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RENOVATION OF PESTICIDE CONTAMINATED RINSE WATERS

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and
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Final Report
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JUSTIFICATION

Many instances of severe contamination of groundwater by pesticides have been traced to spills at pesticide mixing/loading sites. Under Wisconsin law, farmers and commercial applicators handling more than 1500 lbs of pesticides per year must install containment pads at mixing/loading sites. Rinsates generated during use of the pads must be collected in sumps and transferred to holding tanks. Disposal of the rinsates is frequently achieved by utilization in new tank mixes of pesticides, but where crop damage is possible due to pesticide incompatibility, this may not be an option. New technologies to treat pesticide contaminted waters of this kind are needed, since few other disposal options are available. Photocatalytic oxidation using titanium dioxide and ultraviolet (UV) light is a promising approach that has been demonstrated to mineralize a wide array of recalcitrant organic compounds such as PCBs. The purpose of this study was to examine the feasibility of using this technology to treat pesticide wastes and to explore ways to optimize treatment conditions. Studies of this nature are continuing under a different grant.

INTRODUCTION AND LITERATURE REVIEW

The anatase crystalline form of titanium dioxide (TiO_2) is an n-type semiconductor and has a band-gap energy (the difference in energy between valence shell orbitals and the lowest-energy conducting band orbital in the mineral catalyst) corresponding to that of 385 nm wavelength light. The process of photocatalytic degradation begins with absorption of ultraviolet light by the catalyst with sufficient energy to excite electrons across the band gap. The photolytically unbonded electron leaves a vacant, positively charged hole in the crystal lattice. Both charged species are mobile, and can migrate to the crystal surface to assume catalytic functions. Each positive hole is a powerful oxidizing agent which can oxidize organic molecules at or near the TiO_2 surface, while each free electron can serve as a reducing agent. Normally the unbonded electrons react with water or water vapor to produce hydrogen. While direct oxidation by holes of organic molecules sorbed to the TiO_2 surface is believed to occur, most oxidations appear to be mediated by hydroxyl radicals ($HO\cdot$) formed when holes remove an electron from surface-bonded hydroxide ions (Turchi and Ollis, 1990; Ollis et al., 1991). Photocatalysis by titania can be carried out in both gas and liquid phases. Competing technologies for degrading organic contaminants that rely on hydroxyl radical production include ozone + UV and H_2O_2 + UV. Titania catalyzed oxidations are dependent upon the presence of an electron acceptor, usually oxygen, although metal ions, hydrogen peroxide and other compounds may serve this function as well. Mineralization of many compounds including chlorinated aromatic hydrocarbons, surfactants, fluorinated and brominated compounds, heterocyclic aromatic compounds, and organic compounds containing nitrogen, sulfur and phosphorus, has been demonstrated. The only molecules so far observed to resist mineralization are a few fully oxidized species such as cyanuric acid, a product of *s*-triazine degradation (Pelizzetti et al., 1990) and carbon tetrachloride; other chlorinated saturated hydrocarbons are degradable through abstraction of hydrogen atoms.

TiO_2 is used in photocatalysis as a slurry, a thin film on a glass support, or porous, sintered aggregates or pellets of particles. The primary particles in the various forms of titania range in size from 3 to 30 nm.

Many important factors must be considered in the development of a practical photocatalytic reactor including:

1. The selection of affordable lamps that efficiently convert electricity into useful light.
2. Configuring the reactor so that most of the light is directed onto the catalyst.
3. Arranging the catalyst so that most of the light reaching it is absorbed.
4. Selecting a form of the catalyst that will utilize most of the light in electron-hole separation without electron-hole loss by recombination with mobile electrons.
5. Configuring the reactor to minimize limitations to the mass tranfer of solutes to the catalyst surface.
6. Sizing the reactor so that the contaminants are reduced to the desired levels with single throughputs.
7. Ensuring that adequate concentrations of oxygen or other electron acceptor are present in all parts of the reactor so that this does not become a limiting component.

In considering these criteria while designing the two bench-scale reactors used in this study, several basic approaches were adopted. A third reactor of the annular thin film type is briefly described but proved to be highly inefficient. Fluorescent black lights were selected because they are inexpensive, efficient and most of the light produced is of wavelengths between 320 and 385 nm, with peak intensity at 366 nm (Rizzuti and Brucato, 1988); light with a wavelength longer than 385 nm lacks the energy to bridge the anatase titania band gap, while light of wavelengths shorter than 320 nm is absorbed by borosilicate glass. Although quartz glass is transparent to light of wavelengths well below 320 nm, it is prohibitively expensive. While many reactor configurations are possible, an annular design was adopted for one of the reactors constructed to capture as much of the light as possible.

Work with thin films of titania supported on glass have shown that films thicker than 1 μm tend to separate from the support in fast flowing or stirred solutions.

Titania films of this thickness absorb only a fraction of the light reaching them; the loss of light here has led to considerable unsuccessful efforts to fabricate thicker films. Titania pellets offer a better solution to this problem. Reactor columns packed with TiO_2 pellets effectively absorb all of the light reaching them and appear to be stable in solution. The tortuosity of the packed bed also increases turbulance in the liquid, increasing the Reynold's number and improving mass transfer of solutes to the surface.

Titania prepared by sol-gel methods are 100% anatase, while materials prepared by other methods usually contain anatase mixed with some rutile. Pure anatase is believed to perform better in photocatalytic processes.

Light intensity appears to influence the efficiency of photocatalytic reactions. High intensity light may increase the frequency of electron-hole pair recombination due to the higher density of both species. Smaller sized particles may also influence efficiency by decreasing the mean distance to the surface of the catalyst, making interactions of holes with solutes more likely.

The reaction kinetics in heterogeneous photocatalysis with titania tend to follow a Langmuir-Hinshelwood model (Matthews, 1987). This model predicts that at high solute concentrations, degradation will proceed in a zero-order fashion. As the concentration drops, the reaction will become first-order. Information of this kind is important to design the residence time necessary to achieve a satisfactory level of treatment. The half-life is a useful parameter that can be derived from the first-order rate expression for a given compound, but will not be valid at high concentrations, where the rate is closer to zero order. Determination of all of the parameters of the Langmuir-Hinshelwood expression requires that rate data be obtained across a wide range of initial solute concentrations.

A basic factor in reaction kinetics in titania systems is the adsorption properties of the compound. It has generally been observed that intermediate degradation products, particularly of hydrophobic parent compounds, are more hydroxylated and have a higher affinity for the surface and are therefore degraded much faster than the parent compound (Rizzuti and Brucato, 1988). In this way, the initial conversion of the parent is usually the rate limiting step in mineralization.

METHODS

TITANIA PREPARATION

Titania preparations used in this study were made by sol-gel methods involving hydrolysis of the metal alkoxide and stabilization in an acid medium (Anderson et al., 1988), followed by dialysis: 15 mL of titanium isopropoxide (Aldrich Co., Milwaukee, WI) was added to a stirred solution of 180 mL distilled deionized water with 1.3 mL concentrated nitric acid, stirred for 3-4 days, then dialyzed through Spectra Por dialysis tubing (3500 molecular weight, Fisher Scientific, Pittsburgh, PA) against 15 L reagent grade water, with daily water changes until the pH of the dialysis water is above 4. The primary particles produced by this method range from 3-7 nm in diameter.

Titania films were prepared by spin-coating at 2000 rpm on microscope slides followed by drying at room temperature and firing. In some cases, multiple layers of titania film were applied to glass, with firing taking place between application of each layer.

Titania pellets were prepared by removing water from the sol by rotary evaporation until gelation begins to occur. At that time the gel is poured into syringes or onto a teflon sheet as a slab and allowed to set. The gel is dried further and then extruded as a bead or cut into smaller pieces. When completely dry, the pellets are fired, then sized and broken up if necessary to obtain desired sizes (0.5-2 mm diameter). Firing in all cases was at 300 C for 4 hours. Pellets prepared in this manner have a porosity of approximately 50% and a surface area of 200 m^2/g.

REACTOR DESIGNS

i. Flat plate reactor

Several reactors have been constructed for laboratory studies of photocatalysis with titania. The simplest configuration incorporates an array of flow cells made from rectangular blocks of teflon (Figure 1). Nipples were machined at both ends of the blocks to accept tubing, and holes drilled through to allow liquid to flow to a shallow rectangular trough (64 x 20 x 2 mm) mortised into the top of the block. A glass

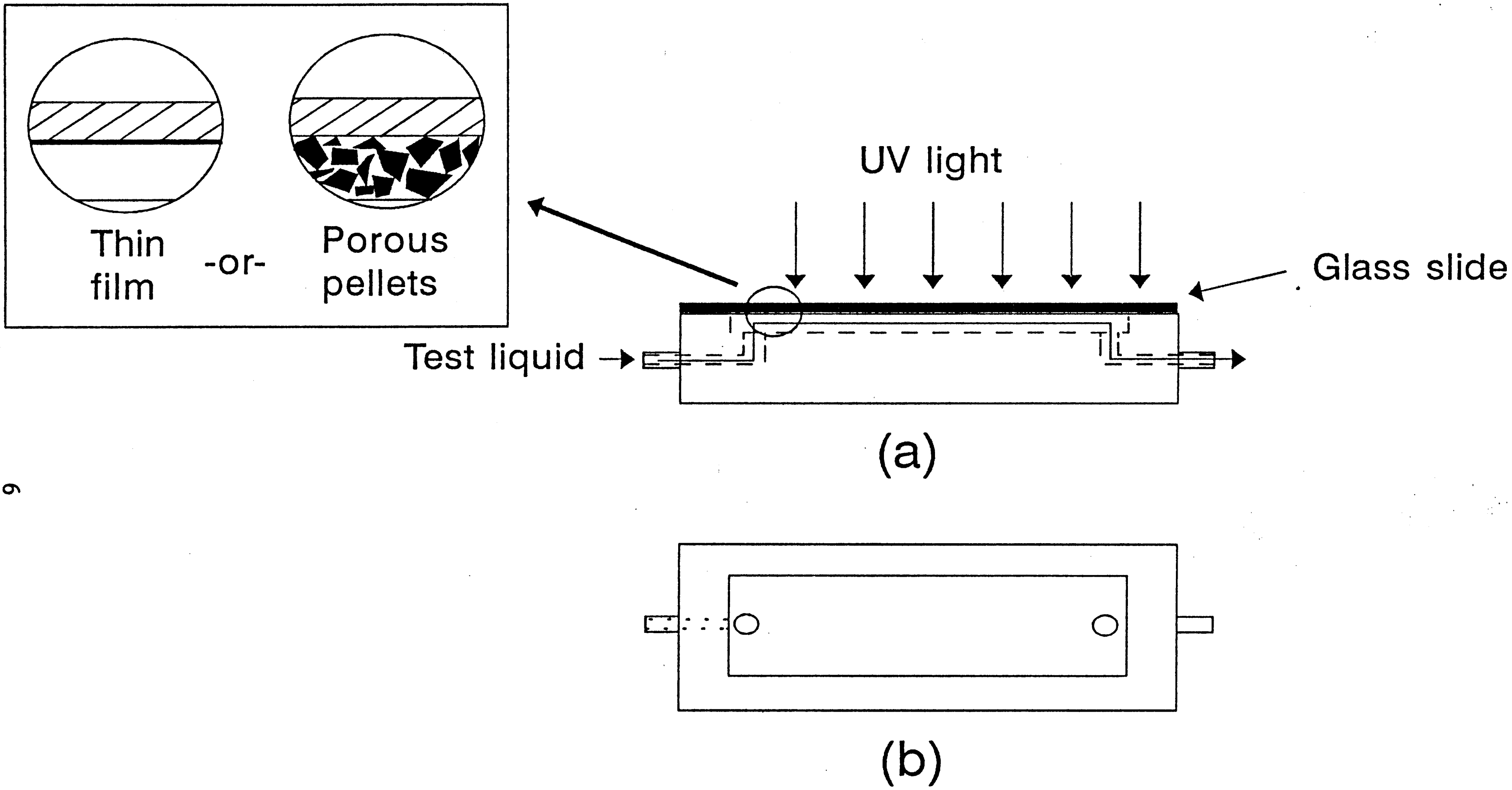

Figure 1. Flow cell used in flat plate reactor, showing (a) side view and (b) top view.

microscope slide was secured to the top of the block with clamps, a seal being formed between the slide and the rim of the trough. In this manner, the test liquid entering the cell passed through a chamber into which light could enter (Figure 2). A thin film of titania was applied to the underside of the slide (in ongoing work, the chamber has been packed with titania pellets). The test liquid was pumped to the cells from 225 mL capacity glass reservoirs by a peristaltic pump (Isthmatec model 7624-62, Cole-Parmer, Chicago IL). The tubing used was neoprene for formic acid experiments, teflon for atrazine experiments and PharmMed-brand silicone tubing for the pump (all from Cole-Parmer). Air was bubbled into the reservoirs through ports in their tops at a sufficient rate to ensure that the liquid was saturated, verified by measuring dissolved oxygen concentrations using an oxygen electrode, Orion model 97-08-00 (Fisher Scientific, Pittsburgh, PA). Additional ports facilitated temperature measurement and sampling. The liquid was stirred by means of magnetic stir bars driven by air-driven stir plates (GFS Chemical, Columbus, OH). UV light was supplied by arraying two 15 W fluorescent "black lights" in a fixture backed with a parabolic mirror (UVP Co. Model XX-15L, San Gabriel, CA). Light intensity was varied by adjusting the height of the fixture and was measured using a model 380 optometer with a model 1222, 1 cm^2 photodiode detector (United Detector Technology, Hawthorne, CA). The detector was calibrated at 366 nm. With the light positioned 15 cm above the cells, the light intensity was 2 mW/cm^2 or 8×10^{-8} einsteins/sec in each reactor cell.

ii. Annular pellet-packed reactor

An annular, column-like reactor was constructed by machining concentric grooves in two telfon disks (17 mm x 45 mm in diameter) that serve as ends for the column (Figure 3). The grooves act as receptacles for two concentric sections of borosilicate glass tubing, each 50 mm long. The tubes were sized to fit with approximately 2 mm of space between them (the inner tube has a 32 ±0.7 mm OD while the outer piece has a 36 ±0.9 mm ID; the inner and outer tubes are 1.8 and 2.0 mm thick). Five holes drilled through each of the teflon ends allow liquid to pass through the annular flow cell. The flow cell was packed with titania pellets, with a small amount of glass wool at each end to prevent efflux of the smaller pellets from the liquid ports. PVC blocks (25 x 60 x 60 mm) were machined to cup the teflon

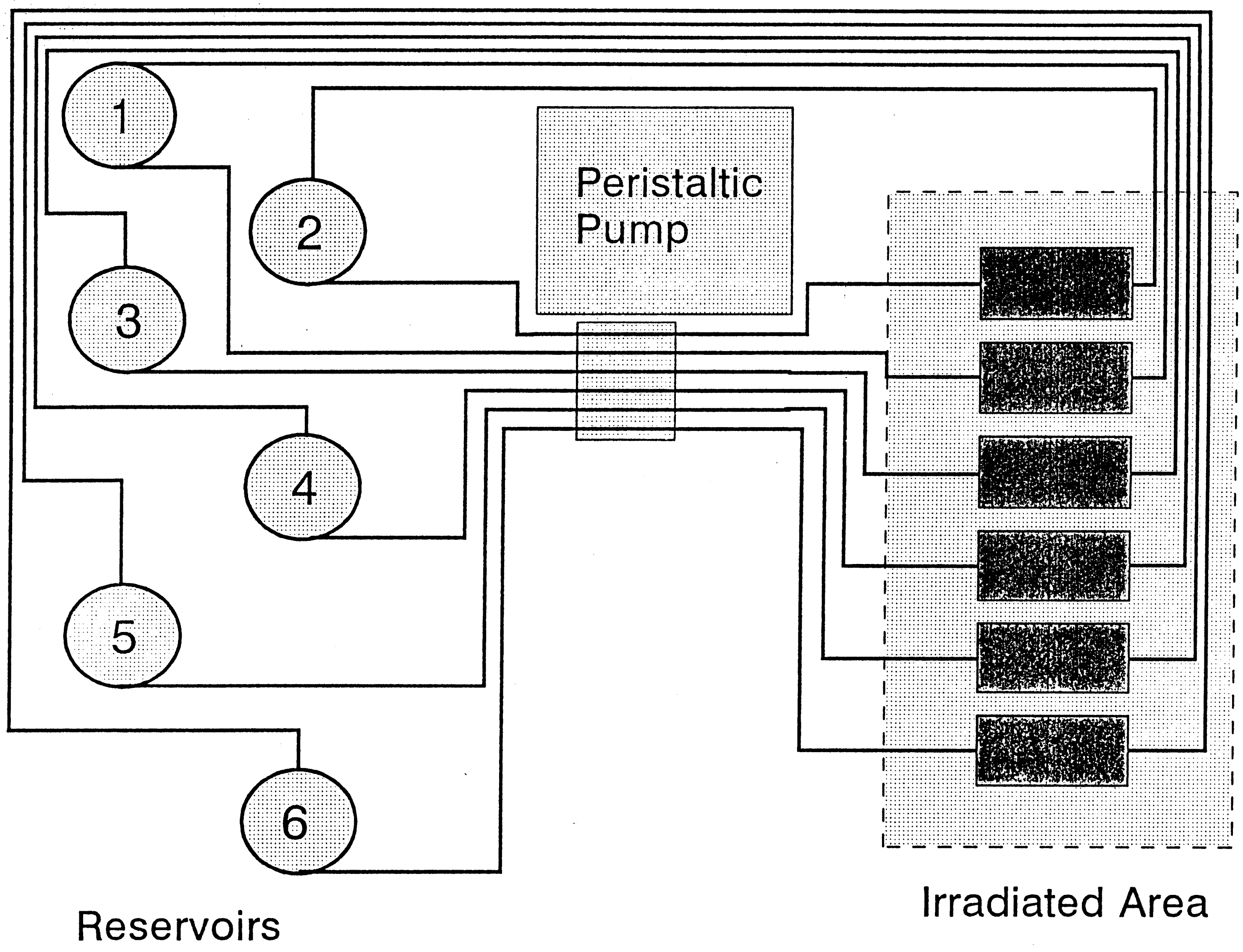

Figure 2. Schematic of flat plate reactor.

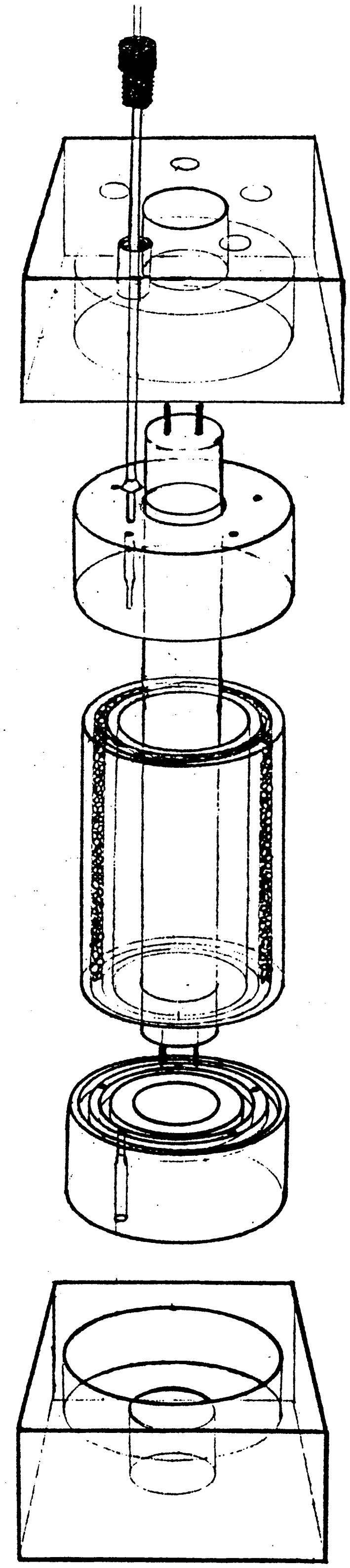

Figure 3. Flow cell used in 4W annular reactor.

ends. Holes aligned with the liquid port holes in the teflon block were drilled and tapped to accept nylon ferrule nuts to seal tubing with tefzel (a little harder than teflon but with similar adsorption properties) ferrules on 3.17-mm (0.125 in) teflon tubing against the teflon ends. A 4-watt fluorescent black light (courtesy of Fotodyne Co, Milwaukee, WI) was inserted through 16-mm holes drilled in the center of each of the teflon ends. A seal was made between the ends of the tubes and the teflon disks by inserting washers cut from teflon tape into the grooves in the teflon ends and by pressing the ends together by means of threaded rods inserted through the corners of the PVC blocks. Liquid travelling to the reactor first passes through a distributor where it is split into five streams, each leading to one of the five port holes in the teflon ends. The distributor consists of a rectangular block of teflon with a nipple machined on one end with a hole drilled into the block. Short holes drilled into one side of the block intersect the main hole. The block is recessed in a plastic block with threaded holes aligned with the short connecting holes to accomodate nuts and ferrules on tubing, sealing against the teflon. A similar arrangement collects the five streams of liquid leaving the reactor and consolidates them into one. The reservoir and peristaltic pump used are those used in the flat plate reactor (Figure 4).

iii Annular thin-film reactor

A third reactor used in some experiments was built with a high-power mercury vapor lamp and a large-volume reservoir. We have concluded that reactors using high-wattage short-wave UV lamps are not practical because short-wave UV does not penetrate common types of glass, requiring that the shortwave bands be wasted or that the reactor be constructed of expensive quartz glass and because TiO_2 irradiated at high-intensity exhibits low photochemical efficiency. This reactor is no longer in use and and will not be described in detail. Summary characteristics of all three reactors are presented in Table 1.

Actinometry experiments were performed for each reactor to measure the amount of light actually entering the reactor by determining the rate of the light-driven, UO_2- catalyzed oxidation of oxalate. A solution of sodium oxalate and UO_2 (Fluka, Ronkonkoma, NY) was circulated in the reactor, and periodically, samples were taken and oxalate determined by titration with permanganate. Using the actinometry data, manufacturers' data on the spectral distribution of light emitted from the lamps,

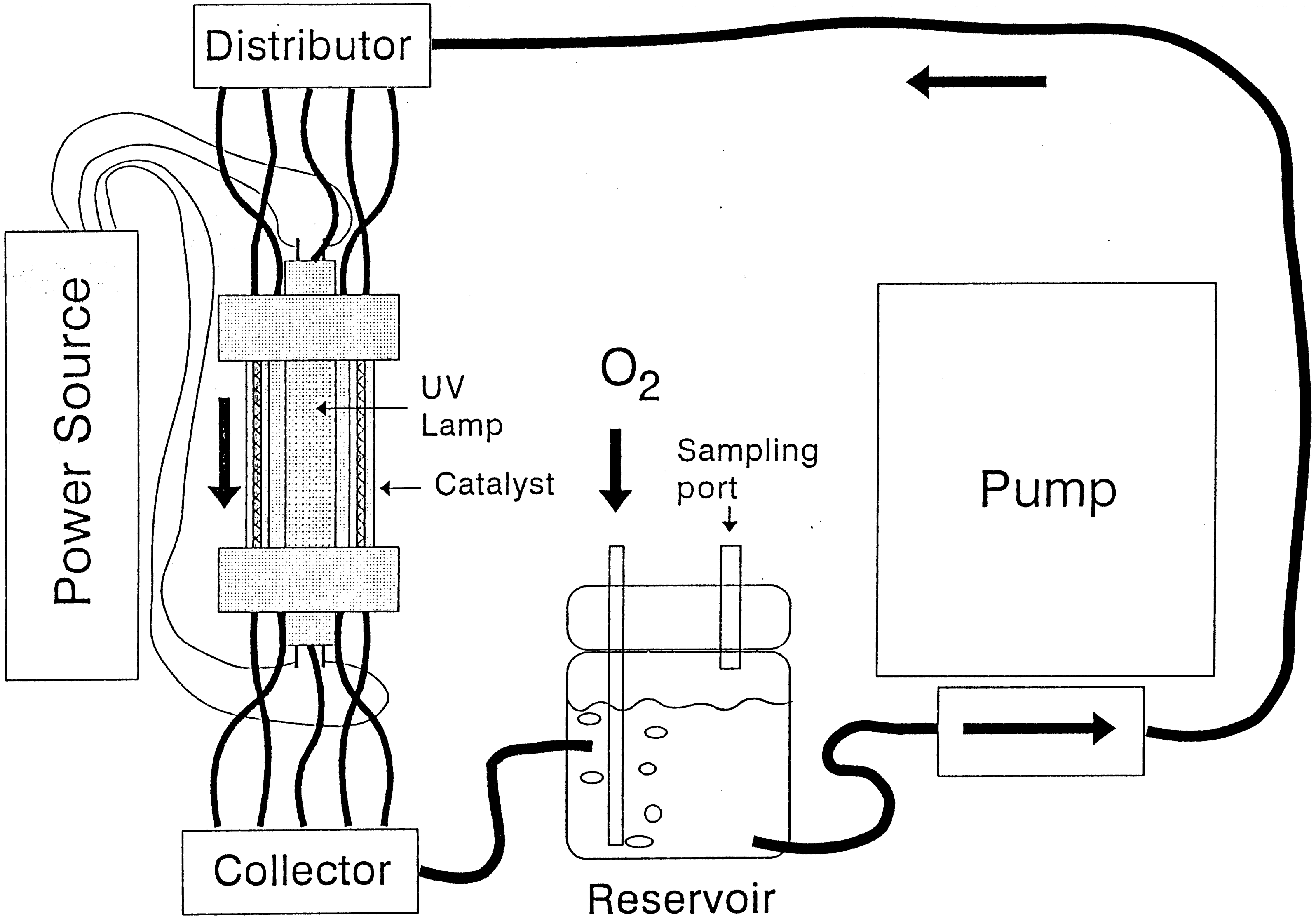

Figure 4. Schematic of 4W annular reactor.

reactor geometry, the light absorbance characteristics of the TiO_2, the absorbance characteristics of the actinometer (UO_2 + sodium oxalate), and the borosilicate glass reactor walls, a calculation was made using a computer program to estimate the number of photons entering the reactor. The estimate (Table 1) permitted assessment of reactor photochemical efficiencies (the ratio of photons used in degradation reactions to photons absorbed).

Table 1. Reactor characteristics

Reactor configuration	Light source, watts	Volume, mL	Form of TiO_2	UV flux, E/sec cm^2
i. Flat Plate	2 x 15	150	Porous film	5.5×10^{-9}
ii. Annular	4	180	Porous pellets	5.8×10^{-9}
iii. Annular	1,500	3,000	Porous film	6.7×10^{-7}

Experiments to determine rates of photocatalytic degradation were carried out using formic acid and atrazine. Formic acid (Aldrich, 96%) was selected because its concentration can be conveniently estimated with a conductivity meter (Model 604 VWR Scientific, Chicago, IL), and it is mineralized in one step, is strongly sorbed on TiO_2 and serves as a good probe for the maximum activity of the catalyst. Atrazine (>99% purity, donated by Ciba-Geigy, Greensboro, NC), was selected because it is a widely used herbicide in the midwest and based on published rate constants for reaction with hydroxyl radical, is relatively slowly oxidized compared with other herbicides (Haag and Yao, 1992). Atrazine was determined by high pressure liquid chromatography (HPLC).

Atrazine solutions were prepared by dissolving appropriate amounts of atrazine in 50 to 100 mL HPLC grade methanol (Fisher Scientific) in a round-bottomed flask (1-L for large batches; 250 mL for smaller batches), removing the methanol slowly under low vacuum on a rotary evaporator, leaving a film of atrazine coating the walls of the flask, which could be dissolved by filling halfway with reagent-grade water and spinning the flask without vacuum for about 20 minutes. The water was then decanted and the process repeated until the appropriate total volume of atrazine solution (1-4 L) was obtained.

Samples collected during the experiment were placed directly into amber glass vials with septum-lined caps. Without further processing, the samples were chromatographed using a Gilson 714 system HPLC (Gilson Medical Electronics, Middleton, WI) equipped with a differential UV detector and a 150 mm x 4.5 mm C_8/cation mixed-mode reverse-phase/ion exchange column (Alltech Co, Waukegan, IL). The mobile phase consisted of 70% phosphate (Malinckrodt) buffer (50 m*M*, pH 6.7) and 30% HPLC-grade methanol (Fisher Scientific). The column effluent was monitored at two wavelengths (220 and 240 nm). Comparisons were made to results with standards that included atrazine and 7 of its metabolites (also from Ciba-Geigy, shown in Table 2). Based on these comparisons, some of the degradation products were tentatively identified, and the unreacted parent atrazine was quantified.

Table 2. Atrazine and metabolite standards used in analysis of products.

Compound abbreviation	Chemical name	Common name
AT	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine	Atrazine
OHAT	2-Hydroxy-4-ethylamino-6-isopropylamino-*s*-triazine	Hydroxyatrazine
DIAT	2-Chloro-4-ethylamino-6-amino-*s*-triazine	Desisopropylated atrazine
DEAT	2-Chloro-4-amino-6-isopropylamino-*s*-triazine	Desethylated atrazine
DDAT	2-Chloro-4,6-diamino-*s*-triazine	Diamino-chloro-*s*-triazine
DEOH	2-Hydroxy-4-amino-6-isopropylamino-s-triazine	Desethylated hydroxyatrazine
DIOH	2-Hydroxy-4-ethylamino-6-amino-*s*-triazine	Desisopropylated hydroxyatrazine
DDOH	2-Hydroxy-4,6-diamino-*s*-triazine	Diamino-hydroxy-*s*-triazine

DATA

FORMIC ACID STUDIES

Degradation experiments carried out in the reactors using solutions of formic acid (Figures 5 and 6) showed that increasing light intensity raises degradation rates but lowers the photochemical efficiency. Using similar conditions in the three reactors, the highest photochemical efficiency observed approached 25% using the pellet-based reactor. In the thin-film systems, only about 50% of the light reaching the titania is absorbed while almost 100% is absorbed in the pellet system. The light actually absorbed by the titania is used to calculate the photochemical efficiency.

Preliminary data indicates that higher efficiencies, approaching 100% for formic acid, are attainable with the pellet-based system; interpretation of this data is complicated by the fact that the pellet-based reactor has roughly 1000 times as much catalyst as the thin film reactors (gram vs mg quantities). While both pellets and films have surface areas on the order of 200 m^2/g, the greater quantity of TiO_2 used in the pellet system adsorbs significant amounts of the formic acid in the reactant solution. Distinguishing between degradation and adsorption can only be accomplished by operating the reactor over a period of days, slowly adding fresh formic acid solution to the recycle loop while removing an equivalent volume, until the reactor appears to reach a steady state.

ATRAZINE STUDIES

Atrazine degradation studies were carried out in the annular thin-film reactor (see iii, Table 1) and the flat-plate reactor (see i, Table 1). Figure 7 shows the rate of disappearance of atrazine in both reactors. As with the photodegradation of formic acid, the low-powered flat-plate reactor exhibited greater efficiency: 890 versus 49 μmole of atrazine degraded/einstein. Pelizzetti et al. (1990) reported a higher efficiency (1,310 μmole/einstein) in a study of atrazine photocatalysis in a TiO_2 slurry-based system using a high-intensity light source with the wavelengths shorter than 340 nm filtered out.

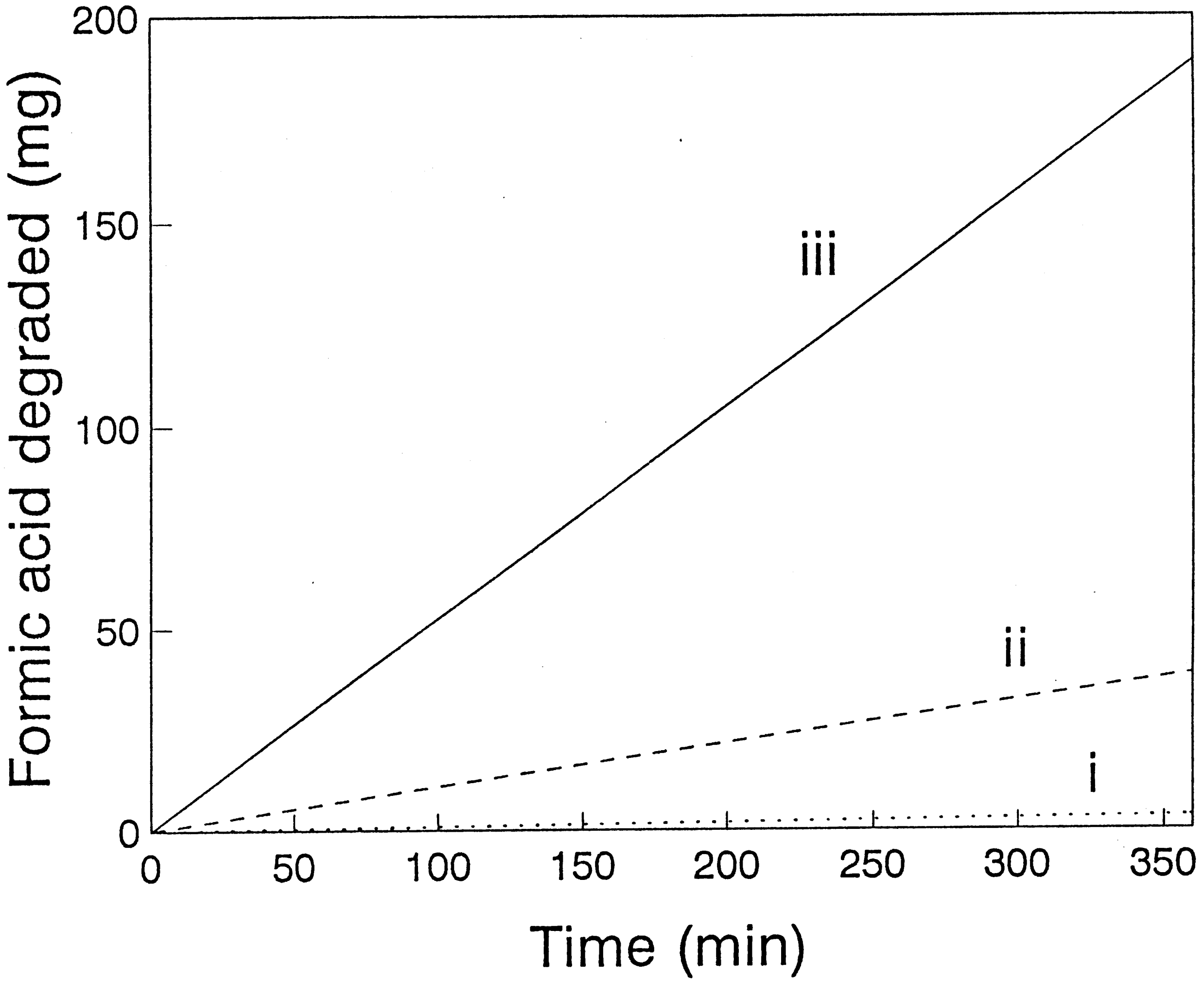

Figure 5. Formic acid degradation with time for the three TiO_2 photocatalytic reactors; i = 2x15W, flat plate reactor; ii = 4W annular pellet reactor; iii = 1500W, annular thin film reactor.

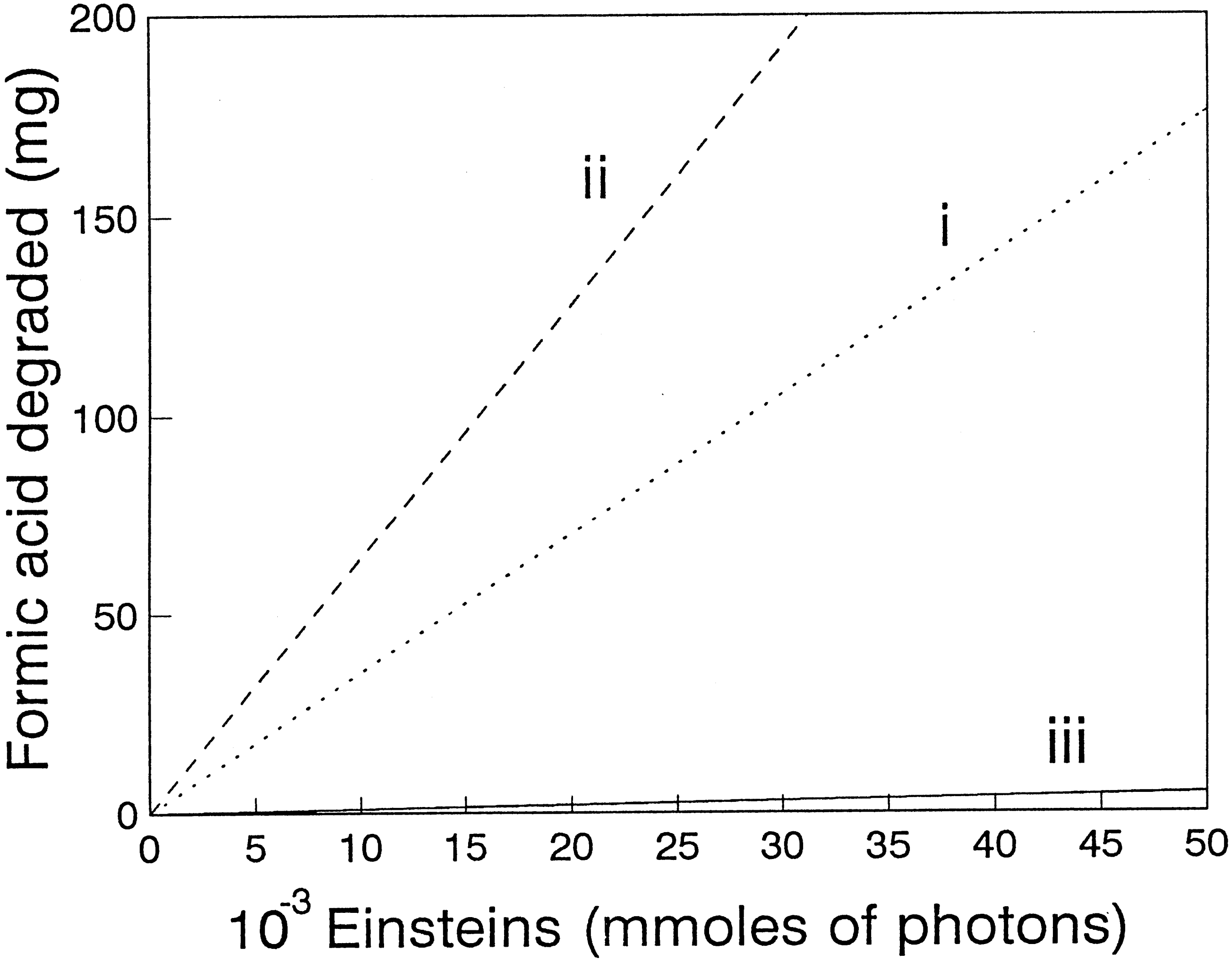

Figure 6. Formic acid degradation as a function of light flux for the three TiO_2 photocatalytic reactors; i = 2 x 15W, flat plate reactor; ii = 4W annular pellet reactor; iii = 1500W, annular thin film reactor.

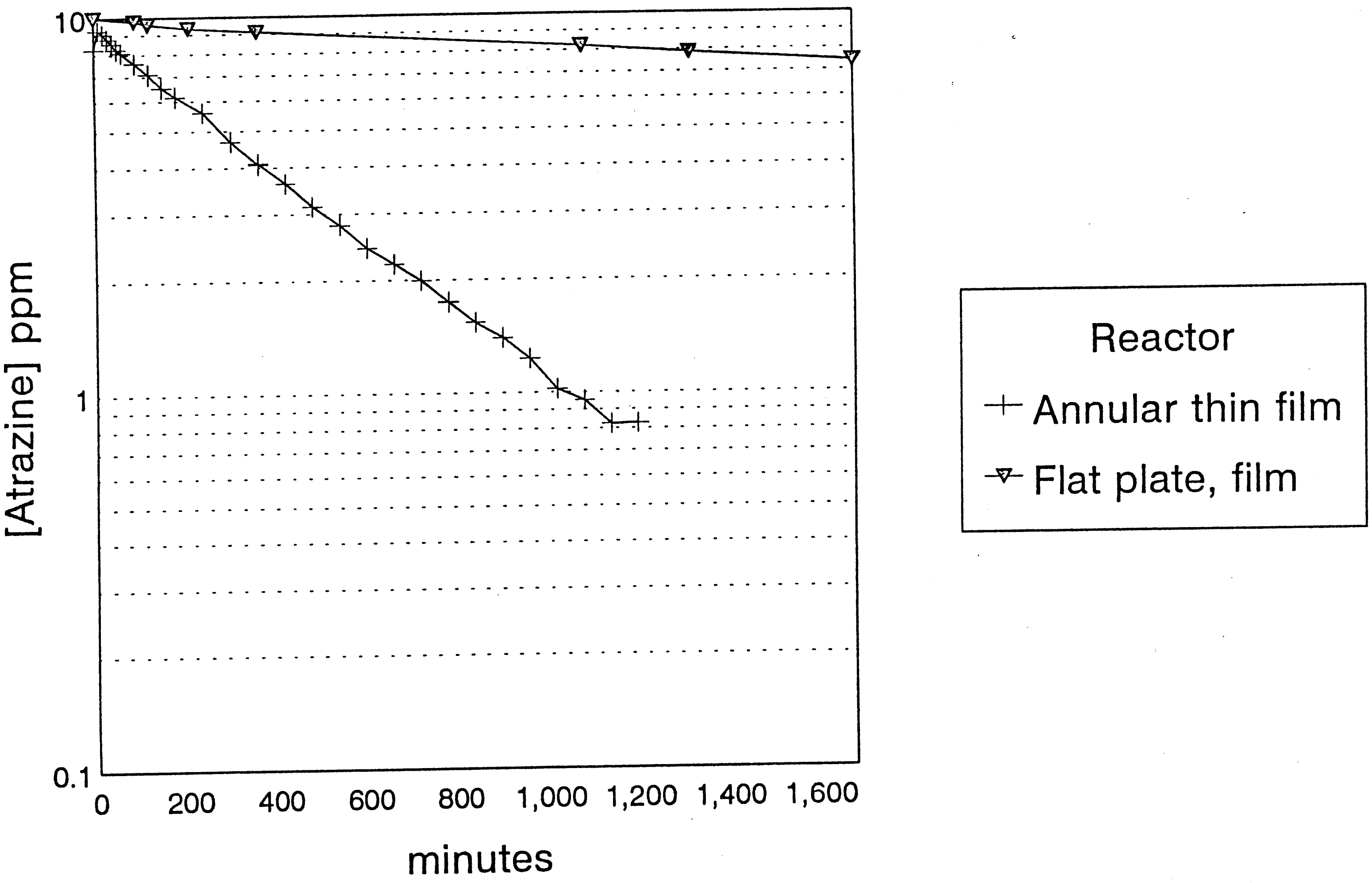

Figure 7. Photocatalytic degradation of atrazine with time in two photocatalytic reactors; i = 1500W thin film reactor; ii = 2 x 15W flat-plate reactor.

An array of degradation products was observed, some of which were tentatively identified based on matching their HPLC retention times with standards. Unidentified products were classified as either chlorinated or hydroxylated based on a characteristic spectral shift that occurs with hydrolysis--the ratio of absorbance at 240 nm to that at 220 nm is higher for the hydroxy derivatives--and the concentration estimated by using an average of the absorbances and molecular weights of the hydroxy- or chloro- metabolites for which standards were available.

After 22 hr of irradiation in the annular thin-film reactor, the concentration of atrazine decreased to 0.8 ppm. On a molar basis, approximately 35% of the atrazine had been dechlorinated. The distribution of the major intermediates (expressed as the mole percentage of the starting concentration of atrazine) is shown in Table 3.

Table 3. Distribution of the major intermediates produced by the photocatalytic degradation of atrazine, expressed as a percentage of the initial molar atrazine concentration, and arranged in order of elution on HPLC; -Cl and -OH designate two unidentified chloro- and one hydroxy- metabolites.

Time, hr.	DDOH	DDAT	DIAT	DIOH	-Cl	DEOH	DEAT	-OH	-Cl	AT
0	0	0	0	0	0	0	0	0	0	100.0
3	3.6	1.6	7.3	2.4	1.6	6.7	4.6	7.5	5.8	64.4
8	9.3	5.0	21.6	3.7	2.6	12.3	9.4	11.8	4.7	32.4
15	15.0	7.7	30.9	7.6	3.9	11.1	9.4	11.1	4.2	15.4
22	19.4	11.1	38.9	9.6	4.3	9.5	8.2	8.2	2.7	7.9

The sums of the percentages at each time point are greater than 100, probably due to experimental error and to the uncertainty of the concentrations of unidentified products. Pelizzetti et al. (1990) carried the reaction to completion, i.e. to nearly 100% conversion to cyanuric acid and documented the appearance and disappearance of intermediates. They determined that the first intermediates formed were DIAT, OHAT and DEAT reaching maxima of 15, 9, and 7 percent of the initial atrazine concentration before conversion into other products. We did not detect any OHAT and found more DIAT (38.9%) and DEAT (9%); otherwise, the distribution of intermediates shown in Table 3 is similar. The literature suggests that degradation rates of non-*s*-triazine herbicides will be significantly faster.

DISCUSSION

For both reactors tested, the atrazine data appear to fit a first-order model, but the flat-plate reactor is a closer approximation of the safer, cheaper kind of low light intensity (1-10 x 10^{-9} einsteins/sec cm^2) system that will be practical for scale-up. Using the rate equation determined by linear regression on the logarithmically transformed data, the half-life for atrazine in this system is approximately 4000 minutes. To lower an initial 10 ppm concentration of atrazine to below 10 ppb, degradation must proceed for 10 half-lives. However, utilizing an annular design of 1.8 cm diameter x 1 m long with a standard 40W fluorescent black light will increase the light intensity by a factor of six and the illuminated surface area by a factor of 45. With such a reactor, the $t_{1/2}$ for atrazine would be approximately 15 minutes. With a starting concentration of 10 ppm, about 2.5 hr would be required to bring the atrazine concentration down to 10 ppb, and could continuously process liquid at a rate of 1 mL/min. An additional 50-60 minutes would be required to reduce the concentration to less than 1 ppb, for a flow rate of 0.75 mL/min. Electric power costs (at 6¢/kWh) work out to $1.60/gallon or $88 to treat the liquid in a 55 gallon drum to the 10 ppb level. Formic acid degradation did not appear to follow first-order kinetics, but the rate was about 49 times faster than the zero-time rate for atrazine. It is expected that the degradation rates of most compounds will fall within these bounds. Use of this technology in treating drinking water contaminated with pesticides might not be accepted by the public unless the levels could be decreased to 10% of Wisconsin's Preventative Action Limit (PAL). For atrazine, the PAL is 0.3 ppb and therefore 0.03 ppb is likely to be an acceptable level. For a well contaminated at the enforcement standard (3 ppb), about seven half-lives would be needed.

Many studies have shown the diminished phytotoxicity of the dechlorinated, hydroxy-analogs of atrazine, and in the standard setting process in Wisconsin that only chlorinated metabolites are included in the state standards. Thus the assertion appears to have been accepted that hydrolysis reduces the human toxicity of atrazine and its chlorine-containing metabolites.

These calculations suggest that photocatalytic degradation is a relatively slow process, but faster degradation is expected with the titania pellets. Improvements in catalyst efficiency and optimization of reactor design promise to increase the rate significantly. Earlier studies in this laboratory indicate that improvements in quantum efficiency may be obtained with platinum doping. A pellet-filled reactor similar to that described above would be inexpensive to build and operate.

Current work is now focusing on degradation of mixed pesticide rinsates collected from a commercial applicator in Wisconsin and of other pure pesticides. Experiments are being designed to determine rate equation parameters for compounds of interest and for mixed wastes. The use of hydrogen peroxide and other electron acceptors in these systems is also of interest.

REFERENCES

Anderson, M.A., M.J. Gieselmann and Q. Xu (1988) Titania and alumina membranes. J. Membrane Sci. **39**, 243-258.

Haag, W.R. and C.C.D. Yao (1992) Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ. Sci. Technol. **26**, 1005-1013.

Matthews, R.W. (1987) Photooxidation of organic impurities in water using thin films of titanium dioxide. J. Phys. Chem. **91**, 3328-3333.

Ollis, D.F., E. Pelizzetti and N. Serpone (1991). Destruction of water contaminants. Environ. Sci. and Technol. **25**, 1523-1529.

Pelizzetti, E., V. Maurino, C. Minero, V. Carlin, E. Pramauro and M.L. Tosato (1990) Photocatalytic degradation of atrazine and other s-triazine herbicides. Environ. Sci. Technol. **24**, 1559-1565.

Rizzuti, L. and A. Brucato (1988) Photochemical reactor engineering fundamentals. In M.Schiavello (Ed.) *Photocatalysis and Environment*, Kluwer Academic Publishers, Boston. pp. 623-636.

Turchi, C.S. and D.F. Ollis (1990) Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. J. Catal. **122**, 178-192.