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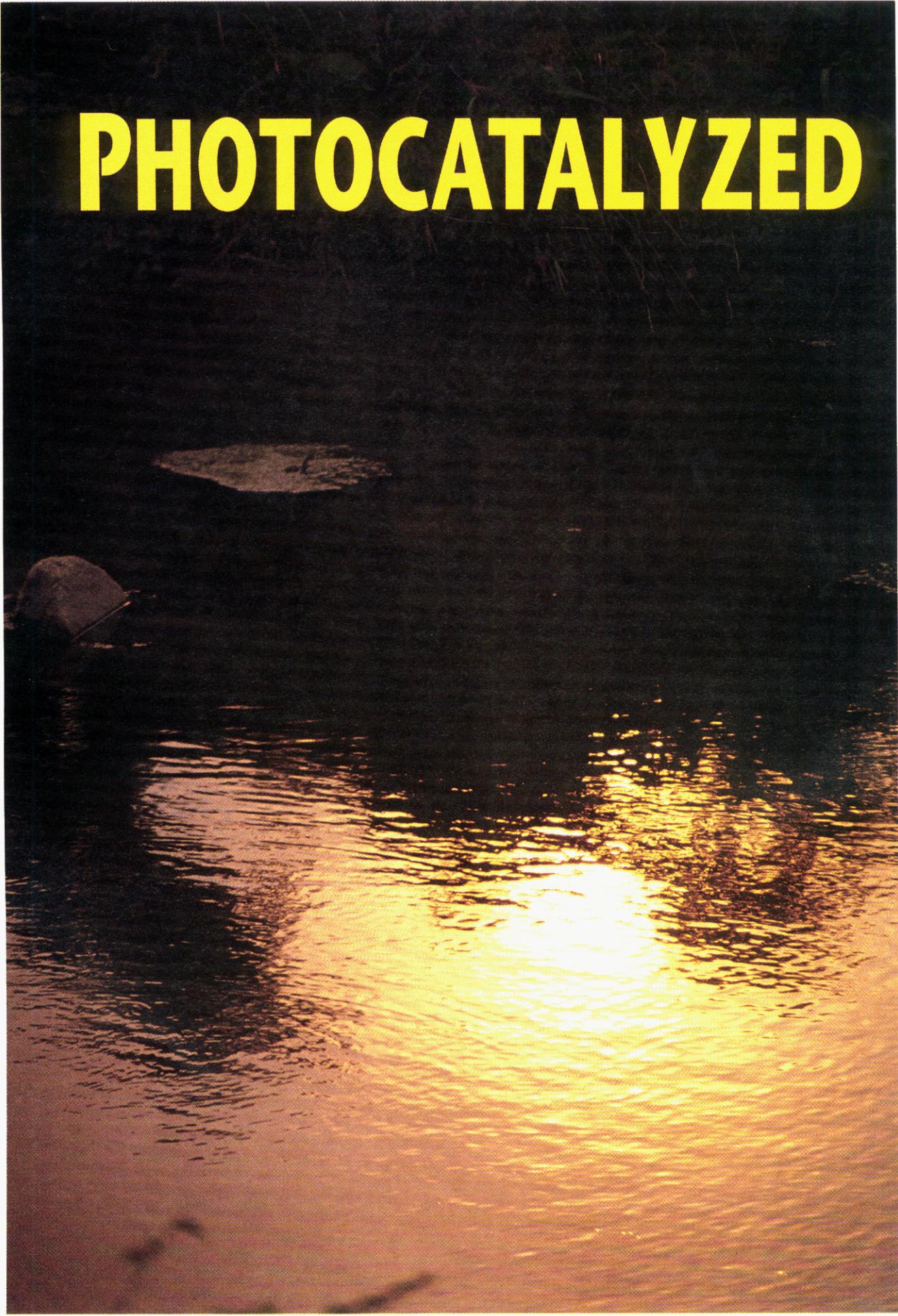
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DESTRUCTION OF WATER CONTAMINANTS

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Heterogeneous photocatalysis is a process in which the illumination of an oxide semiconductor, usually the anatase form of titanium dioxide, produces photoexcited electrons (e^-) and holes (h^+). These can migrate to the oxide surface and participate in half-cell reactions that are part of a closed, catalytic cycle. In the aqueous phase, the illuminated surface is widely regarded as a producer of hydroxyl radicals (e.g., $h^+ + OH^- \rightarrow \cdot OH$), and these and other highly oxidizing initial products of this indirect photochemistry go on to attack oxidizable contaminants.

In the six years since a 1985 *ES&T* review on photocatalysis applied to water purification (1), two NATO conferences (2, 3) and a NATO Advanced Study Institute course have been held (4), and one monograph (5) and more than 100 papers have been published on this topic. Like closely related photooxidation processes employing light plus ozone, light plus hydrogen peroxide (H_2O_2), or light/ O_3/H_2O_2 , photocatalysis research is driven by legisla-

tion in industrialized countries that encourages water purification (decontamination, detoxification, decolorization, deodorization) and simultaneous contaminant destruction. Although light alone or oxidant alone (H_2O_2 , O_3) produces contaminant partial destruction, only the simultaneous use of either light and an oxidant [O_3 , H_2O_2 , or O_2 (with photocatalyst)] or of the dual oxidants ($O_3 + H_2O_2$) has often been shown to yield complete mineralization of organic carbon to carbon dioxide; this is the principal advantage of these advanced oxidation approaches to water treatment.

This article highlights recent developments in photocatalysis that are applicable to water treatment. Topics discussed include the generality of photocatalysis for complete contaminant destruction (mineralization); some specific contaminant classes of interest (chlorinated aromatics, surfactants, herbicides, and pesticides); the use of solar versus artificial illumination; the influence of additional oxidants such as H_2O_2 ; catalyst forms (suspended vs. immobilized); and related potential applications of photocatalysis [metal recovery and total organic carbon (TOC) analyses].

Generality

The complete mineralization of simple and complex chlorinated derivatives of alkanes, carboxylic acids, alkenes, and aromatics has been demonstrated repeatedly (6, 7). So far, the only chlorinated molecule

found to be resistant to initial photocatalytic attack is the saturated molecule of carbon tetrachloride, which contains no abstractable hydrogen (1). [Even trichloroacetic acid can be dechlorinated photocatalytically (7)]. Although chlorinated hydrocarbons have been the example contaminants most studied via photocatalysis, the complete destruction of brominated compounds [bromoform (8) and ethylene dibromide (9)] and fluorinated compounds [fluorophenols (10)] also has been achieved.

Actual water treatment challenges characteristically will be multicomponent in several senses. First, multiple organic contaminants are routinely expected from materials such as gasoline [benzene (B), toluene (T), xylenes (X)] or from leaks in halogenated solvent tanks [perchloroethylene (PCE), trichloroethylene (TCE)] into underground or surface waters. Second, in the course of mineralization of any organic contaminant, oxidation will logically involve a series of intermediates of progressively higher oxygen-to-carbon ratios on the way to CO_2 . Such intermediates make the conversion process multicomponent, even if only a single contaminant exists in the feed. Hence demonstration of the formation and elimination of intermediates also is important for showing complete removal of undesirable compounds. The same point has become a focus in homogeneous photooxidation (11).

Demonstrated mineralization

All advanced oxidation processes have the potential to carry the original organic contaminant through a series of increasingly oxidized intermediates to carbon dioxide. Because complete mineralization usually is desirable in a water-polishing operation, increased attention has been drawn to demonstrating not only reactant disappearance but also carbon dioxide appearance kinetics. For example, with PCE, reactant disappearance and CO₂ appearance are complementary (12), which indicates a virtual lack of kinetically stable important intermediates (Figure 1a). In contrast, benzene clearly passes through several stable intermediates; at least two are required to fit the CO₂ evolution data of Figure 1b.

Matthews has demonstrated that organic compounds containing phosphorus, sulfur, and halogen heteroatoms may be oxidized quantitatively, yielding phosphate (PO₄³⁻), sulfate (SO₄²⁻), and halide (X⁻), respectively (13). Oxidations of nitrogen-containing compounds present the most complex results (14). The photocatalyzed conversion of rings containing a single nitrogen atom results in the early appearance of inorganic nitrogen in the form of ammonia, and later as nitrate (14). Nitrate, a presumed secondary product, appears last but eventually dominates the product spectra.

The ring structure of *s*-triazine herbicides contains three nitrogens and is very stable; only partial degradation to cyanuric acid is achieved (15).

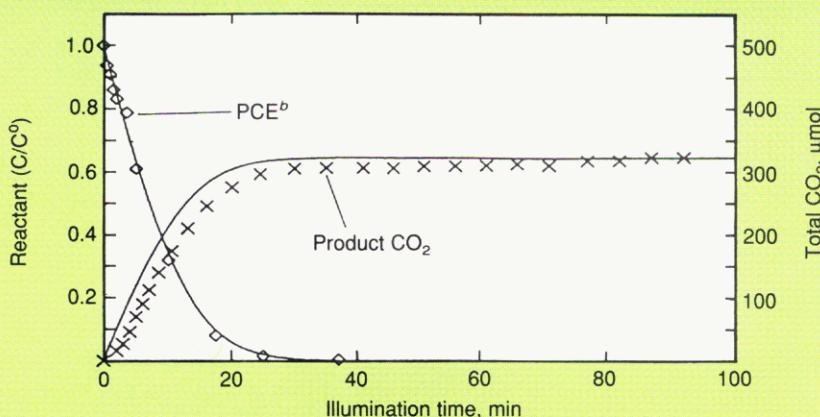
Pelizzetti et al. (16) have demonstrated complete mineralization of such long-chain alkanes as dodecane, dodecyl sulfate, 1-bromododecane, 1-decanol, and decanoic acid. Stoichiometric recovery of sulfate and bromide also was claimed when anion adsorption on the titanium dioxide photocatalyst was included.

Chlorinated aromatics

Since our 1985 summary of photocatalysis (1), spectacular progress has been made in demonstrating the complete photocatalyzed mineralization of chloroaromatics, including chlorophenols, chlorobenzenes, chlorinated biphenyl, chlorinated dioxins, and DDT. A sample of such compounds appears in Figure 2 (17, 18).

Dioxins are so water-insoluble that they can be examined only by

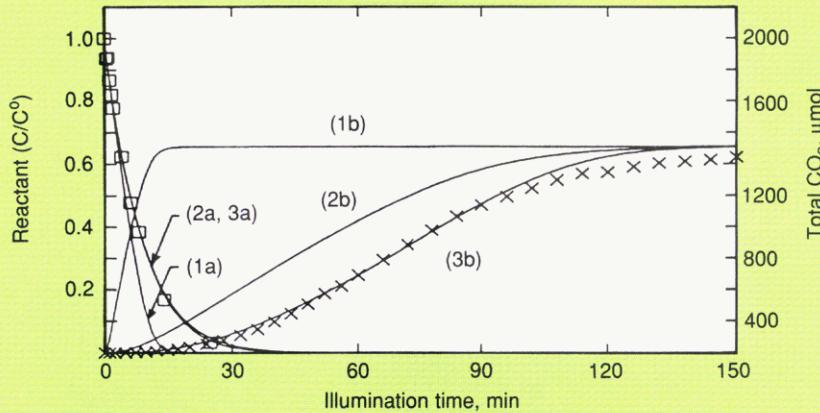
FIGURE 1
(a) Photocatalyzed mineralization of perchloroethylene (PCE)^a



^a Solid curves represent kinetic models for PCE disappearance and for carbon mass balance for CO₂ appearance, respectively.

^b Initial concentration PCE₀ = 207 μmol.

(b) Photocatalyzed benzene mineralization^a



^a Solid curves represent kinetic models for benzene disappearance, assuming:

1a, 1b = no intermediates;
2a, 2b = one important intermediate;
3a, 3b = two important intermediates.
Source: Reference 12.

loading them onto the catalyst via dissolution in hexane, contact with the catalyst, and solvent evaporation. Interestingly, this approach may allow direct hole (h⁺) attack of adsorbed organics, and only by this solvent-loading approach are other oxides such as WO₃ and ZnO shown to be nearly as effective as TiO₂ for the decomposition of the chloroaromatic 3,3'-dichlorobiphenyl (DCB) (19).

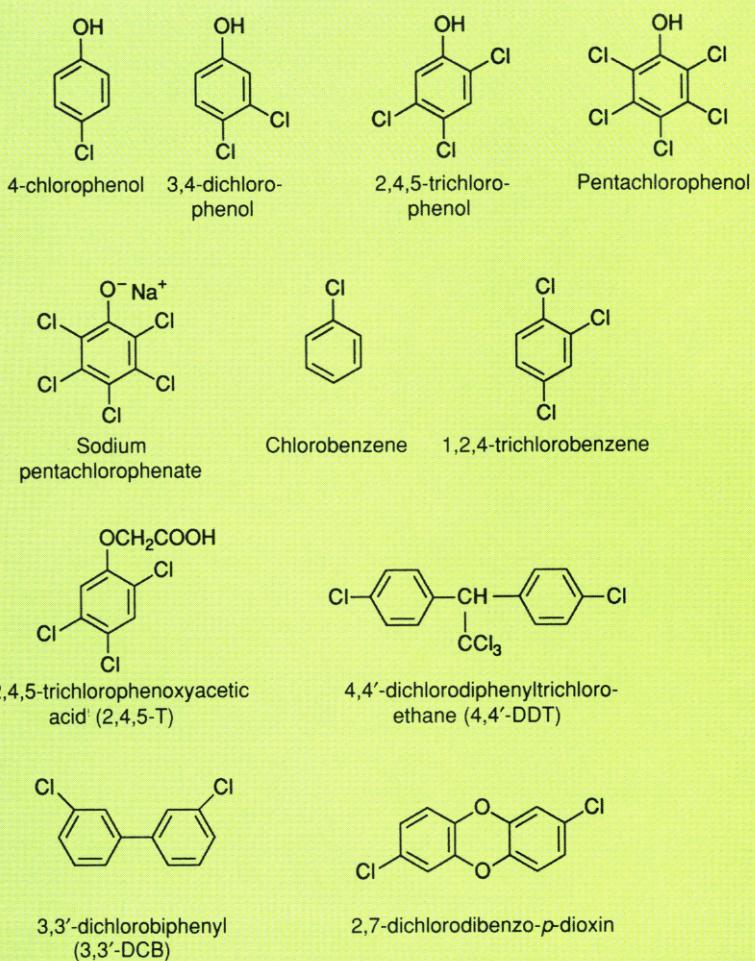
Photocatalyzed destruction of DDT proceeds without evidence of significant formation of the more toxic DDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene] which forms by OH⁻ attack or biodegradation. This absence of DDE suggests a photocatalyzed ·OH radical attack on the aromatic ring, followed by ring opening; chlorine appears to be released only after ring opening, in contrast with most results with single-ring chloroaromatics (20).

The use of photocatalysis in series with conventional chlorination also may be envisioned, because the rates of 2-chlorophenol or of atrazine disappearance have been shown to be largely unaffected by 3 × 10⁻⁴ to 10⁻³ M chlorine (21).

Surfactants

Earlier studies (22–25) of anionic, cationic, and non-ionic surfactants indicated that aromatic (benzyl) and hydrophilic moieties (e.g., C-SO₃Na) are relatively easily attacked and, for benzyl groups, fully mineralized, whereas the long hydrocarbon chain is converted slowly. Significantly, virtually complete loss of surface active behavior was demonstrated in parallel with loss of benzyl groups, a rare example in photocatalysis in which the elimination of the nuisance or hazard value of the reactant did not require complete reactant mineralization.

FIGURE 2
Structural formulas of chloroaromatics degraded photocatalytically



Source: Reference 4.

Recently, the photocatalyzed degradation of alkyl phenols and the non-ionic nonylphenol ethoxylate were examined (25). The surfactant and alkyl phenols were susceptible to complete mineralization, as indicated by the demonstration of a carbon balance all the way to carbon dioxide for polyethoxylated 4-nonyl-phenols with average numbers of 2, 5, and 12 ethoxy units (26). The related solvents 2-ethoxy- and 2-butoxyethanol also were easily mineralized (27).

Herbicides and pesticides

The complete disappearance of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4,5-trichlorophenol (TCP) as well as ~ 100% recovery of initial chlorine as free chloride ion in the final state (reaction time of 30–90 min) was demonstrated (28). The ratio of free chloride to TCP converted was always 3:1, suggest-

ing a very rapid mineralization and absence of appreciable accumulated intermediates. In contrast, the photocatalytic destruction of 2,4,5-T yielded smaller chloride-to-reactant converted ratios prior to complete mineralization, and major intermediates detected were 2,4,5-TCP and 2,4,5-trichlorophenylformate (28). These and other results indicate slow to moderate attack of ring compounds, followed by rapid mineralization once simple phenolics or opened rings have been achieved.

DDT is one of the most complicated chlorocarbons examined in photocatalysis: the complete dechlorination of 1-ppm solutions is reported (29) with a half life of ~ 40 min. An initially rapid DDT disappearance was followed by much slower final disappearance and chloride recovery, as would be expected for a reactant with a number of important kinetic intermediates.

The herbicide bentazon (3-isopropyl-2,1,3-benzo-thiadiazin-4-one-2,2-dioxide) is efficiently converted to give nearly quantitative yields of sulfur as sulfate ion and carbon as carbon dioxide (30).

The *s*-triazine herbicides (atrazine, simazine, trietazine, prometon, and prometryne) are degradable but are singularly resistant to complete mineralization. In all cases, the starting material is degraded to the very stable six-membered ring cyanuric acid ($-\text{N}=\text{C}(\text{OH})-$)₃; virtually stoichiometric recovery of nitrogen, sulfur, and chlorine in ring side groups as nitrate, sulfate, and chloride ions has been demonstrated (15). Pathways for atrazine may include dehalogenation, dealkylation, and deamination (15) as summarized in Figure 3. Because cyanuric acid has a very low toxicity, these partial mineralization results are encouraging. Complete atrazine disappearance has been demonstrated even at parts-per-billion levels.

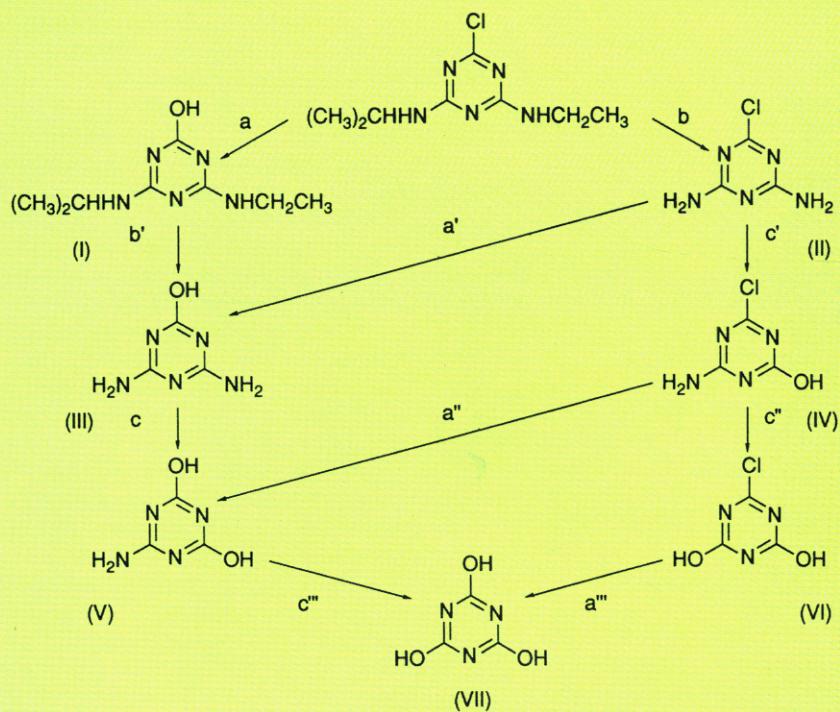
Rate enhancement by H₂O₂

Photocatalyzed reactions have, at times, been reported to exhibit appreciable, even substantial, rate increases when H₂O₂ is added to an aqueous photocatalyst slurry. Degradations showing increased rates include trichloroethylene and perchloroethylene (31), chloral hydrate (32), and phenol (33). The last study found that the photocatalyzed oxidation rates increase according to O₂ < H₂O₂ < (H₂O₂ + O₂). Such enhancements are potentially very important for water treatment. The explanations for the observed enhancements may be several, depending on the following reaction conditions.

First, hydrogen peroxide is a better electron acceptor than molecular oxygen; hence it may increase the photocatalyzed rate by removing surface-trapped electrons, thereby lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as OH[·] + h⁺ → ·OH (34). This is a desired reaction because the hydroxyl radical is widely thought to be required to initiate photocatalyzed degradation.

Second, hydrogen peroxide may be split photolytically to produce ·OH directly, as cited in studies of homogeneous photooxidation using UV/(H₂O₂ + O₂) (35). Because many lamp sources, including solar simulators, have 300-nm and shorter wavelengths, this contribution will depend strongly on the individual

FIGURE 3

Proposed pathways for the degradation of atrazine^a^aIn the presence of titanium dioxide.

Note: Pathways are postulated from the nature and time evolution of intermediates; compounds I-III, V, and VII were detected experimentally.

a, a', a'', a''' = path of dehalogenation.

b, b', b'', b''' = path of dealkylation.

c, c', c'', c''' = path of deamination.

Source: Reference 15.

lamp and reactor wall material.

Third, the solution phase may at times be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer; peroxide addition thereby increases the rate toward what it would have been had an adequate oxygen supply been provided.

These and other possibilities will require further examination before the influence of hydrogen peroxide "enhancement" is clearly established and understood.

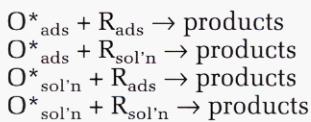
Other oxidants, such as peroxydisulfate and periodate, also have been shown to enhance the overall reaction rate (36). As with H_2O_2 , these may either trap surface electrons (rate enhancement by prevention of recombination of electrons and holes) or participate directly in an oxidative step. The resolution of the various possible heterogeneous steps, as well as the inclusion of any homogeneous phase chemistry, remains to be accomplished, as does an economic analysis of optimal oxidant addition levels.

Heterogeneous photocatalysis

Although it is widely presumed that titanium dioxide-mediated photocatalysis is initiated at the

liquid-solid surface, the location of the subsequent steps is being intensely investigated for the following reasons.

A recent kinetic analysis (37) showed that if the photoactivated oxygen (O^*) and the contaminant reactant R interact according to any of the following rate-limiting elementary steps, the global rate of reaction, usually modeled as a Langmuir-Hinshelwood form, will have the same general dependence on reactant concentration R:



Thus, the widely observed fit of rate initial data to Langmuir-Hinshelwood equations of the form

$$r = \frac{k \cdot K \cdot R}{1 + K \cdot R}$$

offers no direct insight or verification of a given mechanism of O^* attack on R. (Here k = rate constant and K = binding constant.)

Recent experimental studies have identified active oxygen at the titanium dioxide surface (38, 39) and in solution (40). The reaction therefore may proceed at either or both loca-

tions. Moreover, the various light sources used may allow the simultaneous presence of homogeneous and heterogeneous photochemistry.

Where homogeneous photo-initiated chemistry also may occur, the situation is not unlike that suggested by Peyton et al. (41) for homogeneous photooxidation involving ozone. In that case, a four-term rate equation was written to account for reactant disappearance via photolysis, direct ozone attack (dark reaction), volatilization, and photolytic ozonation. Clearly, these reactions will require considerable further study. The contribution of homogeneous photochemistry will depend strongly on the optical density of the solution as well as the catalyst. A reactor analysis of this homogeneous plus heterogeneous photochemical problem has been published (42, 43).

Immobilized photocatalysts

Most photocatalysis studies to date have used ~0.1 wt% slurries of titanium dioxide particles, of gross size 0.1–30 mm depending on the source. Because recovery of micron-size particles from a treated liquid may be an awkward process, a number of papers have examined means of catalyst immobilization on beads (44), on inside tubes of either glass (45) or Teflon (46), on fiberglass (47), or on woven mesh (48). As with all other areas of heterogeneous catalysis (49), the convenience of catalyst immobilization on progressively larger particles is bought at the expense of increased average convective-diffusion distance from fluid to catalyst surface. This circumstance invites reactant mass transfer influence because, at pseudo-steady state, the mass transfer rate to the surface, r_m , must equal the surface catalyzed rate, r_c . Thus,

$$\begin{aligned} r_m &= k_m (C_b - C_s) \\ r_c &= k_c f(C_s) \end{aligned}$$

where C_b and C_s are the bulk solution and surface concentrations of reactant, $f(C_s)$ represents the concentration dependence of the surface photocatalyzed rate, and k_m and k_c are the mass transfer coefficient and the reaction rate constant, respectively.

In 0.1 wt% slurries, the average interparticle distance is so small that the measured rate of TCE conversion is much less than the potential mass transfer limit (50). In contrast, with the catalyst immobilized on walls of tubes several millime-

ters diameter, mass transfer influence may exist and has been demonstrated with data for salicylic acid conversion in a coiled tube (51). Here, a clear variation of reaction rate with flow rate exists, and a reactor analysis (50) indicates that the data is strongly influenced by mass transfer. A similar influence of fluid flow rate on the first-order rate constant has been noted in the degradation of chlorophenol on photocatalyst-coated glass tubes (52).

Intensity: Optimal power question

Almost all of the few studies of photocatalyzed rate versus illumination intensity in systems that are not transport limited indicate that at illumination levels appreciably above 1 sun equivalent, the reaction rate increases with the square root of intensity. At sufficiently weaker levels of illumination (catalyst dependent), on the other hand, the rate is first-order in intensity (53–58). Because absorption of photons is first-order in intensity, it follows that at low intensity, the quantum efficiency (the number of molecules transformed per absorbed photon) is a constant, and at higher levels it decreases as $I^{-0.5}$, indicating an efficiency penalty for sufficiently intense lamps or concentrated solar sources. To be sure, increased intensity always results in an increase in volumetric reaction rate, until the mass transfer limit is encountered.

Thus, the quantum efficiency Φ varies with intensity as follows:

Low I :

rate varies as I

Φ = constant

Intermediate I :

rate varies as $I^{0.5}$

Φ varies as $I^{-0.5}$

High I (mass transfer limit):

rate varies as $I^{0.0}$ (const)

Φ varies as $I^{-1.0}$

When reactor cost is the most expensive part of the process, increased intensity increases the rate per volume (below the mass transfer limit) and is worthwhile, whereas if photon collection or generation is a major cost, a lower intensity will provide cheaper treatment. Because the $I^{1.0}$ to $I^{0.5}$ rate transition depends on catalyst material (46), and because the $I^{0.5}$ to $I^{0.0}$ rate transition depends on immobilized catalyst configuration and on flow-influenced mass transfer (58), the transition points between these regimes will vary with each application. Extension of the first-order regime to higher intensities may be

possible by addition of better electron acceptors, such as H_2O_2 , Cu^{2+} , and Ag^+ , but much work in this area is needed to maximize the efficiency of the overall process.

A similar application-specific circumstance exists in photolytic ozonation (59), in which laboratory and field sample reaction rates varied with intensity as follows:

rate $\alpha I^{1.0}$ (distilled water)

and

rate $\alpha I^{0.4}$ (lake water)

These dependencies occurred in the dominant photolytic ozonation terms in the rate kinetics. Thus, the latter fractional order dependence of rate on intensity may be found commonly in environmental applications of homogeneous or heterogeneous photolytic oxidations in general. Such a circumstance is not surprising, because increased intensity should increase recombination processes (second-order) faster than oxidation processes (first-order in excited oxidant), regardless of the photochemistry involved.

Illumination: Artificial vs. solar

The spectral distribution of solar illumination versus that of some solar simulators that have been used in photocatalysis studies differs appreciably in the critical range of 280–300 nm, in which solar radiation itself is negligible (57). Because these wavelengths may initiate homogeneous photochemistry, care must be taken in assigning equivalency to solar illumination (58). Nonetheless, such studies using suitable filters have been fruitful in suggesting solar action, because compounds photocatalytically degraded by true solar illumination include trichloroethylene and trichloromethane (60), surfactants (61), salicylic acid (62), and dioxins and biphenyls (19).

Experiments with a Solarbox simulator (Xe lamp) and a 340-nm cut-off filter provide a unit air mass (AM1) spectral distribution to the photocatalyst. The broad range of contaminant structures that has been mineralized via this simulated solar illumination includes chlorophenols, chlorobenzene, and multi-ring structures (DDT, dioxins) (63, 64).

Metals stripping and recovery

A number of heavy metals have been demonstrated to be recoverable via photocatalyzed metal deposition on the illuminated catalyst (65). The selective, nearly sequential removal of platinum, gold, and

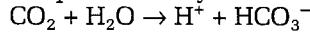
rhodium from a mixed solute solution is achievable (Figure 4); a finite dissolved oxygen level is important to prevent rhodium reduction (66).

Gold is easily recovered from aqueous chloride media (67), and its recovery from gold–cyanide solutions has been demonstrated via sequential photooxidation processes such as UV/ H_2O_2 oxidation of CN^- to OCN^- , followed by removal of excess H_2O_2 and photocatalyzed gold deposition in the presence of TiO_2 and added methanol (68).

Mercury ($Hg[II]$) chloride and methylmercury(II) chloride solutions can be treated photocatalytically to deposit elemental mercury. Conditions differ substantially, however; mercury is removed at the natural pH of $HgCl_2$ air-equilibrated solutions, whereas methylmercury solutions yield mercury metal deposition only when oxygen is removed and a substantial amount of methanol (20% v/v) is added (69). Also, platinized anatase TiO_2 can remove lead (Pb^{2+}) photocatalytically to give Pb^0 on platinum and PbO_2 on the metal oxide (70).

Analysis of organic carbon

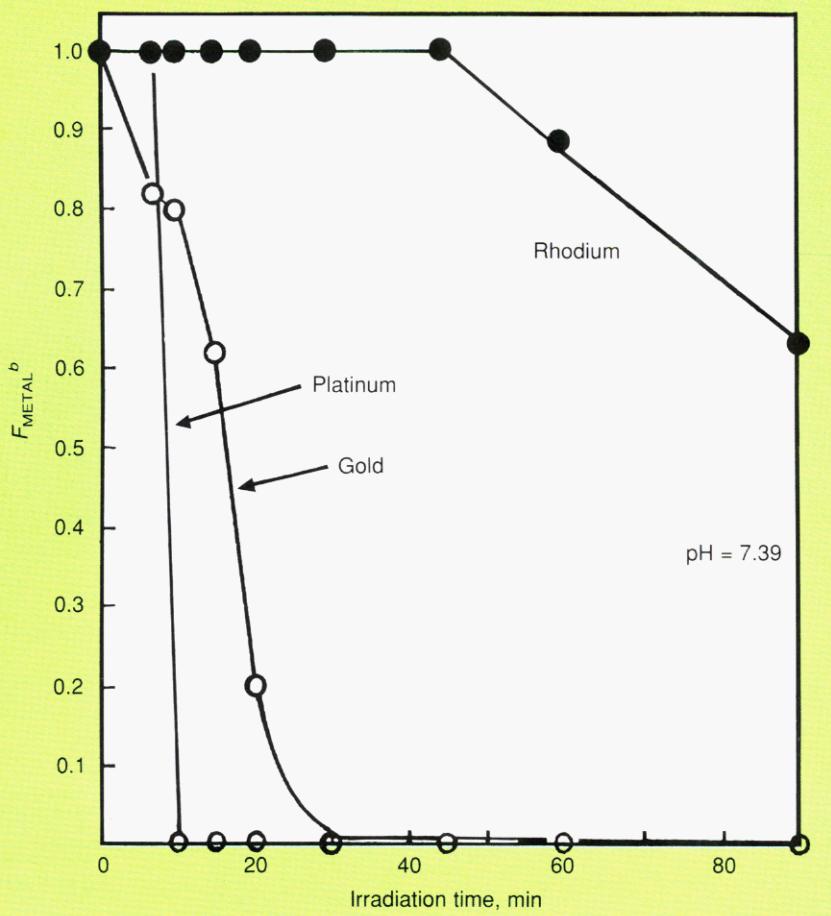
The mineralization of organic contaminants produces dissolved CO_2 which, at near neutral pH, yields bicarbonate ion (HCO_3^-) almost quantitatively:



Matthews has demonstrated that carrying out photocatalyzed sample mineralization, followed by equilibrating the dissolved CO_2 between the product sample and a separate conductivity loop, allows the loop to be used as a total organic carbon (TOC) analyzer (71, 72). This method is claimed to be suitable for the direct analysis of 0.1–30 ppm organic carbon and sample volumes of 1–40 mL. Higher level TOC samples can be diluted before analysis. Complete photocatalyzed mineralization (> 99% oxidation to CO_2) usually is accomplished in 5–10 min.

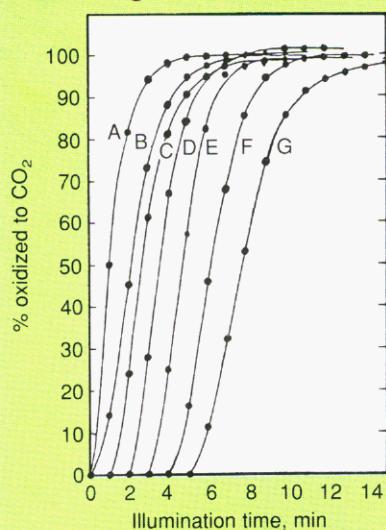
This approach represents a possible basis for an analytical device. Example data for CO_2 generation versus time in a device prototype are shown in Figure 5, which indicates total oxidation times of 5 min for formic acid, 8 min (acetic acid), and 15 min (estimated) for nitrobenzene. Also important from a sample analysis viewpoint is that the mineralization time for benzoic acid appears to be slowed most by HCl and less by phosphoric and sulfuric acids; perchloric and nitric acid have little effect.

FIGURE 4

Selective photocatalyzed separation of gold and platinum^a^a By metal deposition from gold–platinum–rhodium solution.^b Fraction of each metal remaining in solution vs. irradiation time.

Source: Reference 66.

FIGURE 5

Time for total oxidation of various organic solutes^a^a Oxidation or mineralization to carbon dioxide. Data for solutes C–G are shifted progressively to right for ease of comparison.

A = formic acid, 119 µg.

B = sucrose, 144 µg.

C = benzoic acid, 168 µg.

D = salicylic acid, 168 µg.

E = umbelliferone, 126 µg.

F = acetic acid, 120 µg.

G = nitrobenzene, 144 µg.

Source: Reference 72; ©1990, *Anal. Chim. Acta*; reprinted by permission.

A total organic carbon analyzer based on a photocatalytic device has been patented (73), in which the active titanium dioxide is coated inside a borosilicate glass spiral within which is set a 20-W near-UV light source. A flow injection configuration also has been demonstrated that uses an internally coated Teflon tubing wrapped around a 20-W near-UV tube (74). Complete oxidation of an appropriately diluted sample is attainable, provided there is sufficient dissolved oxygen.

The next decade's challenges

The literature has by now largely succeeded in establishing the general ability of photocatalysis to mineralize a host of water contaminants and to serve as a photochemical process basis for metals recovery and total organic carbon analysis. Over the next decade researchers who wish to use and commercialize photocatalysis will need to design reactors that increase the efficiencies of photon utilization and to

demonstrate economic feasibility beyond that cited in the initial reports (75).

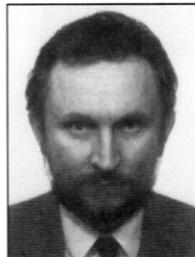
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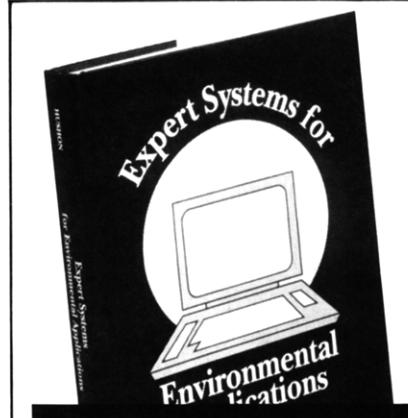


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