-600, Branford, Conn.) used in the studies had a reactor chamber 10" in diameter and 10 1/2" 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 by using a gas chromatograph (HP 5890 series II, Hewlett Packard, Wilmington, DE) equipped with an FID detector; the lead concentration in the solution was analyzed by using an atomic absorption (AA) spectrophotometer (model 200 A, Buck Scientific, East Norwalk, Conn.). The sample solutions were preserved in a 1% nitric acid solution (pH<2) before being analyzed.

Adsorption studies for the target contaminants were carried out in the laboratory; a shaker table (Eberbach Co., Ann Arbor, Mich.) was used 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.

RESULTS AND DISCUSSION

Adsorption Rate and Adsorption Capacity of TiO₂ Photocatalyst

The adsorption rate and adsorption capacity of lead, as well as the target organic compounds, over either treated or untreated TiO₂ photocatalysts were investigated before any UV irradiation had been performed. 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. The pH of the irradiated solutions was adjusted to about four. Changing the pH value of the solution changes the surface charge of TiO₂, as well as the extent of hydrolysis and species distribution of the metal ions, and as a result the adsorption capacity of the photocatalysts to metal ions changes. It has been reported that there was no adsorption of Pb²⁺ ions on TiO₂ photocatalyst semiconductor particles in the dark and at pH 1.4. If another chemical compound, such as naphthalene or phenol, is present in the solution, the lead ions will compete with the added chemical compound for the adsorption sites on the surface of the photocatalyst, which may result in a lower adsorption capacity for the target compound.

Adsorption equilibrium between the target compounds and the photocatalysts was assumed to be reached after 72 h of contact, although it was reported that adsorption equilibrium between pyridine and TiO₂ photocatalyst could be reached within one hour of contact time²⁸. 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 TiO₂ photocatalyst is

appreciably higher than that of the untreated photocatalyst. Adsorption data on lead ions also reveal that the adsorption rate of the treated photocatalyst is much faster than that of the untreated photocatalyst. The coated cysteine compound behaves as a strong active site for capturing the dissolved metal ions in solution.

The adsorption rate and adsorption capacity may have significant effects on the reaction rates of the photo-induced REDOX reactions. During a typical UV irradiation with a photocatalyst in 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.

In the experiments, 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 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 in that 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 inorganic compounds. The disappearance of the introduced lead ion and naphthalene in the irradiated aqueous solution is represented in Figs. 1 and 2, respectively. The degradation of phenol compound with or without the presence of lead ions is not shown here but is presented in a separate poster session. However, the phenol results are discussed below.

PLACE FIGS. 1 AND 2 HERE

The removal of lead ions in solution was verified from the residual lead analysis (using AA) of the irradiated solution, along with the observation of black particulates (believed to be metallic lead) generated in the solution. From an 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; more than 95% of dissolved lead ions were 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.

During the UV irradiation, the lead ions were recognized to be adsorbed onto the surface of TiO_2 photocatalyst and then reduced to elemental lead. However, it is uncertain how many lead ions were removed from the solution through photoreduction to their metallic form and how many were removed only by adsorption on the TiO_2 photocatalysts.

Figure 2 shows that 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 TiO₂ photocatalysts was statistically insignificant. The introduced naphthalene may be degraded through direct adsorption of UV energy or through oxidation by the radicals generated by the excited TiO₂ photocatalysts or by the photocatalysts themselves.

UV irradiation of phenol compound in aqueous solution using the two photocatalysts exhibited similar results. Initial phenol concentrations of about 100 mg/L decreased to less than 20 mg/L within 30 min of irradiation and leveled out over irradiation times of 30 to 60 min. Approximately 80% of the phenol was removed within the first 30 min of irradiation. The phenol degradation rate using treated TiO₂ photocatalyst was somewhat faster than that with untreated photocatalyst. With lead ions present in the irradiated solution, the phenol degradation rate decreased slightly with the use of untreated photocatalyst in the solution, but the change was insignificant. It appeared that the phenol degradation rates were unchanged when using treated TiO₂ as the photocatalyst in the experiments.

Simultaneous Removal of Lead and Organic Compounds

Experiments were also carried out in which lead ions and organic compounds (such as naphthalene and phenol) were simultaneously treated with the UV-TiO₂ photocatalyst. When organic compounds, such as naphthalene and phenol are present, they may compete with lead ions for the adsorption sites on the surface of TiO₂ photocatalyst during UV irradiation, resulting in a decrease in the lead removal rate, or serve as additional electron donors and enhance the photoreduction rate of lead ions. Under our experimental conditions, the removal rate of lead ion in the irradiated solution seems to have a minor effect on the existing phenol compounds. The decay in lead concentration remained unchanged in this case. However, noticeable differences were obtained when naphthalene was added to the solution. As shown in Fig. 3, the presence of naphthalene resulted in a "lag-time" effect on the photoreduction of lead from the irradiated solution. The removal rate of lead ions decreased significantly within the first 30 min of UV irradiation. In both cases (using untreated and treated TiO₂ photocatalysts), the use of cysteine-modified TiO₂ photocatalysts resulted in faster and more effective removal/recovery than was obtained for the untreated TiO₂ system.

PLACE FIG. 3 HERE

With inorganic and organic compounds in solution in the same system, the presence of lead ions would provide additional electron-acceptors, resulting in an increased removal/degradation rate for the organic compounds. However, probably due to the low organic concentrations in the irradiated solution, the experimental results (as shown in Fig. 4) showed that the presence of lead ions had little effect on the removal/degradation of naphthalene from solution. The presence of lead ions also had an insignificant effect on the photooxidation of phenol compound. The degradation rate remained unchanged with or without the presence of lead ions in the solution.

PLACE FIG. 4 HERE

SUMMARY AND CONCLUSION

The experimental results indicate that simultaneous removal of organic compounds (such as naphthalene and phenol) and inorganic compounds (such as lead ions) in aqueous solution can be achieved by using a UV-irradiated TiO₂ photocatalyst system. The removal rates of organic and inorganic compounds can be enhanced through surface modification of the TiO₂ photocatalyst using an organic substance such as cysteine. The cysteine-modified TiO₂ 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. The photoreduction rate of lead ions were significantly affected by the presence of some organic compounds, such as naphthalene, but had little effect on the presence of other organic compounds such as phenol. The photodegradation rates of organic compounds were not significantly affected by the presence of metal ions.

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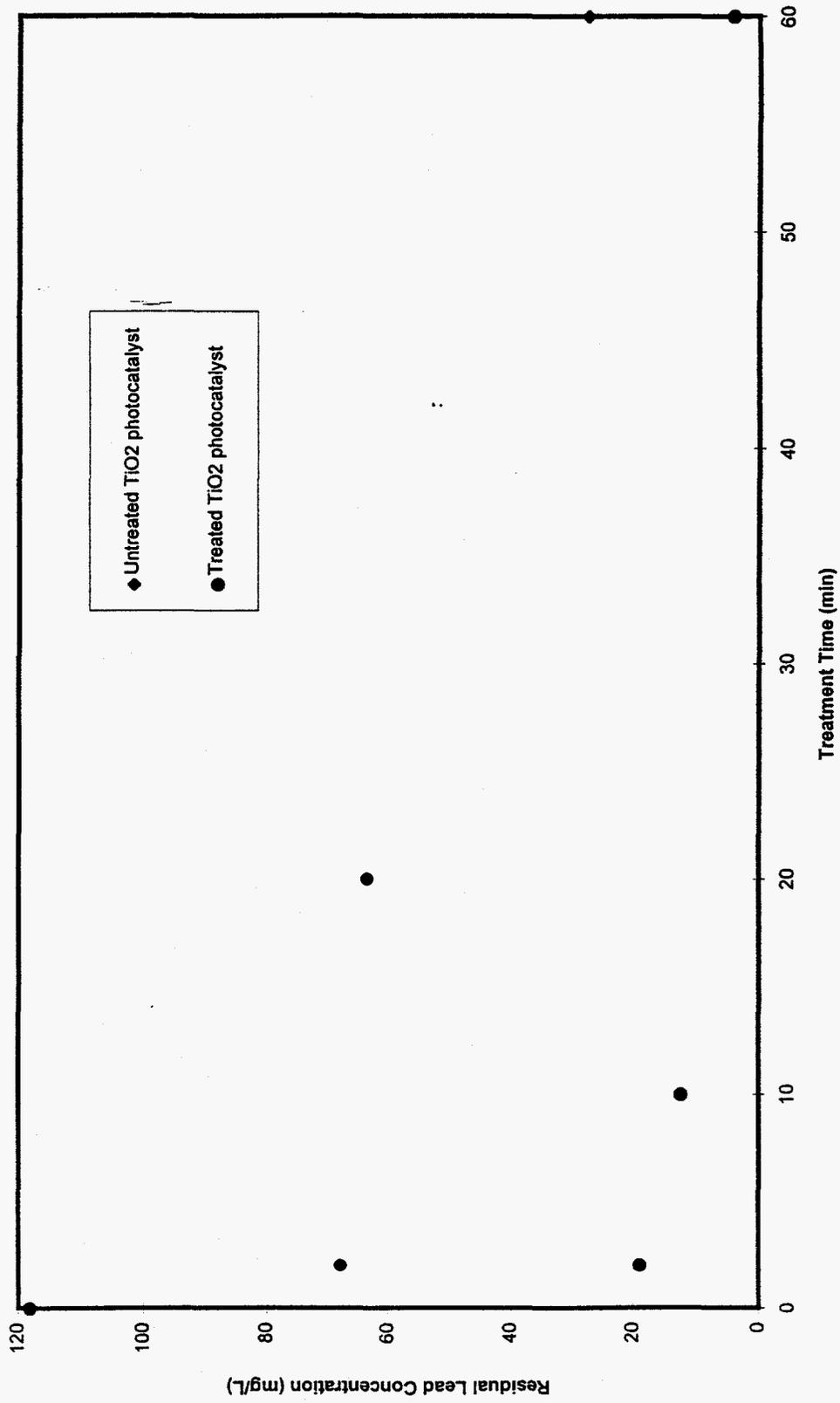


Figure 1. Effect of Irradiation Time - Lead Only

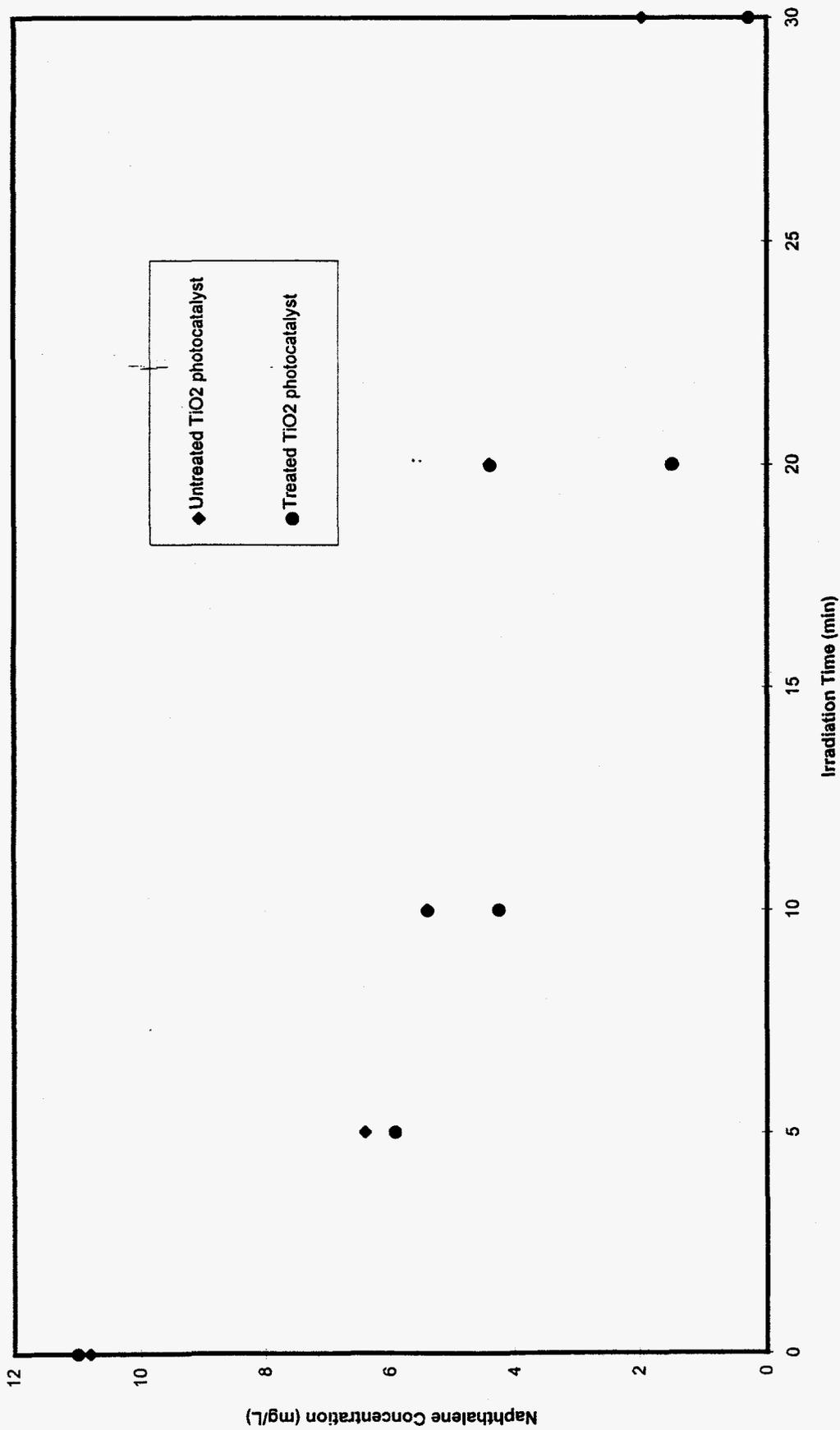


Figure 2. Effect of Irradiation Time - Naphthalene Only

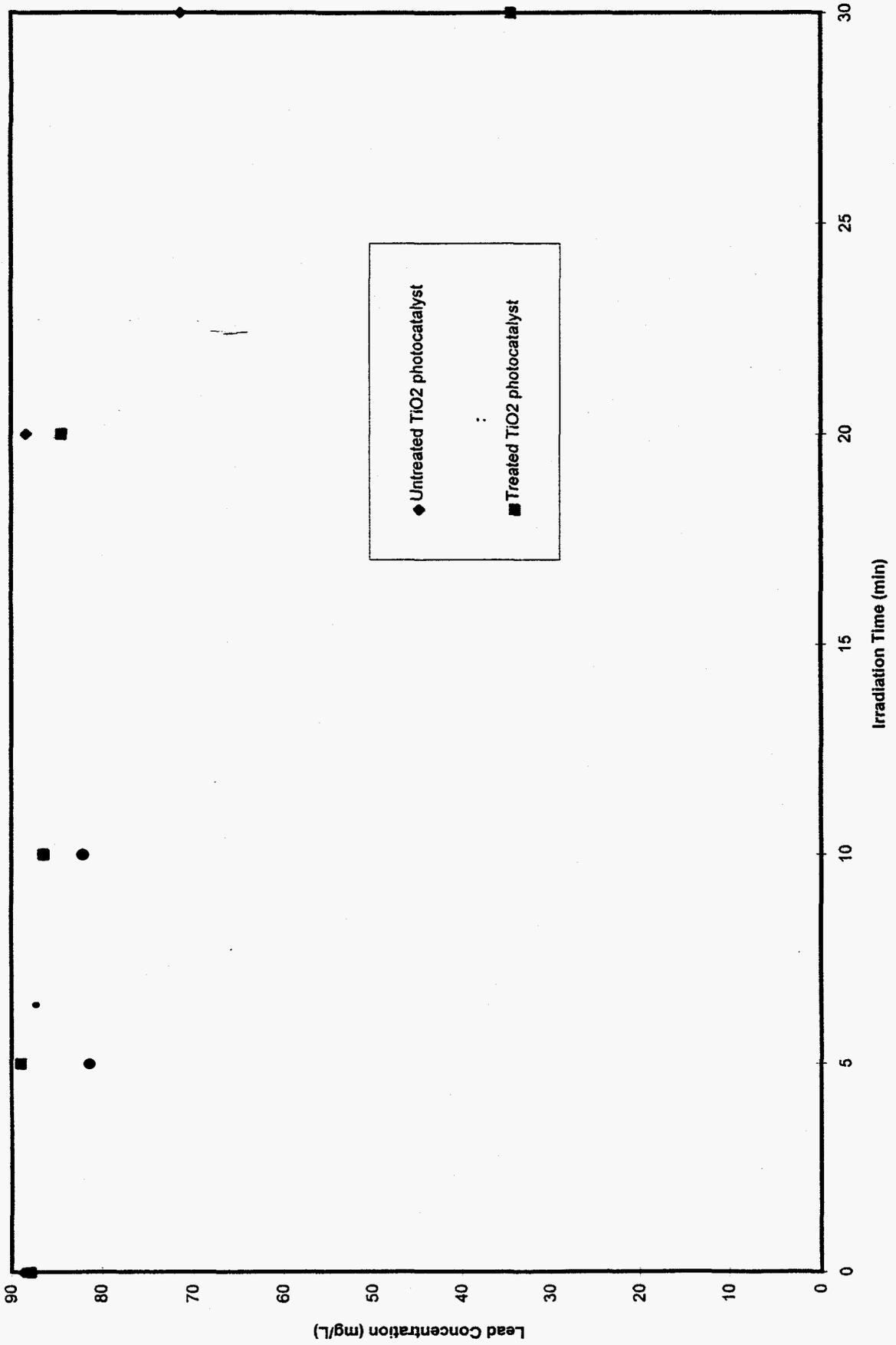


Figure 3. Combined Naphthalene-Lead System - Lead Concentration

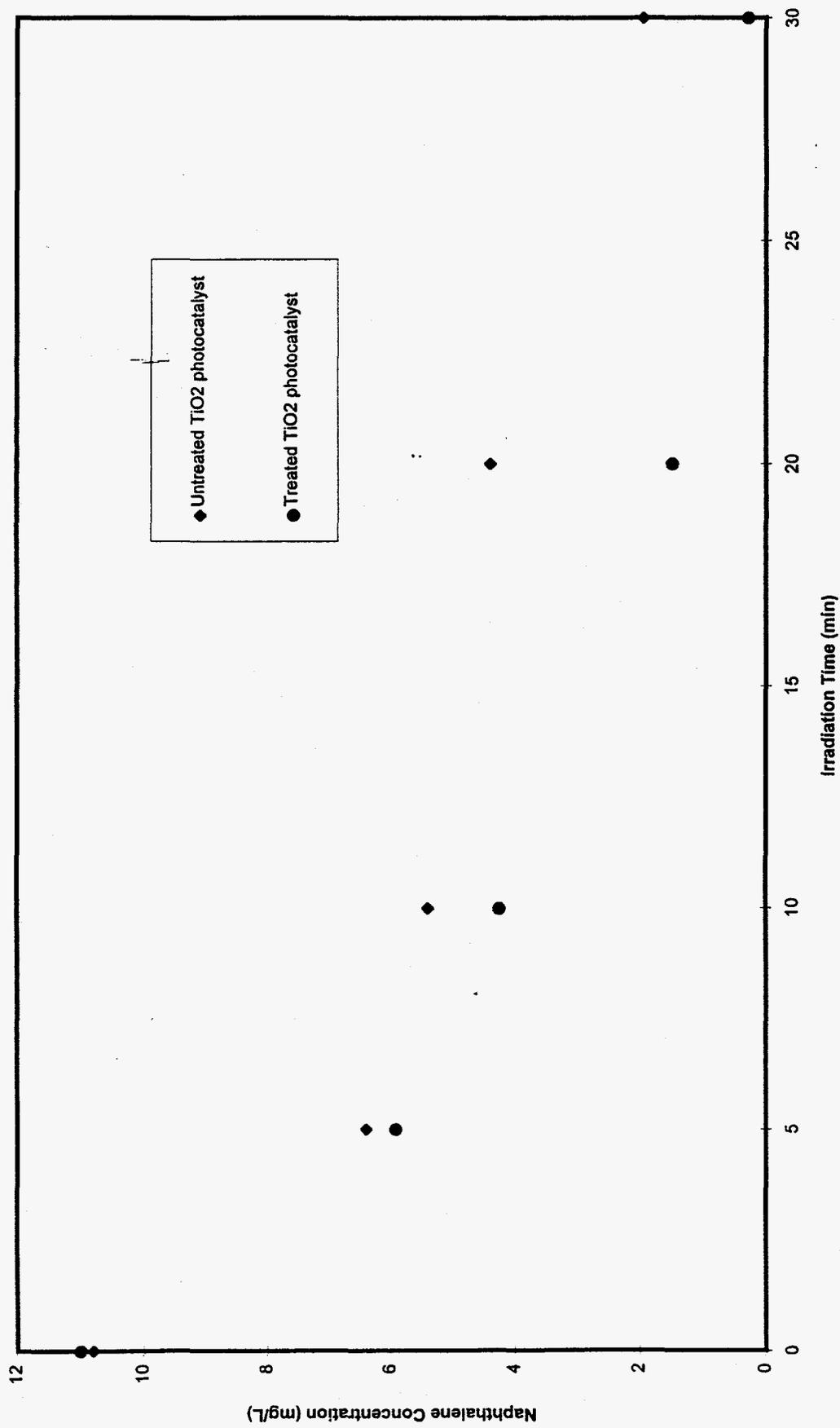


Figure 4. Effect of Irradiation Time - Naphthalene Only