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16. ABSTRACT The use of a solid photocatalyst, titanium dioxide, as an amendment incorporated into pavement surfaces was investigated as a basis for controlling nonpoint hydrocarbon runoff. Titanium dioxide is an inexpensive and conservative material that, when activated by sunlight, generates oxygen radicals capable of degrading common hydrocarbon contaminants characteristic of nonpoint highway runoff. Six materials were evaluated for fixing the photocatalyst onto pavements; paint base and concrete sealant were most effective. A number of contaminants were effectively degraded using the photocatalytic process including hexadecane, anthracene, and 2,4,6-trichlorophenol. Standard procedures (e.g., chloride analysis, addition of scavengers) were used to assess the applicability of photocatalytic pavement borders to a range of waste compounds; the data showed that the process has potential to degrade most compounds present in nonpoint highway runoff. The results of this laboratory study indicted that photocatalytic pavement borders have significant potential for mitigating nonpoint highway runoff.			
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CATALYTIC PAVEMENT BORDERS

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CATALYTIC PAVEMENT BORDERS

STUDY SUMMARY

The contamination of sensitive surface waters from the runoff of gasoline, diesel, and motor oil originating from highway traffic is an important water quality concern. Petroleum hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs), may pose toxic hazards to aquatic biota.

The destruction of hydrocarbons on the surface of pavements using photocatalytic pavement borders was investigated to reduce nonpoint runoff contamination to roadside soils and receiving waters. The process is based on attaching titanium dioxide (TiO_2) to pavement surfaces incorporated into a fixant. The fixed metal oxide photocatalyst (TiO_2) enhances rates of natural photodegradation and oxidizes contaminants before they can migrate in runoff. The system was used to enhance the photodegradation of hexadecane and anthracene (common hydrocarbon constituents of petroleum products) on experimental surfaces.

Titanium dioxide was fixed to sample surfaces in a number of fixants and the sample surfaces were spiked with three organic contaminants. Degradation of these contaminants was monitored over time under near-UV lights at varying mass per mass concentrations of titanium dioxide to investigate the feasibility of such a system.

The type of fixant used in attaching the photocatalyst to the surface affected the ability of TiO_2 to effectively assist in degradation. Six fixants containing TiO_2 were evaluated for photocatalytic activity and results showed concrete sealant and paint base to be the most effective test fixants. The results indicated that the concrete sealant was more effective than paint base when incorporated with TiO_2 in degrading hydrocarbons on the sample surfaces. More detailed studies were conducted using sample surfaces fabricated of the selected test fixants incorporated with titanium dioxide in appropriate mass per mass fractions. Results indicate that the titanium dioxide-sealant formulations were effective in promoting the surface degradation of hexadecane, providing >99% degradation in 48 hours

on a 50% TiO₂-sealant surface. Although the TiO₂-paint base formulation was less effective than the TiO₂-sealant, 98.2% degradation of hexadecane occurred on a 50% TiO₂-paint base surface in 72 hours. The results showed that, due to the absorption spectrum of anthracene, degradation was more likely to take place by direct photolysis. The structural integrity of fixed titanium dioxide was also investigated using test surfaces on an active roadway. Based on the capability of fixed TiO₂ to enhance rates of hydrocarbon photolysis, this system has potential to become an effective control measure for the *in situ* destruction of nonpoint highway runoff.

The most important prerequisite in the investigation of a new remediation process is to 1) document that it actually works and 2) determine the range of chemicals that it works on. To study these important parameters, the use of special model contaminants must be used. For example, to document that the process is working, chlorinated compounds (e.g., 2,4,6-trichlorophenol) are used as a model waste compound, and the release of chlorine to free chloride as the compound breaks down can be confirmed by chloride analysis. Another technique that is commonly used is the addition of scavengers, such as bicarbonate, 1-octanol, and tetranitromethane. These chemicals, which scavenge specific reactive intermediates, when added in excess, provide data on how applicable the process is to a range of contaminants such as aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, ketones, halogenated aliphatics, and halogenated aromatics.

The photocatalytic oxidation of 2,4,6-trichlorophenol (TCP) on the surface of dry titanium dioxide was investigated as a basis for the *in situ* treatment of spills on pavements and other surfaces. 2,4,6-Trichlorophenol was degraded to 20% of its original concentration over 24 hr; the release of chloride confirmed the degradation of the parent compound on the surface of the dry TiO₂. Addition of water to the TiO₂ increased the rate of TCP photocatalysis resulting in degradation of TCP to below detectable limits with a water content of ≥ 25% (mass/mass) after 20 hours. Based on competition studies using the hydroxyl radical scavengers bicarbonate and 1-octanol and the electron scavenger

tetranitromethane, the proposed mechanism responsible for the photocatalytic degradation of TCP is direct oxidation by the valence band hole on the surface of the TiO_2 particle. This mechanism was supported by the addition of the hydroxyl radical scavengers, which did not affect the dry system, but slowed the rate of degradation in a 50% water system. Tetranitromethane addition resulted in no change in the rate of TCP degradation, confirming that reductive processes were not occurring. When spiked with TCP concentrations of up to 10,000 mg/kg, the results showed that the capacity of the TiO_2 was not exhausted. The potential for using fixed TiO_2 as an *in situ* remediation system on surfaces was supported by the results of this research.

The photocatalytic pavement borders process represents a minimal capital cost because anatase can be purchased at a cost of less than \$1 per pound. Using a photocatalytic pavement border 0.5m wide with 5g of anatase/m², the chemical cost for one mile of highway would be \$8.80. The primary advantage of photocatalytic pavement borders over other methods of controlling nonpoint runoff is the minimal operation and maintenance costs. Although a benefit-cost ratio cannot be calculated at present, the minimal capital and operational costs suggest that photocatalytic pavement borders may be a cost-effective process for the *in situ* destruction of nonpoint hydrocarbon runoff.

Based on both the success of fixed TiO_2 in the degradation of common petroleum constituents and the exploration of the pathways of degradation of a common chlorinated organic contaminant, this system has the potential to become an effective *in situ* remediation system for the destruction of nonpoint runoff contamination on surfaces.

CONCLUSIONS AND RECOMMENDATIONS

The results of this study showed that photocatalytic pavement borders may have potential for an effective *in situ* treatment for potential runoff contamination. A photocatalyst, titanium dioxide (TiO₂), was successfully attached to experimental surfaces to effectively enhance the photodegradation of hydrocarbons (hexadecane and anthracene) deposited on the surface.

Although six fixant-TiO₂ formulations were evaluated for their photocatalytic ability, only two, concrete sealant and paint base, were selected from a preliminary investigation to use in more detailed surface evaluations. Hexadecane, when spiked on the TiO₂-fixant formulations, photodegraded at a faster rate with the addition of TiO₂ into the surface system. Undetectable levels of hexadecane were achieved in 48 hours on a 50% TiO₂-sealant surface. Although the paint base formulations were less effective, 98.2% hexadecane degradation was still achieved in 72 hours. The photodegradation of anthracene was not affected by the addition of TiO₂ onto the surfaces, possibly due to blockage of the light that activates the photocatalyst. The results suggest that the primary mechanism responsible for anthracene degradation was direct photolysis, because it absorbs in the 300-400 nm spectrum of the near-UV region available through sunlight. Conversely, hexadecane absorbs in the 290 nm region and, therefore, was more likely to be degraded with the enhancement of TiO₂. Compounds that are light sensitive, such as anthracene, may not pose a significant threat to sensitive adjacent environmental areas. However, compounds such as hexadecane, which are not as light sensitive, have the potential to be degraded at a faster rate using photocatalytic pavement surfaces.

The effectiveness of the surface catalysis system is dependent on a number of factors. The type of fixant used to attach the photocatalyst affects the ability of the activated titanium dioxide particles to contact the contaminant and promote degradation. The type of contaminant and the amount of time before surface runoff also affect the degradation capability of the surface catalysis system.

We recommend that field studies be conducted to determine the areal requirements for application of this system. The sensitivity of the surrounding environmental area, as well as the location of the contamination surface (e.g., gasoline station, industrial area), controls the extent of titanium dioxide-fixant application.

The photocatalytic borders process not only show potential for the destruction of hydrocarbons along sensitive stretches of highways, but also ferry docks, parking lots, bridge decks, and other confined spaces.

Because preliminary tests indicate 34% catalyst loss in 26 days on pavement surfaces, more detailed field studies should also be conducted on the structural integrity of the TiO_2 -fixant formulations. In addition, future studies should be conducted on the reactions of solid-phase TiO_2 with other types of hydrocarbons. The results obtained from this study warrant more in-depth research on the use of solid-phase photocatalytic systems to enhance the natural photodegradation of hydrocarbons and other organic compounds on contaminated surfaces.

INTRODUCTION

RESEARCH OBJECTIVES

The objective of this research was to investigate the potential for mitigating nonpoint highway runoff from highways using narrow borders of titanium dioxide, a powerful photocatalyst.

THE PROBLEM

The contamination of ground and surface waters resulting from nonpoint pavement runoff has received considerable attention. Contaminated runoff from roadways and parking lots commonly migrates from the pavement surface and pollutes adjacent soils and surface waters (1-3). Major components of nonpoint runoff are hydrocarbons (3-4) including, but not limited to, long-chain aliphatics and polycyclic aromatic hydrocarbons (PAHs). Furthermore, other hazardous organic compounds are deposited onto surfaces such as concrete or asphalt by leaking containers in hazardous waste storage areas, or by the leakage of petroleum products in refineries, fuel depots, and gasoline stations (5).

A number of methods have been implemented to control the migration of nonpoint pollutants including overland flow channels, grassy swales, detention basins, and wetlands (1). Although hydrocarbon runoff may be controlled using these methods, the system storage capacity is eventually exhausted which results in periodic maintenance to ensure that the basins or channels retain their ability to remove the contaminants. Furthermore, catch basins or detention basins do not effectively remove the smaller particles, which make up a large percentage of the pollutant load (1). All of these methods take up space and have high costs associated with construction and maintenance to control pollution from highway

and parking lot runoff. An ideal solution would be to control the pollutants before they migrate off of the pavement surface and subsequently pollute the environment.

A potential process for oxidizing hydrocarbons on the pavement surface is the use of catalytic pavement borders, in which the photocatalytic activity of titanium dioxide (TiO_2) is utilized by fixing it to the surface of the pavement. Titanium dioxide has been the most commonly studied metal oxide photocatalyst due to its conservative nature, relatively low cost, and high photoactivity under sunlight (6).

This research was conducted by first screening a number of fixants to successfully promote the degradation of hydrocarbons on surfaces. More detailed investigations were then conducted using anthracene (a polycyclic aromatic hydrocarbon) and hexadecane (an alkane) as model contaminants because they are common to petroleum products that are generally found in nonpoint runoff. To provide a basis for the development of solid-phase surface catalysis systems, 2,4,6-trichlorophenol (TCP) was used as a model contaminant to monitor chloride release and competition studies were then conducted to isolate the mechanisms involved in the destruction of TCP on the surface of solid-phase TiO_2 .

REVIEW OF CURRENT PRACTICE

The mechanisms of titanium dioxide photocatalysis have been studied extensively. Titanium dioxide behaves as a semiconductor particle when illuminated by the near-UV region ($< 400 \text{ nm}$) of sunlight. Absorption of photons at the surface of the photocatalyst greater than its bandgap energy of 3 eV transfers an electron from the valence band to the conduction band, producing an electron vacancy or hole in the valence band and an electron in the conduction band (7). Oxidation and reduction reactions then occur at the surface of the particle to produce radicals that can potentially react with organic compounds (Figure 1).

The electron hole in the valence band ($h\nu_{\text{VB}}^+$) can react with hydroxide ions or oxidize water adsorbed at the surface to form hydroxyl radicals ($\text{OH}\cdot$). In addition, the

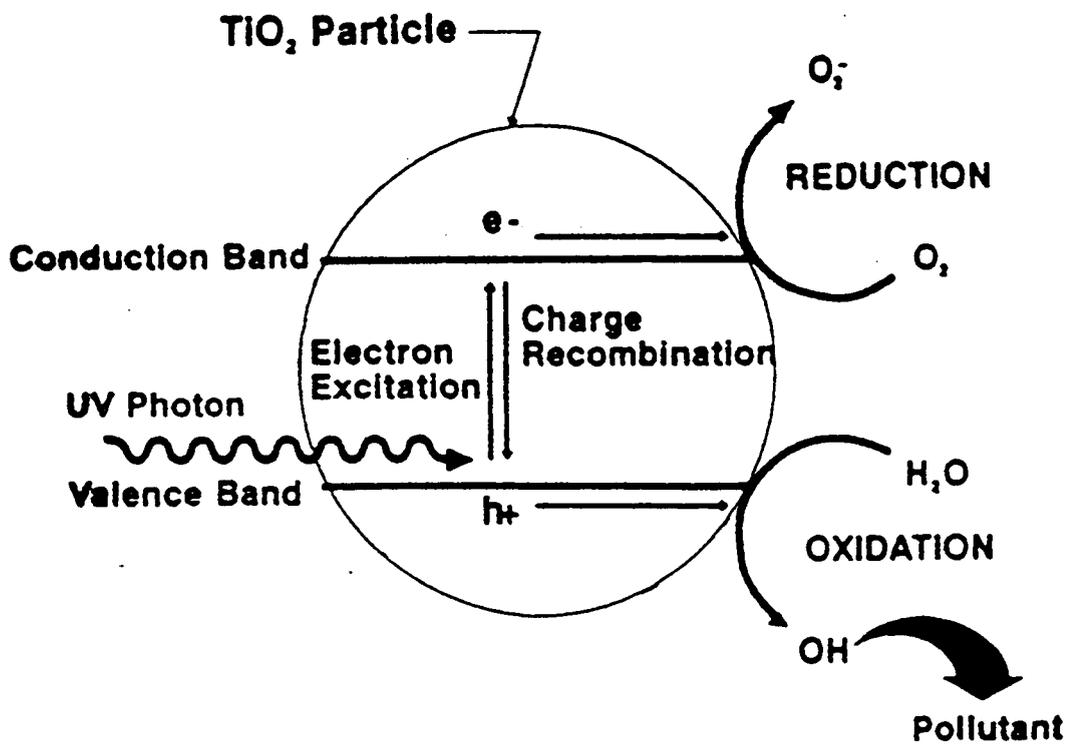


Figure 1. Primary reactions occurring at the surface of an illuminated TiO_2 particle. From Mehos and Turchi, 1993 (8).

conduction band electron (e_{CB}^-) can reduce adsorbed oxygen to form superoxide ion radicals ($O_2^{\bullet-}$) which can further disproportionate to form OH^\bullet through various pathways (9). In the absence of O_2 , the e_{CB}^- may also react directly with the contaminant via reductive processes. The redox reactions occurring from the hole-electron pairs at the surface of the semiconductor can then degrade organic compounds into oxidized or reduced products.

The degradation of toxic compounds by TiO_2 photocatalysis has been the focus of extensive research. The process has been shown to oxidize numerous toxic compounds in water including tetrachloroethylene (10), 4-chlorophenol (11), trichloroethylene (12), chloroform (12), and cyanides (13). In addition, the inactivation of coliform bacteria and viruses in wastewater effluents has been documented using TiO_2 -mediated photocatalysis (14-15).

Because of the difficulty of removing TiO_2 suspensions from water (16), the photocatalytic activity of TiO_2 has recently been examined by fixing the photocatalyst on stationary supports. For example, Matthews coated both sand (17) and the inside of glass tubes (18) with TiO_2 to degrade compounds using these stationary photocatalysts. Serpone *et al.* (19) developed a method to attach TiO_2 to glass beads and successfully treated water contaminated with 2,4,5-trichlorophenol. In other recent investigations, TiO_2 has been supported on silica-based material and used in a fixed bed system to treat water contaminated with trichloroethylene (20).

Essentially all of the research accomplished on TiO_2 -mediated photocatalysis has been performed in aqueous solution. Contamination of surfaces has become a problem, which is evident in the contaminant load of nonpoint runoff from pavements. Because photooxidation on surfaces is a prominent pathway of degradation (21), TiO_2 photocatalysis has the potential to assist in this natural process and enhance the photodegradation of organic contaminants on pavement surfaces. In such an application, TiO_2 would be fixed to the pavement surface and the hydrocarbons dropping onto the

surface would be oxidized in place by the radicals generated from photoactivation of the TiO₂, preventing migration to roadside soils and surface waters. Titanium dioxide is a common constituent in paint and, therefore, has the potential for attachment to pavements in a stable manner. This could be accomplished by incorporating the photocatalyst in a fixant, e.g., concrete sealant, paint base, etc. and applying the matrix to the pavement. If effective, the contamination stored in grassy swales and catch basins could be avoided by using photocatalytic pavement borders and destroying the organic contaminants in place or *in situ*.

EXPERIMENTAL METHODOLOGY

MATERIALS

Titanium (IV) oxide in anatase form (99.9+% purity), 2,4,6-trichlorophenol (98% purity), and 1-octanol (99.3% purity) were obtained from Aldrich Chemical Company; anthracene (scintillation grade) was purchased from Eastman Chemicals; hexadecane (99+% purity) was obtained from EM Science; sodium bicarbonate (99.8%-100.3%), reagent grade acetone, ethyl acetate, hexane, and toluene were acquired from J.T. Baker, and tetranitromethane (98% purity) was purchased from Chem Service. All chemicals were used without modification. Deionized water was prepared by a Barnstead NANOpure II water purification unit.

The fixants used included concrete sealant (BossWorks, Shakopee, MN), paint base (Columbia Paint Co., Spokane, WA), cement patch (Hartline Products Co., Cleveland, OH), asphalt sealer (Gibson-Homans Co., Twinsburg, OH), concrete (PakMix, Inc., Toledo, OH), and mortar (PakMix, Inc., Toledo, OH). The supports onto which titanium dioxide was fixed were 25 x 75 mm (18.75 cm²) glass plates obtained from VWR Scientific. Roadway evaluation surfaces were sections of industrial grade reinforced cloth fiber supplied by Dewalt (Hampstead, MD).

For chloride measurement, a 0.1 M chloride solution and a chloride ionic strength adjuster solution were supplied by Fisher Scientific. The teflon which covered the sample plates during mechanistic investigations was DuPont Tedlar PVF film.

LIGHT SOURCE

The irradiation source for illuminating the samples was a bank of ten unfocused F40BL lamps, which contain wavelengths (< 400 nm) in the lower solar spectrum and sufficient to simulate sunlight (Figure 2). Samples plates were kept at a distance of 12 cm from the lamps. Potassium ferrioxalate actinometry was used to quantify the light intensity (22-23) which was determined to be 0.50 mW/cm^2 .

TITANIUM DIOXIDE-FIXANT EXPERIMENTS

Fixation of Titanium Dioxide

Titanium dioxide was mixed with the fixant (concrete sealant or paint base) in the appropriate mass/mass fraction of 0%, 10%, 25%, or 50%. The mixture was applied to the sample plates and allowed to dry. The test surfaces were then spiked with anthracene, hexadecane, or 2,4,6-trichlorophenol (TCP).

Experimental Procedures

In a typical screening experiment, dry TiO_2 anatase was fixed to a sample surface using concrete sealant, paint base, cement patch, asphalt sealer, concrete, or mortar. Anatase concentrations of 0%, 25%, and 50% (mass/mass) were added to the fixant. Each sample surface was spiked with 0.5 mL of 6000 mg/L TCP in acetone and the acetone was allowed to evaporate resulting in a spike of 3.0 mg/cm^2 . The test surfaces were then exposed to the bank of F40BL lamps, which contain wavelengths (< 400 nm) approximately the same intensity as the lower solar spectrum and sufficient to simulate sunlight. Samples were taken from under the lights at 72 hours and TCP concentrations

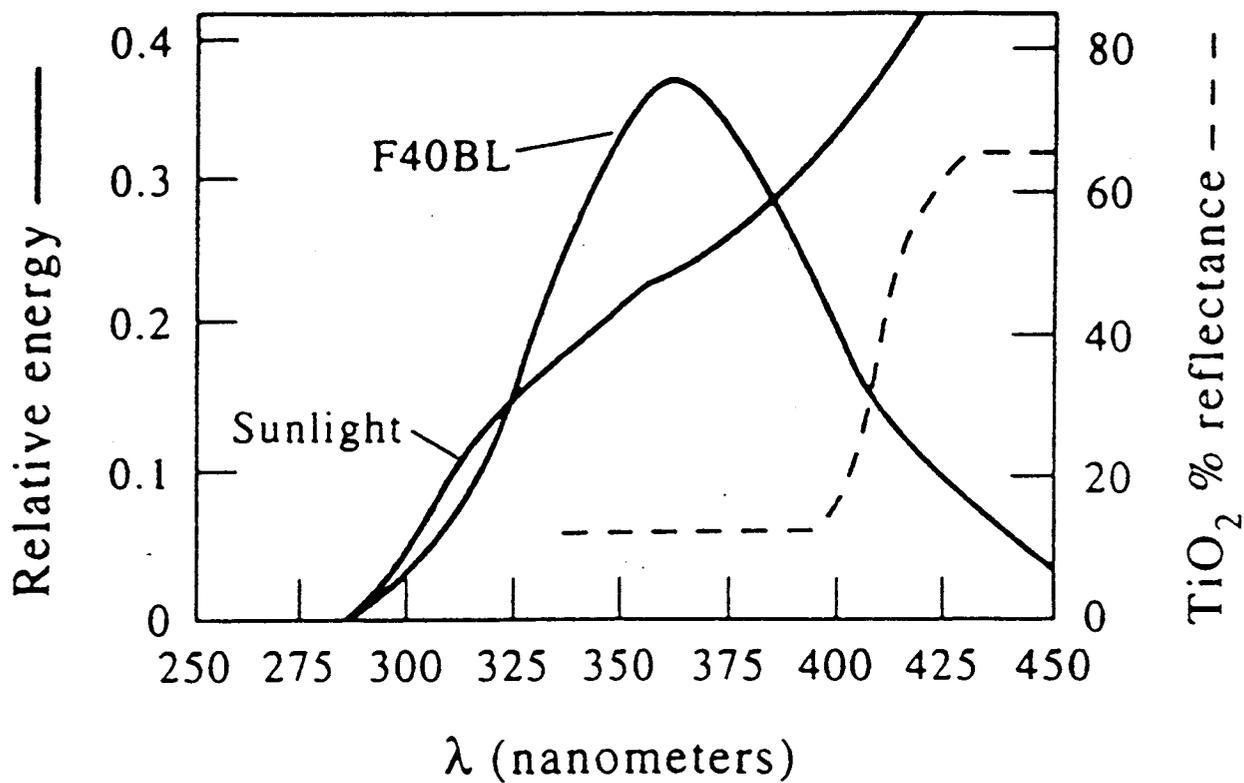


Figure 2. Emission spectrum of sunlight and F40BL lamps and reflectance spectra of titanium dioxide. From Watts *et al.*, 1995 (15).

were analyzed. Controls were established by conducting parallel experiments in the dark and all experiments were performed in triplicate.

The two most effective fixants (concrete sealant and paint base) were investigated in more detail using TiO₂ concentrations of 0%, 10%, 25%, and 50% (mass/mass) and the typical petroleum constituents, hexadecane and anthracene. Test surfaces were spiked such that each surface contained 8.1×10^{-4} mmol/cm² of contaminant. Surfaces were contaminated with 2.33 mg of anthracene per 18.75 cm² of sample plate area by spiking 0.5 mL of 4650 mg/L anthracene in toluene to each test surface and the toluene was allowed to evaporate in the dark. In a similar manner, 0.5 mL of 6870 mg/L hexadecane in hexane were spiked to individual test surfaces, leaving 3.44 mg of hexadecane per 18.75 cm² sample surface. Test surfaces were placed under the F40BL lamps and irradiated. Samples were taken from under the lamps at varying times and analyzed for contaminant concentrations. Controls were established by keeping samples in the dark and periodically analyzing the concentration of contaminant on the surfaces. All experiments were run in the absence of water and performed in triplicate.

Analysis

The contaminant concentration for each sample was determined by shake extraction followed by gas chromatographic analysis. Each sample was placed into a 60 mL vial with 10 mL of deionized water and 30 mL of solvent (ethyl acetate for TCP, toluene for anthracene, and hexane for hexadecane). The vials were then placed on a wrist shaker for three hours and centrifuged for ten minutes. The extract was analyzed on a Hewlett Packard 5890A gas chromatograph in conjunction with a Hewlett Packard 3396 integrator using flame ionization detection. The column used during analysis was a Supelco 2-4044 fused silica capillary column, 30 m x 0.32 mm, with a film thickness of 0.25 μm. The conditions under which the extract was analyzed were compound specific: For TCP and hexadecane, the initial oven temperature was 100 °C, the program rate was 20 °C/min, the

final oven temperature was 200 °C, the injector temperature was 240 °C, and the detector temperature was 250 °C. For anthracene, the initial oven temperature was 150 °C, the program rate was 20 °C/min, the final oven temperature was 250 °C, the injector temperature was 240 °C, and the detector temperature was 250 °C.

Roadway Surface Application

A 50% TiO₂-sealant formulation was applied to 3.75 cm x 3.75 cm sample surfaces consisting of industrial grade reinforced cloth fiber. The sample surfaces were selected as a medium for titanium dioxide attachment because of the rough exterior of the surfaces and similarity to an actual pavement surface. The test surfaces were applied with approximately 170 mg of the TiO₂-sealant mixture, allowed to dry, and then numbered and weighed to determine the initial mass of each sample surface. Each surface was attached to a roadway (Washington State Route 270) to investigate the structural integrity of the photocatalyst-fixant formulation in the presence of vehicles and weather. Controls were established by keeping sample surfaces in the laboratory. Samples were taken from the roadway at selected time intervals and weighed to determine the mass loss of photocatalyst-fixant on each test surface.

SOLID-PHASE CATALYSIS EXPERIMENTS

Experimental Procedures

Dry TiO₂ anatase was spiked with 200 mg/L TCP dissolved in acetone. The contaminated TiO₂ was placed in the dark to minimize photodegradation and the acetone was allowed to evaporate, resulting in a total spike of 200 mg/kg TCP. Two grams of TCP-TiO₂ anatase were distributed evenly in a single layer in a 9.0 cm diameter, 1.5 cm deep dish, covered with DuPont Tedlar PVF film, and exposed to the bank of F40BL lamps. Individual spiked TiO₂ samples corresponded to an initial concentration of 3.18×10^{-5} mmol/cm² TCP. Samples were taken from under the light at varying times and TCP

concentrations were analyzed. Controls were established by conducting parallel experiments in the dark.

Chloride Release

Chloride ion concentrations were analyzed to confirm degradation of the parent compound. Using experimental procedures conducted in parallel under the F40BL lights, TCP-TiO₂ samples were collected from the lights at varying times and chloride ion concentrations were analyzed.

Titanium Dioxide Water Content

The water content of the dry TCP-TiO₂ was adjusted by adding 10%, 25%, or 50% deionized water (mass/mass). Each two-gram sample plus the mass of water was then distributed into the glass dishes and placed under the F40BL lights. Parallel dark controls were established, samples were collected at selected times, and the TCP residual was analyzed.

Competition Investigations

The hydroxyl radical scavengers bicarbonate (HCO₃⁻) and 1-octanol (C₈H₁₇OH) were added with the initial spike. Molar ratios of 200 for HCO₃⁻ and 70 for octanol were used (10). Bicarbonate, added as sodium bicarbonate (NaHCO₃), was dissolved in deionized water and added to the TCP-TiO₂. The water was allowed to evaporate in the dark, and the samples with the additive were exposed to the F40BL lamps. The octanol was dissolved in acetone and added to the TCP-TiO₂, and the acetone was allowed to volatilize in the dark. An electron scavenger (tetranitromethane, TNM) was added to the system in acetone in a 6.0 molar ratio (10). The samples were then placed under the F40BL lamps and analyzed for TCP at selected time intervals. All experiments were performed in triplicate with dark controls conducted in parallel.

Surface Loading

The initial amount of TCP was varied on the TiO₂ by varying the concentration of the TCP in the initial spike. The concentrations of TCP spiked on the photocatalyst were 50 mg/kg, 500 mg/kg, 1000 mg/kg, 5000 mg/kg, and 10,000 mg/kg. The two-gram samples of TCP-TiO₂ were distributed evenly on the bottom of the test dishes, placed under the lights, and collected at selected time intervals.

Analysis

TCP samples were collected over time, shake extracted with ethyl acetate, and TCP residual was analyzed using a Hewlett Packard 5890A gas chromatograph (GC). Using flame ionization detection, the initial GC oven temperature of 100 °C was programmed at 20 °C/min to a final temperature of 200 °C. The injector and detector ports were maintained at 240 °C and 250 °C, respectively. The column used was a Supelco 2-4044 fused silica capillary column, 30 m x 0.32 mm, with a film thickness of 0.25 µm. Chloride concentrations were measured using a Fisher Accumet pH/ion meter 910, combined with a Fisher chloride ion selective electrode and a double junction Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

SCREENING OF FIXANTS

The most effective photodegradation of TCP that occurred for each fixant over a 72 hour period is shown by the data in Figure 3. The concrete sealant was the most effective fixant resulting in 97.6% TCP degradation. Titanium dioxide incorporated into paint base provided a maximum effective photodegradation of TCP of 81.1%. All other fixants achieved maximum TCP degradations of 56.8% or less; therefore, the concrete sealant and the paint base were used in formulating the test surfaces for more detailed study.

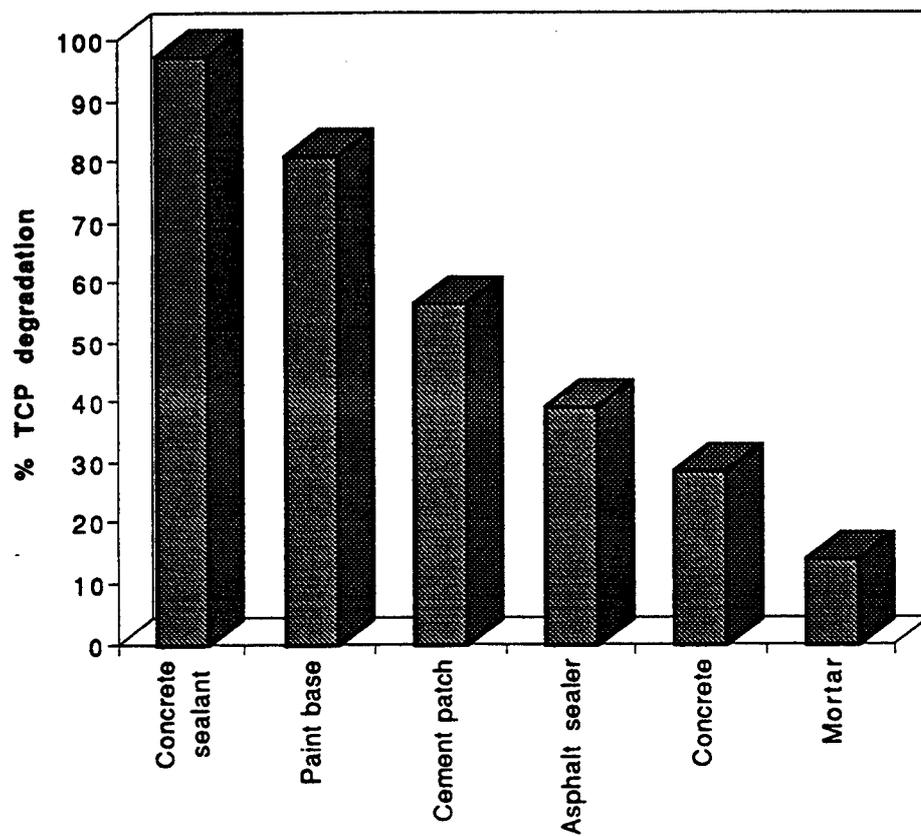


Figure 3. Maximum 2,4,6-trichlorophenol (TCP) photodegradation on various TiO₂-fixant formulations after 72 hours.

TITANIUM DIOXIDE-ASSISTED PHOTODEGRADATION OF HEXADECANE

Titanium Dioxide-Paint Base

The relative disappearance of hexadecane on the TiO₂-paint base formulations is shown by the data in Figure 4. The surface with no TiO₂ resulted in 78% total hexadecane degradation over 72 hours, which then increased as a function of titanium dioxide in the paint base. The 50% TiO₂ samples were characterized by 98.2% degradation of hexadecane in 72 hours. Dark control samples resulted in minimal degradation of the contaminant on the test surfaces.

Titanium Dioxide-Concrete Sealant

Gas chromatograph (GC) analysis documented >99% removal of hexadecane over 96 hours for the photocatalytic destruction of hexadecane on TiO₂ fixed with the concrete sealant. A plot of normalized concentration as a function of time (Figure 5) illustrates the decrease in the concentration of hexadecane on concrete sealant with 0%, 10%, 25%, and 50% TiO₂ by weight. The data of Figure 5 also show that hexadecane on the surface with no TiO₂ incorporated into the mixture degraded at a slower rate than it did on any of the TiO₂-sealant formulations. Using 50% TiO₂ by weight, >99% degradation was observed in 48 hours. With the addition of the photocatalyst, the time required to degrade nearly all of the hexadecane was half the time of the degradation on the surface with no TiO₂. Control samples kept in the dark exhibited some hexadecane disappearance which was most likely due to volatilization, however, its effect was minimal in the time that the samples were exposed to the light.

The accelerated photodegradation of hexadecane in the presence of 50% TiO₂ in the concrete sealant indicated that the photoactivity of the catalyst was enhancing the degradation of the contaminant. Enough radical species were generated by one of the mechanisms of TiO₂ activation to effectively attack and degrade the alkane.

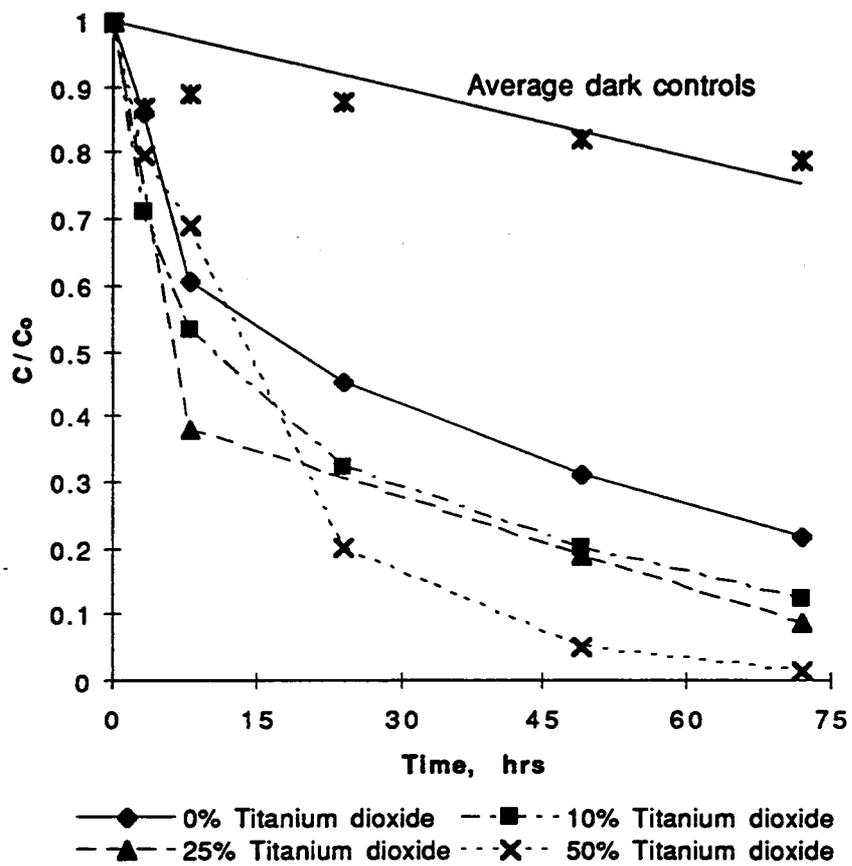


Figure 4. Photodegradation of hexadecane on the surface of TiO₂-paint base.

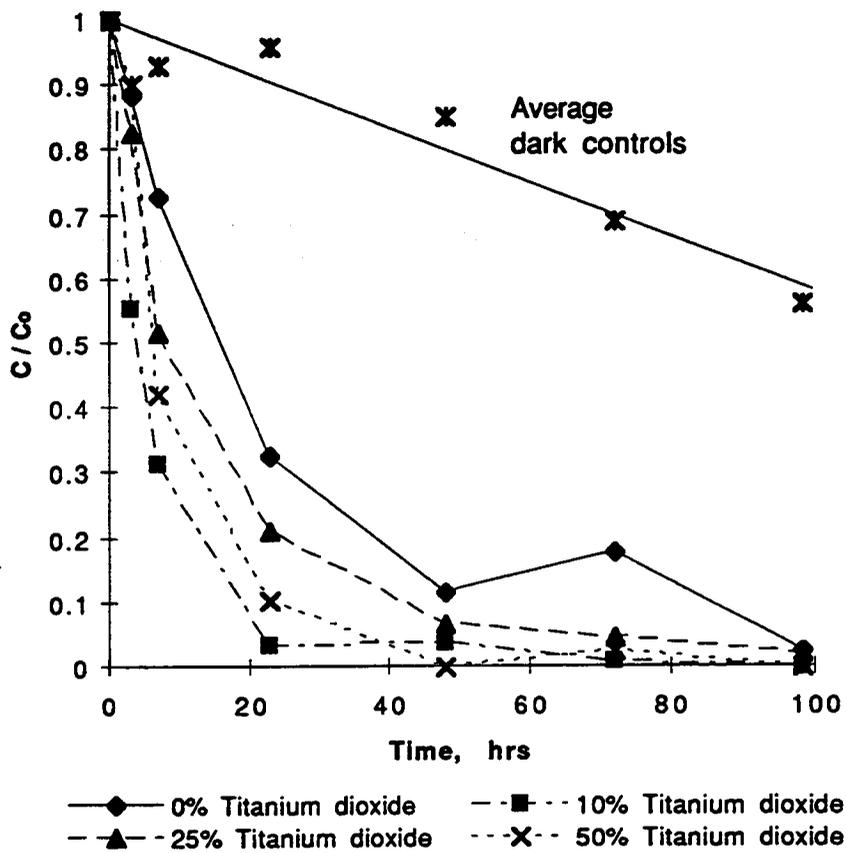


Figure 5. Photodegradation of hexadecane on the surface of TiO₂-concrete sealant.

The TiO₂ incorporated into the concrete sealant was more effective than the paint base. Hexadecane was degraded approximately 150% faster on the concrete sealant surfaces compared to the paint base formulations. These results suggest that the concrete sealant allowed more contact between the TiO₂ particles and the compound, thereby providing more opportunity for the radicals to degrade the compound. The loss of hexadecane on 0% TiO₂ surfaces shows that direct photolysis or volatilization contributed to the contaminant degradation. However, in both the sealant and the paint base, the data illustrate that TiO₂ was effective in accelerating the photodegradation of hexadecane on the surfaces.

TITANIUM DIOXIDE-ASSISTED PHOTODEGRADATION OF ANTHRACENE

Titanium Dioxide-Paint Base

A plot of normalized anthracene concentrations as a function of time on 0%, 10%, 25%, and 50% TiO₂-paint base surfaces is shown in Figure 6. These data demonstrate that titanium dioxide did not affect the photodegradation of anthracene on the test surfaces. The degradation of anthracene ranged from 50.6% to 71.4% over 105 hours with no significant pattern in anthracene disappearance relative to the amount of TiO₂ added to the fixant. Dark controls exhibited little anthracene degradation.

Titanium Dioxide-Concrete Sealant

Titanium dioxide-mediated photolysis of anthracene on the surface of the anatase fixed with concrete sealant is shown in Figure 7. These data show nearly the same relative anthracene degradation (~83%) for all TiO₂ concentrations in the concrete sealant. The 10% TiO₂ formulation showed a slightly lower degradation of anthracene at 73.6%. Dark control samples exhibited minimal anthracene loss. Because the disappearance of anthracene was nearly the same for all the photocatalyst concentrations, the TiO₂ incorporated into the fixant did not appear to affect the photodegradation of anthracene.

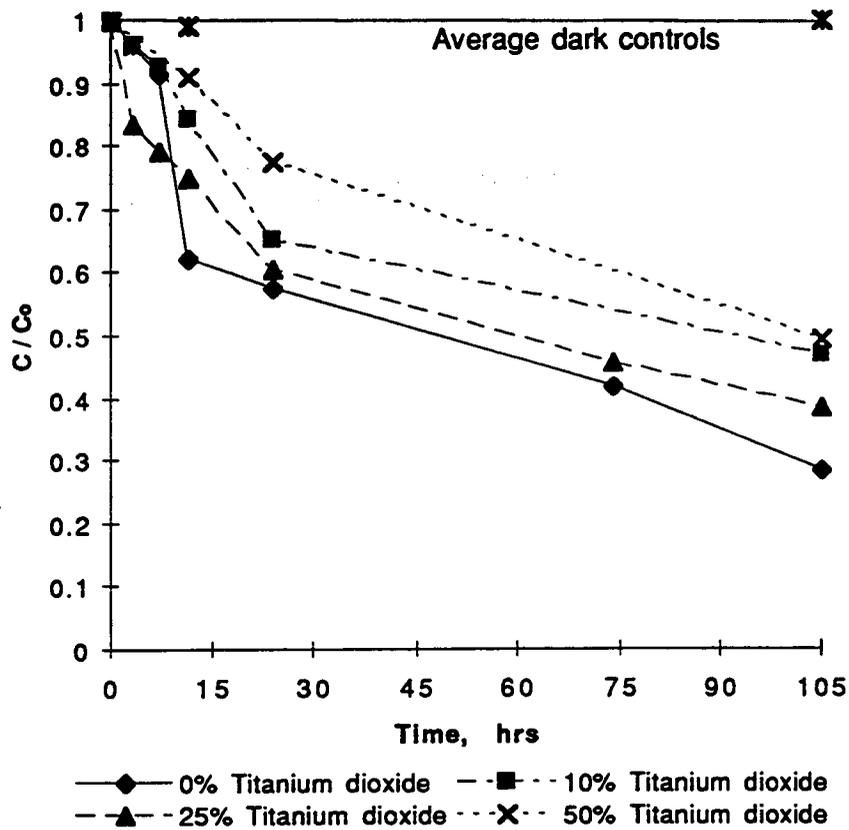


Figure 6. Photodegradation of anthracene on the surface of TiO₂-paint base.

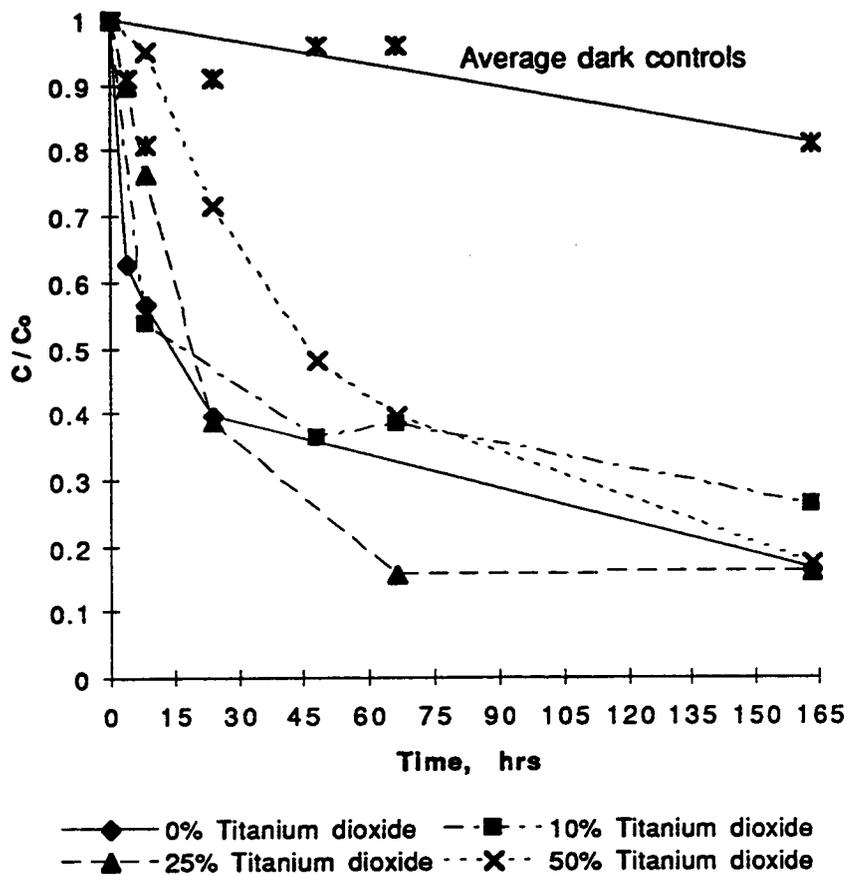


Figure 7. Photodegradation of anthracene on the surface of TiO₂-concrete sealant.

The maximum anthracene degradation (71.4%) that occurred on both fixants after 105 hours was significantly slower than the degradation of hexadecane on the same surface. Because anthracene absorbs the same wavelengths as TiO_2 , the presence of the contaminant may have reduced the effectiveness of TiO_2 photocatalysis by blocking the light needed to excite the TiO_2 .

Because TiO_2 did not appear to assist in the surface photodegradation of anthracene and anthracene is not volatile, any degradation that took place on both fixants was most likely due to direct photolysis. Anthracene photodegraded over a longer time period than did hexadecane on the same type of surface which was probably due to the different absorption spectra of the two contaminants. Anthracene, a PAH, absorbs at a higher wavelength (up to 375 nm) (24) on the solar spectrum than hexadecane, and degradation was less likely to be enhanced by the titanium dioxide (Figure 2). The F40BL lamps emit wavelengths primarily above 300 nm and below 400 nm. Anthracene was more likely to absorb these wavelengths and photodegrade directly without assistance from the photocatalyst. The hexadecane absorption maximum is 290 nm (25); therefore, its absorbance range did not overlap significantly with the emission spectrum of the F40BL lamps and was more likely to be photodegraded with the enhancement of TiO_2 .

Because compounds such as anthracene are light sensitive, they may be degraded by direct photolysis and may not pose a significant threat in nonpoint runoff. Compounds such as hexadecane may be more of a concern because they are not as light sensitive and could, therefore, be degraded using photocatalytic pavement borders.

STRUCTURAL INTEGRITY OF TITANIUM DIOXIDE-FIXANT FORMULATIONS

When applied to actual pavement surfaces, the photocatalyst-fixant mixture attached to the pavement will exhibit some wear and eventually affect the ability of the system to enhance rates of hydrocarbon photodegradation. The effect of the everyday use of roadways and parking lots on the structural integrity of the TiO_2 -fixant formulation was

investigated by applying test surfaces to Washington State Route 270. The test surfaces exhibited mass loss of TiO₂-sealant as illustrated by the data in Figure 8. Over 26 days, the surfaces lost 58 mg of the 170 mg of TiO₂-sealant applied (34% loss). The data was fitted to a line using linear regression which resulted in a linear loss of 2.35 mg/d ($r^2 = 0.937$) of TiO₂-sealant.

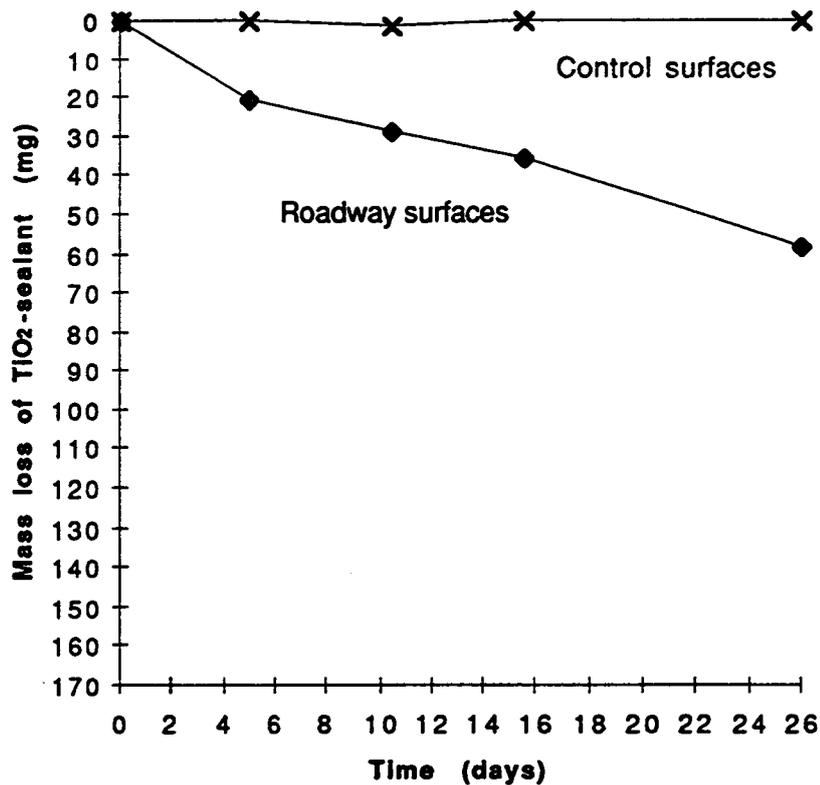


Figure 8. Maximum mass loss of titanium dioxide-sealant on a pavement surface.

2.4.6-TRICHLOROPHENOL PHOTODEGRADATION AND CHLORIDE RELEASE

Approximately 80% degradation of TCP occurred under the F40BL lamps over 24 hours (Figure 9). The dark control experiments conducted in parallel exhibited negligible TCP loss. The results of Figure 9 suggest that TCP, a common biorefractory industrial compound, can be degraded on the surface of TiO₂.

The loss of chlorine from the parent compound was investigated to verify degradation of the TCP. An increase in the concentration of chloride ions corresponded to the disappearance of TCP (Figure 10). Stoichiometric calculations showed that approximately two of the three chlorines on each TCP molecule were released after 24 hours. Pruden and Ollis (26-27) found similar dechlorination during the degradation of trichloroethylene and chloroform using titanium dioxide recirculating photoreactors. Moreover, Barbeni *et al.* (11) observed the dehalogenation of 4-chlorophenol in less than 24 hours in aqueous TiO₂ suspensions. The results in Figure 10 illustrate that even in the absence of water, TiO₂ has the ability to dehalogenate compounds and potentially decrease the hydrophobicity and toxicity of chlorinated organics.

EFFECT OF WATER CONTENT ON 2,4,6-TRICHLOROPHENOL DEGRADATION

The effect of the presence of water in the TiO₂ system on TCP degradation is illustrated by the data of Figure 11. These data demonstrate that degradation occurred at a more rapid rate as the water content increased. Degradation of TCP to below detectable concentrations was achieved at a water content of 25% after approximately 20 hours. As the water content increased, the oxidative pathway on the surface of the particle may have become more significant due to an increase in adsorbed water and hydroxide ions on the surface of the semiconductor (8).



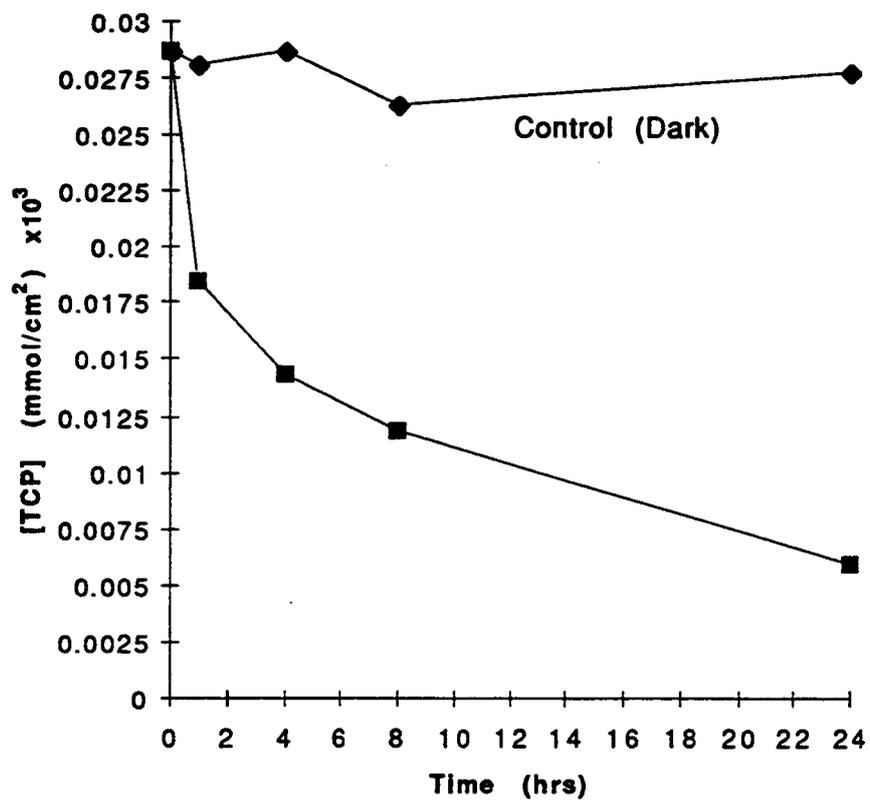


Figure 9. Degradation of TCP under UV-light on the surface of dry TiO₂ anatase.

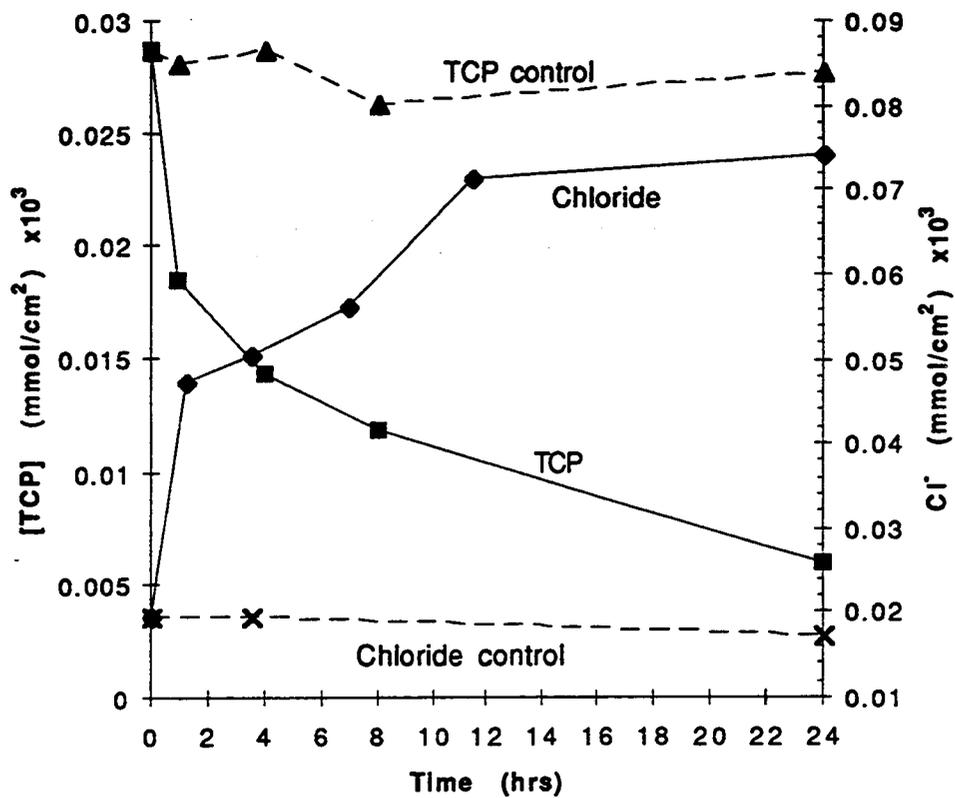


Figure 10. Chloride production compared with TCP degradation on the surface of dry TiO_2 anatase.

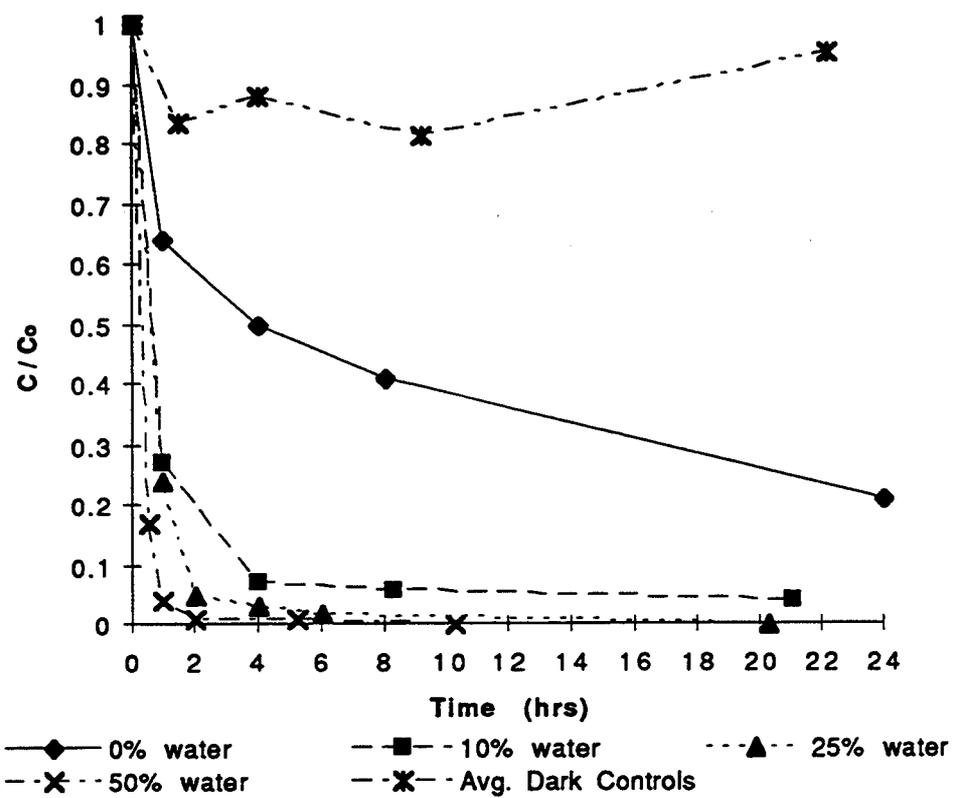


Figure 11. Effect of water content on TiO_2 -mediated surface photodegradation of TCP.

The surface reactions of the electron hole in the valence band of the semiconductor particle likely became an increasingly important mechanism of degradation as the water content increased. With more water incorporated into the system, the electron vacancy had more opportunity to react with water (equation 1) and hydroxide ions (equation 2) and produce more hydroxyl radicals, which react with most organic compounds at near-diffusion controlled rates (28) resulting in the accelerated degradation of TCP.

WIDESPREAD APPLICABILITY OF SURFACE CATALYSIS

To evaluate the mechanisms occurring in dry-phase TiO₂ photocatalysis and accompanying applicability to a wide range of contaminants, hydroxyl radical scavengers (HCO₃⁻ and octanol) were incorporated into the system. Bicarbonate and octanol were added in separate aliquots at molar ratios of 200:1 and 70:1, respectively (10). The degradation of TCP in the samples with no scavengers occurred at the same rate as the samples with added scavengers in the dry system (Figure 12). Statistical analysis by analysis of variance (29) was used to evaluate differences in the slopes of the curves. The analysis showed that there was no significant difference between the system with no scavenger and the systems with bicarbonate and octanol amendments ($p = 0.95$). These data confirm that OH• was not a major component in the degradation of TCP when the system did not contain water.

The role of hydroxyl radicals was also investigated using the same scavengers in a TiO₂ system with the addition of 50% water (Figure 13). Based on the analysis of variance, both the bicarbonate and octanol additions significantly lowered the rate of reaction ($p = 0.95$). Therefore, the TCP degradation rate without the addition of bicarbonate or octanol was significantly greater than the rates with the scavengers. Because the bicarbonate and octanol scavenged the hydroxyl radicals being produced through equations 1 and 2, the rate of degradation of TCP decreased (Figure 13), which indicates that the role of OH• is a dominant mechanism with an increase in water content.

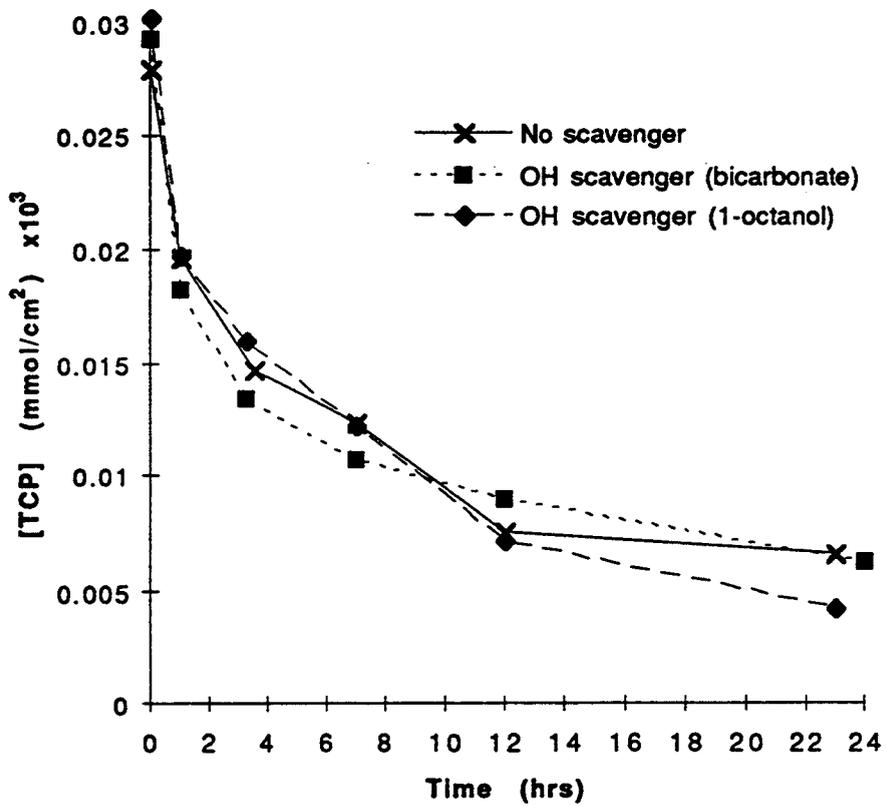


Figure 12. Effect of two hydroxyl radical scavengers on TCP degradation on the surface of TiO₂ powders, 0% water.

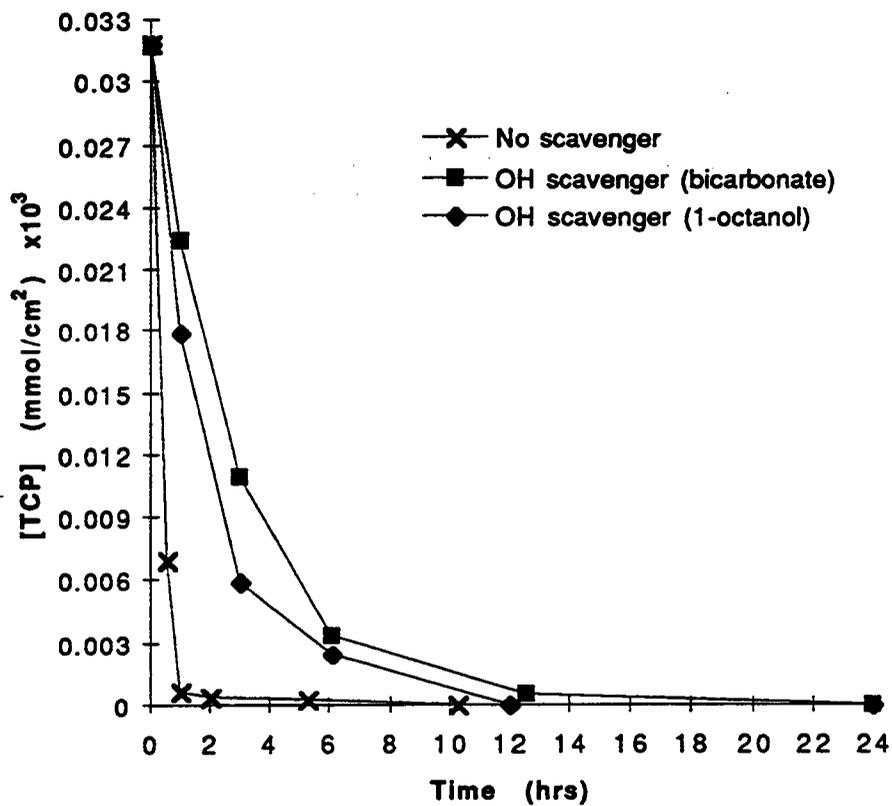


Figure 13. Effect of two hydroxyl radical scavengers on TCP degradation on the surface of TiO₂ powders, 50% water.

Glaze *et al.* (10) obtained similar results when bicarbonate and methanol were added as OH• scavengers to an aqueous system containing tetrachloroethylene (PCE). Bicarbonate addition was increased from 100 to 207 moles per mole PCE with corresponding degradation of PCE ranging from 95% to 70%. Bicarbonate and methanol slowed the overall PCE degradation by scavenging OH•. They established that, although OH• was a major mechanism in the aqueous systems, it was not the only mechanism in the degradation of PCE in the presence of TiO₂ suspensions, and that other mechanisms performed an important role in the degradation of compounds.

The data of Figure 12 confirm a negligible contribution of OH• in the dry-phase TiO₂ photocatalysis of TCP. However, from the data of Figure 13, the addition of water resulted in the production of OH• (equations 1 and 2), confirming that other mechanisms were responsible for the degradation of TCP on the surface of dry-phase TiO₂.

The data of Figure 14 show the effect of the addition of tetranitromethane to the dry TiO₂ photocatalytic system. Statistical analysis using analysis of variance showed that the rate of degradation of TCP with the electron scavenger occurred at the same rate as the system without the scavenger ($p = 0.95$). In addition to the lack of OH• in the dry system, the superoxide ion radicals produced from the reaction of oxygen with the conduction band electron did not react with the TCP to promote its degradation:



The experimental data are in agreement with equation 4 because O₂^{•-} is considered relatively nonreactive with organic compounds (30). Furthermore, TCP was non-reactive with the conduction band electron and was not reduced through the reaction described by equation 5:

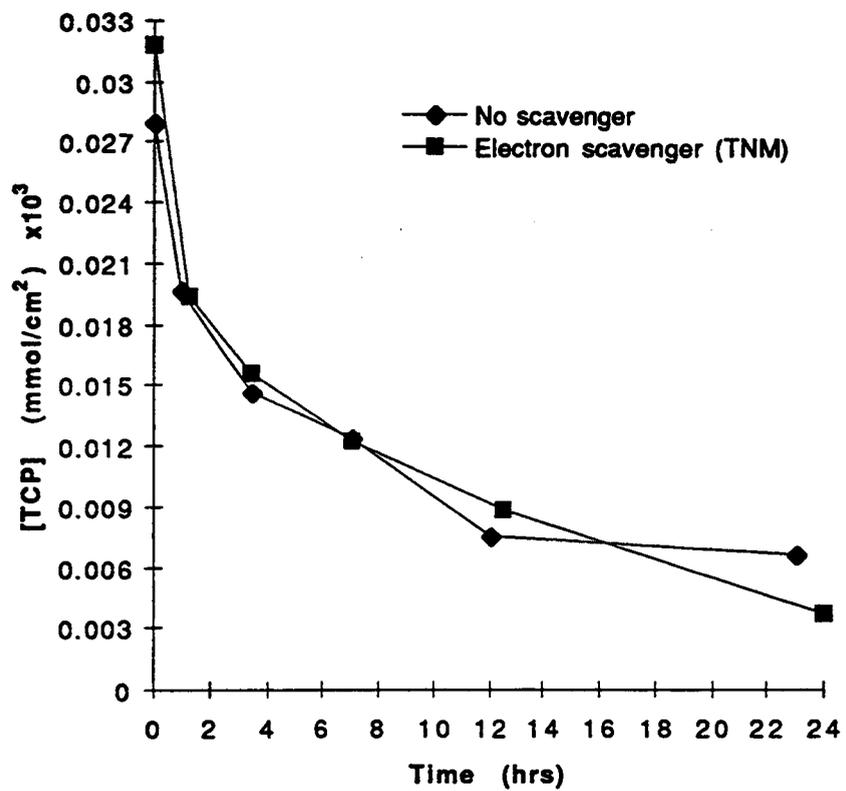


Figure 14. Effect of electron scavenger, TNM, on the photodegradation of TCP on TiO₂, 0% water.



The pathway described by equation 5 would not be expected in the hyperoxic environment of the atmosphere because electrons in the conduction band are transferred preferentially to O₂ over organic compounds. These data confirm that the conduction band electron and the superoxide ion radical do not react significantly with TCP using dry phase TiO₂ photocatalysis, and that the reductive mechanism at the semiconductor surface was not a prominent pathway of degradation. Because OH•, O₂•⁻, and electrons were not significant mechanisms in the dry-phase photocatalytic degradation of TCP, the only potential remaining mechanism is direct oxidation of TCP by the valence band electron hole:



The presence of water (to promote the OH• mechanisms described by equations 1 and 2) or the absence of oxygen (to promote reductive transformations described by equation 5) has usually been considered necessary for TiO₂-mediated photodegradation of organic compounds. However, Izumi *et al.* (8) proposed that the valence band electron hole may potentially promote the direct oxidation of some organic substrates. The results of this study suggest that the electron hole mechanism (equation 6) is the dominant mechanism for the dry-phase TiO₂ photoassisted catalysis of TCP. This mechanism will likely oxidize a wide range of contaminants on pavement surfaces.

EFFECT OF 2,4,6-TRICHLOROPHENOL LOADING

The relative rates of TiO₂-mediated photocatalysis as a function of initial TCP concentration are shown in Figure 15a. These data indicate significantly faster relative rates of degradation at low initial TCP concentrations. At concentrations below 1000 mg/kg,

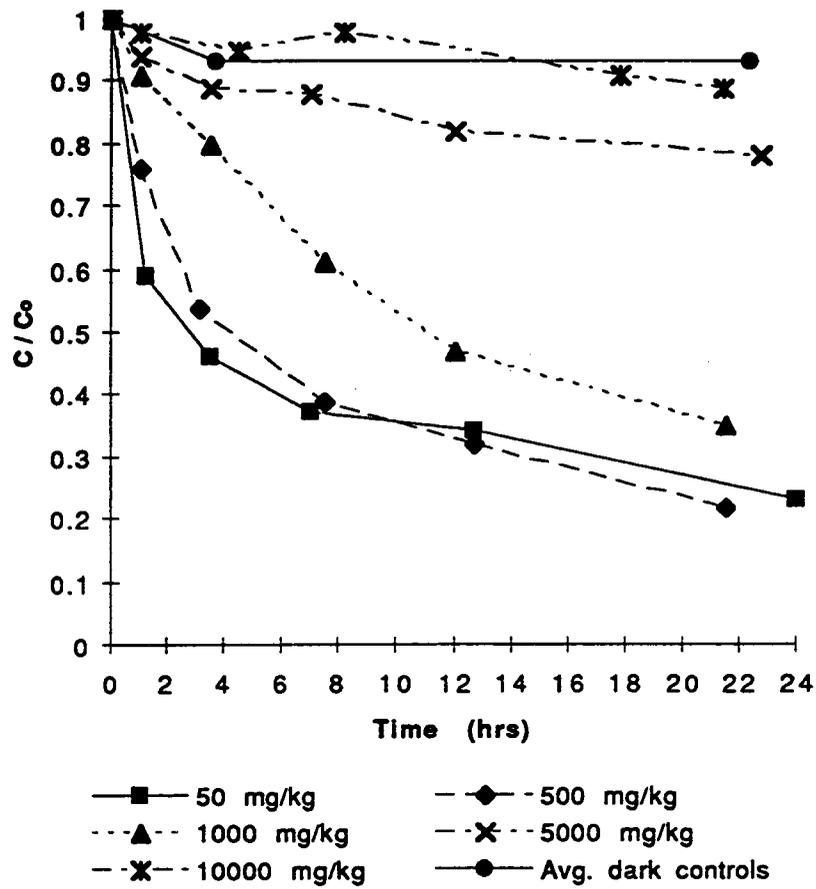


Figure 15a. Effect of increased TCP concentrations on the effectiveness of dry TiO_2 to degrade TCP.

65% to 79% TCP degradation was achieved in approximately 24 hours. However, at concentrations of 5000 to 10,000 mg/kg, only 11% to 22% of the initial spike was degraded in 24 hours. Dark controls exhibited negligible TCP loss. These data suggest that the effectiveness of TiO₂ decreases as a function of TCP concentration. However, the data shown of Figure 15b illustrate that the total mass of TCP degraded increased as a function of initial TCP concentration which was probably due to a second-order phenomenon (equation 7) as the rate of TCP change increased with higher TCP concentrations.

$$\frac{-d[\text{TCP}]}{dt} = k [h\nu_B^+] [\text{TCP}] \quad (\text{Equation 7})$$

Although extended time periods would be needed to degrade the higher concentrations of TCP, these results indicate that the capacity of TiO₂ was not exhausted, even at loadings of up to 10,000 mg/kg TCP. Although high contaminant concentrations may potentially quench excited states or decrease the flux of light reaching the TiO₂ (31), the data of Figure 15b suggest that TCP concentrations to 10,000 mg/kg did not significantly quench TiO₂ excited states or block the light reaching the photocatalyst.

The results of this research show that dry-phase TiO₂ photocatalysis degraded TCP by a non-hydroxyl radical mechanism. Jones and Watts (32) found that the common petroleum constituents hexadecane and anthracene were also degraded by dry-phase photocatalysis. Their results suggest that coating the surface of pavements and other construction materials with TiO₂ has potential as an *in situ* decontamination system. The process may be effective in treating spillage on highways, parking lots, and at gasoline stations and industrial areas which are adjacent to sensitive bodies of water.

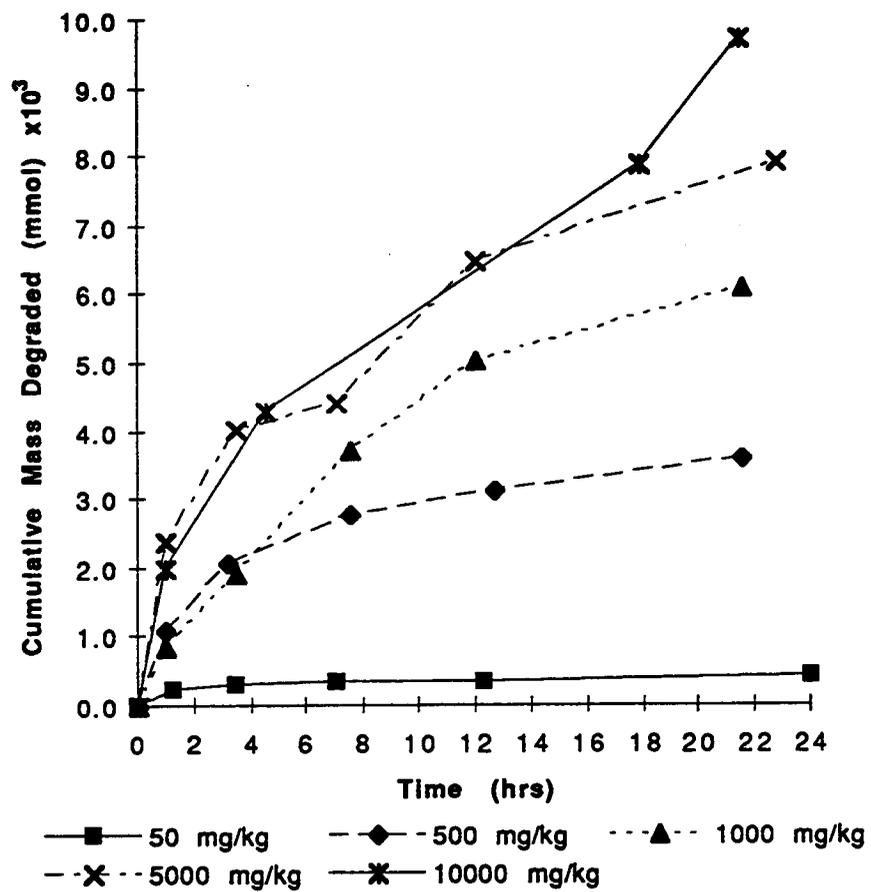


Figure 15b. Mass degraded as a function of time with increased TCP concentrations.

DESIGN CONSIDERATIONS

A range of photocatalytic pavement borders could be designed based on the potential threat of nonpoint runoff to adjacent soils and surface waters. Areas where minimal protection is required may only require a border as wide as a fog line. Some systems, such as a section of highway, parking lot, or service station adjacent to an extremely sensitive body of water (e.g., an endangered species habitat) could potentially mitigate hydrocarbon runoff *in situ* by covering the entire pavement with TiO₂. Field studies will be needed to determine areal design requirements for photocatalytic pavement borders.

The type of contaminant and the amount of time allowed for degradation have a considerable effect on the ability of fixed TiO₂ to enhance the photodegradation of hydrocarbons. On an actual contaminated surface, the varying types of hydrocarbons and the unknown lengths of surface time before runoff increase the difficulty of engineering such a system.

The type of fixant used to attach the TiO₂ particles to surfaces partially controls the amount of contact the contaminant has with the activated photocatalytic particles. The concrete sealant and the paint base used for these test surfaces are but two of the numerous fixants available. The optimal fixant is one that allows sufficient contact between the contaminant and the activated TiO₂ particle, reducing the time needed to degrade the contaminant. Design considerations must also be given to the effect of use (e.g. traffic) and weather on the photocatalytic system. Results show that considerable wear takes place from heavy pavement use and the type of fixant used in attaching the photocatalyst to the surface must be structurally sound when fixed. From such a system, the pollutant load could be considerably reduced before migrating to conventional roadside measures of runoff control.

Based on the contaminant destruction documentation performed through chloride analysis and scavenging techniques to document reactive pathways, surface, dry-phase

photocatalysis is applicable to the destruction of a wide range of organic contaminants such as aliphatic hydrocarbons and polycyclic aromatic hydrocarbons. The process has a wide range of potential applications and deserves implementation on highways in chip seal and fog lines, in parking lots, and highly contaminated areas such as maintenance yards and fuel depots.

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