

The Effect of Titanium Dioxide Alumina Beads on the Photocatalytic Degradation of Picloram in Water

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Photocatalytic degradation of pesticides with titanium dioxide (TiO₂) and other catalysts has shown promise as a potential water remediation method. Titanium-based powders have been used in photocatalytic degradation studies but have limitations. The objective of this study was to determine picloram degradation in water using various UV light sources and low-pressure metal organic chemical vapor deposition titanium dioxide alumina beads (TDABs) as a catalyst. A triple-annular, flow-through photoreactor was used as a degradation chamber. A picloram test solution of 50 μg/mL was introduced to the photoreactor inlet and recycled for 10 h at a flow rate of 50 mL/min. Three ultraviolet light sources were compared for their photocatalytic capacity (UV-A, UV-B, and UV-C) both with and without TDABs. TDABs were added to the photoreactor at 1.8 g/cm³. Dark treatments with and without TDABs were included to quantify hydrolysis or adsorption. A 500-μL aliquot was taken from the test solution 14 times during the 10-h recycling period. Sampling times ranged from 0 to 600 min (10 h). These aliquots were placed in a vial and analyzed by high performance liquid chromatography equipped with a photodiode array detector. Picloram was not significantly hydrolyzed or adsorbed to TDABs during the experiment. The picloram degradation rate with UV-A and TDABs ($t_{1/2} = 119.5$ min) was greater than the degradation rate of UV-A alone ($t_{1/2} = 2288$ min). Picloram degradation was not enhanced by the presence of TDABs with either UV-B or UV-C. This may be attributed to inadequate TDAB densities and/or poor light penetration in the photoreactor. Rapid picloram degradation occurred with both UV-B and UV-C, regardless of the presence of TDABs with mean half-lives ranging from 7 to 18 min. These rates were 8 to 16 times faster than picloram degradation using UV-A with TDABs. TDABs' greatest photocatalytic effect was with the lowest energy light source (UV-A). However, picloram degradation was not enhanced when TDABs were combined with more powerful, shorter wavelength light.

KEYWORDS: Titanium dioxide; alumina beads; photocatalysis; degradation; ultraviolet light; picloram; herbicide

INTRODUCTION

Photolysis is the transformation of a compound through its interaction with light (*I*). This process can be either direct or indirect (*I*). Direct photolysis is commonly referred to as the transformation occurring from direct light absorption causing the breakdown of the chemical species. Indirect photolysis occurs when (1) energy is transferred from an excited to a nonexcited species or (2) when light-induced, reactive species, such as hydroxyl, peroxy, singlet oxygen radicals, degrade the chemical (*I*). There have been examples of indirect photolysis of pesticides. Atrazine (2-chloro-4-(ethylamino)-6-isopropyl-

amino-*s*-triazine) has been shown to go through indirect photolysis in water and soil (2). Atrazine does not significantly absorb light above 290 nm; therefore, direct photolysis is negligible (2). However, in a nitrate rich environment, atrazine degradation was appreciable and attributed to reactions with hydroxy radicals ($\cdot\text{OH}$) during the daylight hours (2, 3). Phenoxy compounds such as mecoprop ((±)-2-(4-chloro-2-methylphenoxy)propionic acid) have been studied in relation to photolysis (4, 5). For mecoprop, the excitation of the molecular form was negligible when exposed to UV-A, UV-B, or UV-C light. The phototransformation of mecoprop was attributed to induced photoreactions (4). Hydroxy radicals from dilute concentrations of nitrite and nitrate contributed to the formation of 4-chloro-*o*-cresol from the parent mecoprop (4). Both direct and indirect processes were determined as contributing processes in the

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photolysis of mecoprop (4). Dichlorprop ((±)-2-(2,4-dichlorophenoxy)propanoic acid) differs from mecoprop in the substitution of Cl for a methyl group on position 2 of the benzene ring. This substitution substantially changed the photochemical behavior. The presence of two chlorine atoms on the ring reduces the quantum yield by 15 to 50 times and potentially curbs the generation of photolysis products (5).

Photocatalysts are solids that promote reactions in the presence of UV light and are not consumed in the overall reaction (6). Titanium dioxide (TiO₂) in the anatase form appears to be the most efficient semiconductor for environmental applications and has been studied as a photocatalyst for potential use in wastewater treatment (6, 7). The use of TiO₂ photocatalysts for environmental cleanup has been of interest, because TiO₂ is stable, harmless, inexpensive, and solar-activated (6, 7). The TiO₂ photocatalysis mechanism has been described by Robert and Malato (8). The basic process of photocatalysis consists of ejecting an electron from the valence band to the conduction band of the TiO₂ semiconductor, creating a hole in the valence band (8). This is due to UV irradiation of TiO₂ with an energy equal or superior to the band gap (>3.2 eV) (8). This is followed by the formation of reactive radicals at the semiconductor surface and/or a direct oxidation of the polluting species (8). The ejected electrons react with electron acceptors such as oxygen adsorbed or dissolved in water (8).

Pesticide photocatalysis with TiO₂ has been conducted with fine TiO₂ particles (Degussa P-25, mean diameter ~30 nm) suspended in an aqueous phase (7, 9–18). Powdered TiO₂ enhanced photocatalytic degradation of propachlor (9); metobromuron (10); isoproturon (10); chlortoluron (10); chlorbromuron (10); cinosulfuron (11); triasulfuron (11); atrazine (12, 13); cyanazine (13); propazine (13); prometryne (13); irgarol (13); dicamba (14); MCPA (15, 16); 2,4-D (15, 17); 2,4,5-T (15); 3,4-xylylmethyl-carbamate (15); 3,5-xylylmethylcarbamate (15); propanil (18); and molinate (18). However, researchers noted several limitations with TiO₂ powder, including (1) problems separating fine powder from treated wastewater, (2) clogging of analytical instruments (particularly liquid chromatographs) from TiO₂ powder, (3) human exposure of TiO₂ powder during water treatment, and (4) inconsistency in slurry suspensions between batches.

TiO₂ may be more photocatalytically effective when coated on larger beads or pellets made from metals, glass, silica gel, zeolite, clay, alumina, etc. (7, 19–20). The photocatalytic decomposition of leather dyes was compared between alumina and glass beads coated with TiO₂ (19). The highest degradation efficiency was observed with TiO₂ supported on alumina rather than on glass beads (19).

Several different methods exist for preparing TiO₂ thin films, such as thermal oxidation, sputtering, pyrolysis, sol-gel, and chemical vapor deposition (CVD) (20). These methods differ substantially in their effective surface area and photocatalytic efficiency. CVD is a promising method to prepare high-quality thin films over large surface areas with consistent and uniform composition and low defect density (20–24). This technology in the form of low-pressure metal organic chemical vapor deposition (LPMOCVD) TiO₂ alumina beads (TDABs) has demonstrated high photocatalytic capabilities of methylene blue when irradiated with UV light (20). It is not known how pesticides will react photocatalytically with LPMOCVD-TDABs.

Picloram (4-amino-3,5,6-trichloro-2-pyridincarboxylic acid) is an herbicide used for broadleaf weed control in pasture and rangeland, wheat, barley, oats, and for woody plant species (25).

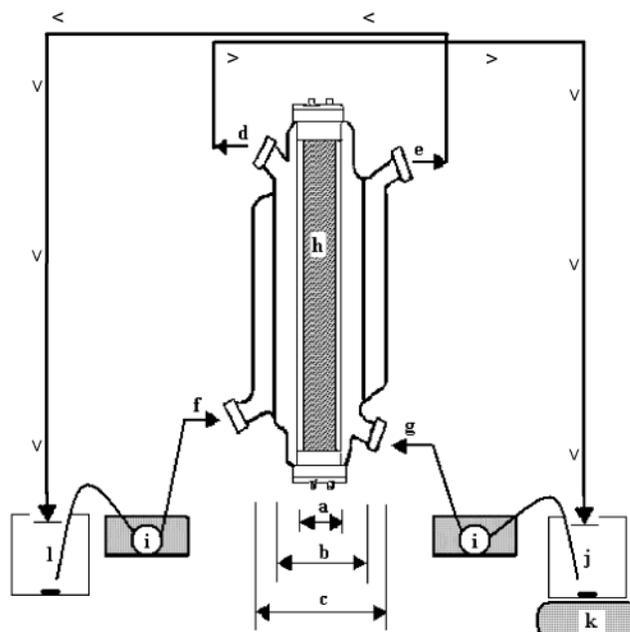


Figure 1. Schematic of photocatalytic reactor: (a) interior quartz chamber containing the light source, (b) glass secondary chamber containing interior test solution volume of 700 mL and TDABs, (c) glass outer chamber for cooling solution, (d) test solution outlet, (e) cooling solution outlet, (f) cooling solution inlet, (g) test solution inlet, (h) UV-light source, (i) circulating pump, (j) test solution (50 $\mu\text{g/mL}$ picloram), (k) magnetic stirrer, (l) cooling solution. Arrows designate flow path of the respective test and cooling solutions.

Picloram is a pyridine carboxylic acid and has a similar chemistry to the phenoxy compounds mentioned earlier, with the exception that it has three chlorine atoms and a pyridine ring rather than a benzene ring. It is susceptible to photodegradation in water, soil, and plant surfaces and has a photolysis half-life of 2.6 days (25). Picloram has a quantum yield of 3.48×10^{-3} mole/mole according to aqueous photolysis studies done with a xenon lamp that mimics natural sunlight (26). It is not known if this compound will demonstrate more rapid degradation in the presence of TDABs and UV light. Therefore, the objective of this study was to evaluate picloram degradation in water with LPMOCVD-TDABs and various UV light sources.

MATERIALS AND METHODS

Chemicals. Technical grade picloram (78% pure) was donated from Dow Agrosciences (Indianapolis, IN). Picloram test and stock solutions were prepared in methanol (chromatography grade, EM Science, NJ). Methanol was also a component in the high performance liquid chromatography (HPLC) mobile phase that will be described later. Sodium phosphate was used as a buffer (chromatography grade, EM Science, NJ). TDABs were prepared using LPMOCVD as described by Jung and Imaishi resulting in a film thickness of 2–5 μm (20). The process used 8-mm diameter alumina beads (Al₂O₃) as a support metal (Nikkado, Japan) coated with a liquid suspension of 99.9% pure titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄) (Sigma-Aldrich, WI) (20).

Apparatus. The photocatalytic apparatus used was a triple-annular photoreactor created by Jung and Imaishi (20) and is shown in **Figure 1**. The triple-annular design is based on the three chambers of the apparatus. The interior chamber consists of quartz and contains the light source. Quartz allows for optimal light permeation. The secondary chamber consists of glass and contains the test solution with the TDABs when used. The amount of TDABs placed in the photoreactor was limited by the volume and weight of the beads as well as the volume of the photoreactor. In our case, the density of TDABs packed in the secondary glass photoreaction chamber was 1.8 g/cm^3 . The outer

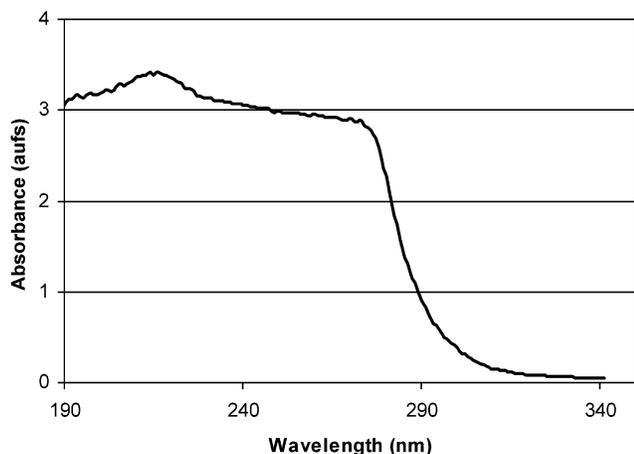


Figure 2. Absorption spectrum of a 1 µg/mL solution of picloram in water.

chamber is also glass and contains the cooling material (water). This apparatus has four ports that include (1) a cooling liquid outlet, (2) a test solution outlet, (3) a cooling liquid inlet, and (4) a test solution inlet. The reactor volume was approximately 700 mL. All sample test solutions were 800 mL in volume. Test solutions were prepared in a 1-L amber glass jar and stirred with a magnetic stirrer during the test period. The test solution was kept at room temperature (22–25 °C) and pumped through the photoreactor with a variable speed Gilson Minipuls 3 pump (Gilson, Villiers Lebel, France).

Flow Rate Determination. Flow rate of the test solution through the photoreactor was determined by a separate experiment. The goal was to determine optimum picloram degradation at various test solution flow rates that would provide a balance of adequate photoreaction time and test solution recycling. TDABs were added to the chamber, and the light used was UV-A. If flow rate were optimized for UV-A, the potential to see differences in degradation of picloram between UV-A and UV-A with TDABs would be optimized. The hypothesis was that the lowest energy light source would be the safest due to its longer wavelength and lower energy. It also would be cheaper to use in a remediation scenario if practical use of this technology were developed.

The test solution was a 50 µg/mL solution of picloram in deionized water. The flow rates of test solution through the photoreactor were 10, 25, 50, 100, 150, 200, and 250 mL/min. Results from all flow rates were compared to the untreated picloram test solution that represented the initial picloram concentration at the beginning of the flow rate study. A 500-µL aliquot of the test solution was removed from the glass jar during the recycling photoreaction process at 0, 10, 30, and 60 min after introduction of the test solution to the photoreactor. This aliquot was placed in a 1-mL glass vial for analysis by HPLC.

The optimum flow rate for picloram degradation in water was 50 mL/min (Figure 3). After 60 min of reaction time, 73% of the picloram remained in the 50 mL/min flow rate, whereas all other flow rates showed greater than 88% remaining. Therefore, this flow rate optimized degradation of picloram and provided an adequate reaction time in the photoreactor and turnover of the recycling volume. This flow rate was also optimum for the degradation of methylene blue using TDABs (27).

Light Sources and TDAB Experiment. The test solution and flow rate were the same as in the flow rate experiment. The treatments included (1) dark, (2) UV-A (15 W fluorescent, maximum λ 365 nm; spectral range 350–400 nm; Philips Electric, Somerset, NJ), (3) UV-B (15 W fluorescent, maximum λ 302 nm, spectral range 280–360 nm; Ultra-Violet Products, Inc., Upland, CA), (4) UV-C (15 W fluorescent, maximum λ 254 nm; spectral range 100 to 280 nm; Philips Electric, Somerset, NJ), (5) dark with TDABs, (6) UV-A with TDABs, (7) UV-B with TDABs, and (8) UV-C with TDABs. The photoreactor was covered with aluminum foil for all treatments, to avoid excess light from entering the test system and for exposure protection for the scientist.

A 500-µL aliquot of the test solution was collected for each treatment at 0, 1, 5, 10, 20, 30, 45, 60, 90, 120, 180, 300, 420, and 600 min. This aliquot was placed in a 1-mL glass vial for analysis by HPLC. A 10-µL injection was introduced by a Waters HPLC equipped with a

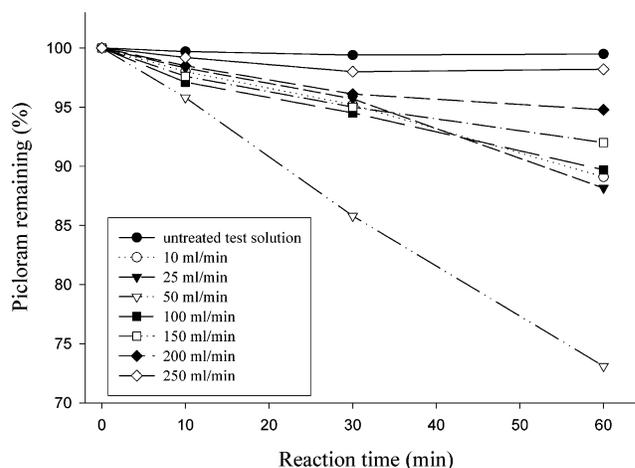


Figure 3. Percentage of picloram remaining after 60 min of recycled flow of the 50 µg/mL test solution through a photocatalytic reactor containing a UV-A light source and TDABs at eight flow rates ranging from 10 to 250 mL/min. The flow rate results were compared with the untreated test solution of picloram at a concentration of 50 µg/mL.

model 717 autosampler, model 600 pump, and a model 996 photodiode array (PDA) detector (Waters Corporation, Milford, MA). The mobile phase of 80% 13 mM sodium phosphate (pH 3.0):20% methanol was pumped through a 2.1 mm diameter X 150 mm length Symmetry Shield, reverse phase, C8 narrow-bore column (Waters Corporation, Milford, MA). The flow rate for the mobile phase was 0.25 mL/min and the column temperature was ambient. Chromatograms were extracted from the PDA data at 225 nm for identification and quantitation of picloram. The wavelength of 225 nm was determined to be a reasonable wavelength for quantitation based on the UV-spectral absorbance from spectrophotometric readings (Figure 2). The retention time of picloram averaged 7.0 min. The level of quantitation (LOQ) was estimated to be 0.1 µg/mL. All quantitations were based on a six-point calibration curve that included 0.1, 1, 5, 10, 20, and 30 µg/mL.

Statistical Analysis. The study was a completely randomized design, with three replications per treatment. Picloram concentrations were converted to percentage of picloram remaining at the selected sampling times. These percentages were fit to a pseudo-first-order degradation equation

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_t is the picloram concentration at time = t , C_0 is the initial concentration of picloram, k is the degradation rate, and t is time. To determine the half-lives and degradation rates from the data, the linear form of the equation was used as shown below.

$$\ln C_t = \ln C_0 - kt \quad (2)$$

In this form, k is the slope, and $\ln C_0$ is the intercept. Analysis of covariance of the linearized equations was done within the general linear models (GLM) procedure in SAS (Statistical Analysis Systems, Cary, NC). This procedure was used to determine slope and intercept differences among treatments. To accurately assess slopes, data were truncated after the first instance where the picloram concentration reached zero for a specified treatment. Estimations of $t_{1/2}$ were made based on the equation

$$t_{1/2} = \frac{0.693}{k} \quad (3)$$

where k is the estimated pseudo first-order degradation rate constant determined from the GLM procedure in SAS.

RESULTS AND DISCUSSION

UV-A and TDABs. Picloram degradation comparing dark, dark with TDABs, UV-A alone, and UV-A with TDABs is

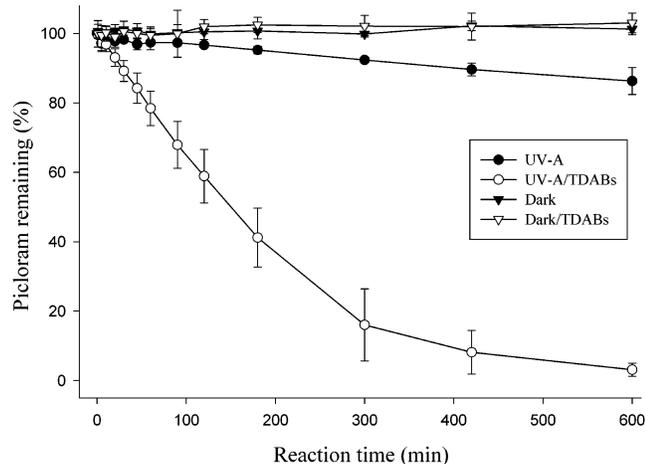


Figure 4. Percentage of picloram remaining after 10 h of recycled flow of the 50 $\mu\text{g/mL}$ test solution through a photocatalytic reactor containing (1) UV-A light source alone, (2) UV-A with TDABs, (3) no light (dark) without TDABs, and (4) no light (dark) with TDABs. Flow rate of the test solution was 50 mL/min.

Table 1. Photocatalytic Rate Constant, Estimated Half-life, Standard Deviation of Determination, and Confidence Intervals for Picloram Degradation in Water Using Various UV Light Sources with and without TDABs

| treatment ^a | k^b ($\times 10^{-3}$) (min^{-1}) | std error ($\times 10^{-4}$) (min^{-1}) | std error of intcpt ($\times 10^{-2}$) | $t_{1/2}^c$ (min) | R^2 ^d | p -value for k^e |
|------------------------|---|--|--|----------------------|--------------------|-------------------------|
| UV-A | ns ^f a ^g | na ^h | na | na | na | 0.5767 |
| UV-A + TDAB | 5.8 b | 3.9 | 8.8 | 119.5 | 0.99 | 0.0001 |
| UV-B | 41.4 c | 29.9 | 12.3 | 16.7 | 0.97 | 0.0001 |
| UV-B + TDAB | 38.8 d | 21.3 | 11.6 | 17.9 | 0.99 | 0.0001 |
| UV-C | 96.7 e | 63.4 | 14.1 | 7.2 | 0.92 | 0.0001 |
| UV-C + TDAB | 78.8 e | 63.4 | 14.1 | 8.8 | 0.92 | 0.0001 |

^a UV-A, ultraviolet max wavelength 365 nm; UV-B, ultraviolet max wavelength 302 nm; UV-C, ultraviolet max wavelength 254 nm; TDAB, titanium dioxide alumina bead. ^b Degradation rate based on pseudo-first-order degradation. ^c Half-life based on pseudo-first-order degradation. ^d Coefficient of determination for the linear form of degradation model. ^e Treatment values greater than 0.05 were not significant, and therefore, were assumed to not demonstrate appreciable degradation of picloram within the time frame of the experiment. ^f Not significant. ^g Values with the same letter are not significantly different from one another based on covariate analysis. ^h Not applicable.

shown in **Figure 4**. Significant picloram degradation was not observed in the dark treatments during the experiment. Therefore, it was concluded that picloram was not significantly hydrolyzed or adsorbed to TDABs during the experiment. Conversely, TiO_2 powders have demonstrated significant propachlor (9), propanil (18), and molinate (18) adsorption with relatively short test periods of less than 60 min. Several other researchers have acknowledged adsorption of the test chemical by TiO_2 and have accounted for it by allowing an adsorption equilibrium to be reached in the dark for approximately 30 min prior to initiating light treatments (10, 11, 13).

Compared with the other light sources, UV-A demonstrated significantly slower degradation rates than UV-B and UV-C treatments either with or without TDABs (**Table 1**). After 10 h of incubation, 86% of the picloram remained in the test solution when treated with only UV-A (**Figure 4**). The degradation rate was not fast enough to demonstrate a significant slope estimation ($p = 0.5767$) from the covariate analysis (**Table 1**). However, a visual estimate of the picloram half-life was 2288 min (1.6 d), which is more rapid than data obtained from earlier picloram

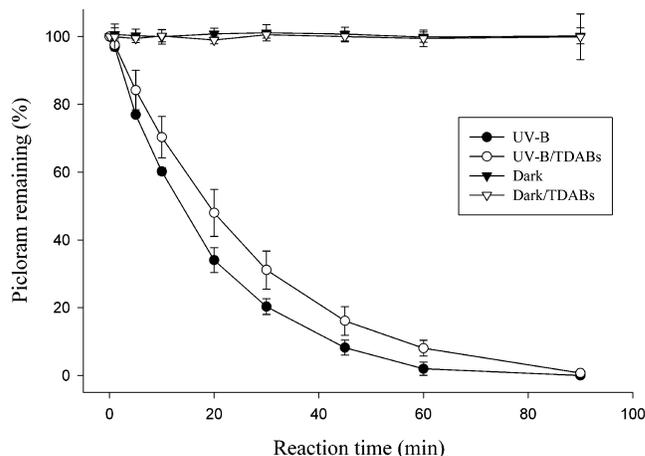


Figure 5. Percentage of picloram remaining after 2 h of recycled flow of the 50 $\mu\text{g/mL}$ test solution through a photocatalytic reactor containing (1) UV-B light source alone, (2) UV-B with TDABs, (3) no light (dark) without TDABs, and (4) no light (dark) with TDABs. Flow rate of the test solution was 50 mL/min.

photolysis studies, in which the half-life was reported to be 2.6 d (24). The picloram degradation rate was significantly greater with TDABs ($t_{1/2} = 119.5$ min) compared to UV-A without TDABs (**Table 1**). Approximately 3% of the picloram remained in the test solution after 10 h, which resulted in an 83% degradation attributed to photocatalytic activity from UV-A with TDABs. Therefore, TDABs enhanced degradation when combined with UV-A light through photocatalytic degradation of picloram as compared to UV-A alone.

UV-B and TDABs. After 90 min, picloram was degraded below the LOQ in both UV-B alone and UV-B with TDABs (**Figure 5**). The degradation rate was faster in the UV-B alone treatment compared with UV-B with TDABs according to the covariate analysis (**Table 1**). Also, both treatments demonstrated a faster degradation than either of the UV-A treatments, but were not as fast as either of the UV-C treatments (**Table 1**). The trend shown with UV-A was reversed when using UV-B, where the presence of TDABs apparently hindered picloram degradation.

UV-C and TDABs. Picloram degradation was the most rapid when treated with UV-C light, where estimated half-lives were less than 9 min (**Table 1**). The degradation rates of UV-C treatments were approximately 2 to 2.5 times faster than that with UV-B treatments and 13 to 19 times faster than UV-A with TDABs (**Table 1**). The picloram concentration was below the LOQ after 45 min of recycling with UV-C alone and 60 min for UV-C with TDABs (**Figure 6**). The presence of TDABs did not significantly increase picloram degradation under UV-C light (**Table 1**).

It appears that the presence of TDABs did not enhance, and perhaps hindered, degradation when the more powerful light sources UV-B and UV-C were used. The authors suspect that there are several reasons for this phenomenon. First, due to the shorter wavelengths from UV-B and UV-C, poor penetration of light energy in the photocatalysis chamber caused fewer of the TDABs to be activated that would have enhanced the degradation. Second, the light sources were so strong that the main photolysis mechanism was probably due to direct photolysis, whether TDABs were present or not. Finally, degradation was so rapid with the UV-B and UV-C light sources that enhancement of degradation would be difficult to detect experimentally.

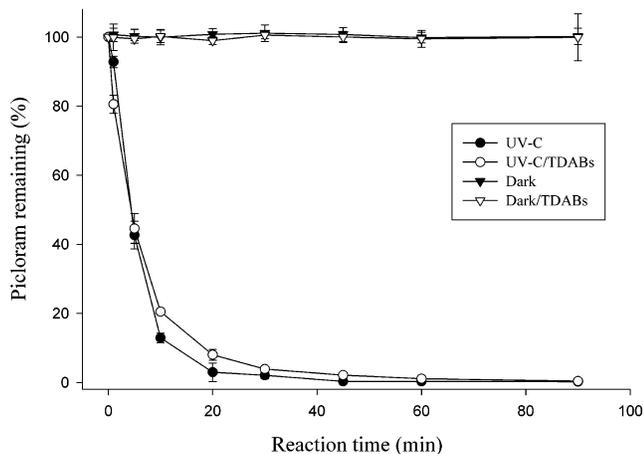


Figure 6. Percentage of picloram remaining after 2 h of recycled flow of the 50 $\mu\text{g/mL}$ test solution through a photocatalytic reactor containing (1) UV-C light source alone, (2) UV-C with TDABs, (3) no light (dark) without TDABs, and (4) no light (dark) with TDABs. Flow rate of the test solution was 50 mL/min.

In the case of UV-A, degradation was slow enough with UV-A light applied to the test solution that enhanced degradation from photocatalysis could be detected. Also, the wavelength of light was long enough to adequately penetrate the photoreactor, thereby activating the TDABs that ultimately initiated indirect photolysis through the creation of oxygenated species. We feel that indirect photolysis could still have been occurring in the UV-B and UV-C treatments but were overwhelmed by the magnitude of direct photolysis from these more powerful light sources.

Similar trends in degradation of methylene blue occurred using TDABs with UV-A, UV-B, and UV-C light sources where UV-A with TDABs showed the slowest degradation and UV-C with TDABs was the most rapid (20). However, the light sources were not studied without the presence of TDABs in this experiment (20). Although highly effective, other researchers have not endorsed using stronger light sources such as UV-B and UV-C, due to additional expense and hazards associated with short-wavelength lamps (28). From a practical view, UV-A with TDABs would perhaps be the best choice, due to TDABs enhancement of photocatalytic activity, increased human safety, due to less damaging light exposure, and for field adaptation of photocatalytic degradation, because its wavelength more closely represents natural sunlight.

Using TDABs compared with TiO_2 powder would appear to have several advantages, because there is no need to filter to recover the catalytic material using the bead technology. Also, the LPMOCVD provides a more uniform deposition of material, more active surface area, and potentially, more consistent photocatalytic activity (20).

Further study is needed to determine photocatalytic sensitivity of other organic compounds to TDABs and UV light. Also, determinations of the most optimum density of TDABs and perhaps the most optimum bead diameter of TDABs in combination with UV light sources would also advance the technology to another level.

ACKNOWLEDGMENT

The authors would like to acknowledge Dr. Vernon Langston of Dow Agrosiences for the donation of analytical grade picloram.

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Received for review December 18, 2002. Revised manuscript received February 27, 2003. Accepted February 28, 2003. Funding for visiting scholar Dr. Do-Jin Lee provided by Sunchon National University.

JF026232U