

REVIEWS

Treatment of Hazardous Organic and Inorganic Compounds through Aqueous-Phase Photocatalysis: A Review

Kavita Kabra,[†] Rubina Chaudhary,* and Rameshwar L. Sawhney[‡]

School of Energy and Environmental Studies, Devi Ahilya University, Takshashila Campus, Khandwa Road, Indore 452017 (M.P.), India

Photocatalysis has been a widely studied technology since the 1970s. Many investigations have been carried out with the aim of understanding the fundamental processes and enhancing photocatalytic efficiencies especially for water, air, and soil pollution control. In this comprehensive paper, studies focused on the treatment of hazardous wastewater (bearing heavy metals and organic compounds) by photocatalysis and the effects of various parameters such as pH, light intensity, dissolved oxygen, etc., are reviewed. In addition, the design features and efficiencies of various photoreactors used for this process are discussed. Some studies on the economic analysis of photocatalytic systems are also included. It can be concluded that the photocatalysis process is suitable for the treatment of drinking water and industrial wastewater. Also, harvesting the energy of the sun for photoreactions would make it a cleaner and more cost-effective treatment method.

1. Introduction

The phenomenon of photocatalysis is probably most often observed in the deterioration of exterior house paints over time as a result of oxidation. Titanium dioxide particles in the paint film use some of the incident solar energy to oxidize organic compounds in that film.¹ Many studies have been carried out on the utilization of this phenomenon for the degradation of toxic pollutants in water, air, and soil.

In 1972, the photocatalytic splitting of water on TiO₂ electrodes was discovered.² Thereafter, various researchers^{3–6} conducted research directed toward understanding the fundamental processes occurring in photocatalysis and enhancing the photocatalytic efficiency of the process.

The major advantages of this technology are as follows: (i) Photocatalysis offers a good substitute for the energy-intensive conventional treatment methods with the capacity for using renewable and pollution-free solar energy. (ii) Unlike conventional treatment measures, which transfer pollutants from one medium to another, photocatalysis leads to the formation of innocuous products. (iii) This process can be used to destroy a variety of hazardous compounds in different wastewater streams. (iv) It can be applied to aqueous-

and gaseous-phase treatments, as well as solid- (soil-) phase treatments to some extent. (v) The reaction conditions for photocatalysis are mild, the reaction time is modest, and a lesser chemical input is required. (vi) Secondary waste generation is minimal. (vii) The option for recovery can also be explored for metals, which are converted to their less-toxic/nontoxic metallic states.

The major applications investigated for this technology are color removal and the destruction of dyes;^{7–12} reduction of COD (chemical oxygen demand);^{13,14} mineralization of hazardous organics;^{15–18} destruction of hazardous inorganics such as cyanides;¹⁹ treatment of heavy metals;^{20,21} degradation of harmful fungicides, herbicides, and pesticides;^{22–24} purification and disinfection of water;^{25,26} destruction of malodorous compounds;²⁷ decontamination of soil;²⁸ purification and decontamination of indoor air;^{29,30} and destruction of cancer cells and viruses.³¹

2. Mechanism of Photocatalysis

Unlike metals, which have a continuum of electronic states, semiconductors exhibit a void energy region in which no energy levels are available to promote the recombination of an electron and hole produced by photoactivation in the solid. The void region that extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap.²

Absorption of a photon by semiconducting solids excites an electron (e⁻) from the valence band to the conduction band if the photon energy, $h\nu$, equals or exceeds the band gap of the semiconductor/photocatalyst. Simultaneously, an electron vacancy or a positive charge called a hole (h⁺) is also generated in the valence

* To whom correspondence should be addressed. Title: Senior Lecturer, School of Energy and Environmental Studies, D.A.V.V., Indore. Tel.: 91-731-2460309. Fax: 91-731-2460737. E-mail: rubina_chaudhary@yahoo.com.

[†] Junior Research Fellow, Ministry of Non-conventional Energy Sources, School of Energy and Environmental Studies, D.A.V.V., Indore.

[‡] Professor and Head, School of Energy and Environmental Studies, D.A.V.V., Indore.

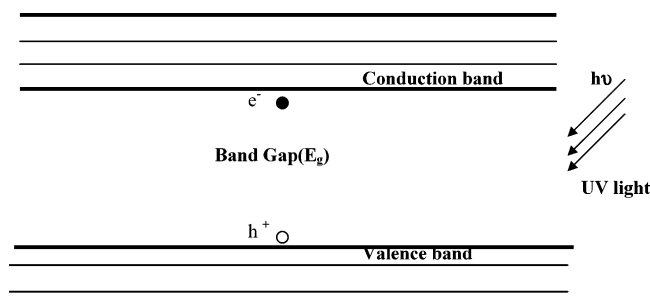
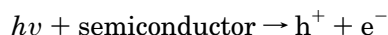


Figure 1. Band-gap diagram [formation of holes (h^+) and electrons (e^-) upon UV irradiation of semiconductor surface].

band (Figure 1). Ultraviolet (UV) or near-ultraviolet photons are typically required for this kind of reaction.

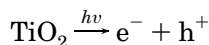


The electron–hole pair (e^- – h^+ pair) thus created migrates to the photocatalyst surface where it either recombines, producing thermal energy, or participates in redox reactions with the compounds adsorbed on the photocatalyst. The lifetime of an e^- – h^+ pair is a few nanoseconds,³² but this is still long enough for promoting redox reactions in the solution or gas phase in contact with the semiconductor.

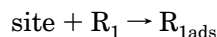
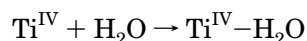
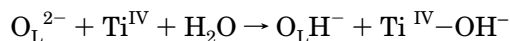
Generally, the hole oxidizes water to hydroxyl radicals (which subsequently initiate a chain of reactions leading to the oxidation of organics), or it can be combined with the electron from a donor species, depending on the mechanism of the photoreaction. Similarly, the electron can be donated to an electron acceptor such as an oxygen molecule (leading to formation of superoxide radical) or a metal ion (with a redox potential more positive than the band gap of the photocatalyst). This metal ion can be reduced to its lower valence states and deposited on the surface of the catalyst. The electron-transfer process is more efficient if the species are preadsorbed on the surface.²

Turchi et al.³³ described a photocatalytic reaction scheme for the degradation of organic water contaminants. The hydroxyl radical (OH^\bullet) was proposed to be the primary oxidant in the photocatalytic system. Four possible mechanisms were suggested, all based on attack of OH^\bullet . The sequence of steps representing the proposed mechanisms is as follows

- (i) Excitation of the catalyst by photon energy greater than the band gap, generating electrons and holes

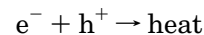


- (ii) Adsorption on the catalyst surface and lattice oxygen (O_L^{2-})

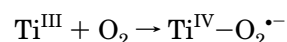
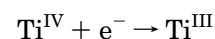
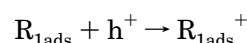
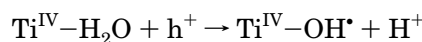
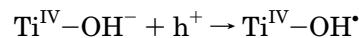


where R_1 represents an organic molecule, R_{1ads} represents an adsorbed organic molecule

- (iii) Recombination of the e^- – h^+ pair, producing thermal energy



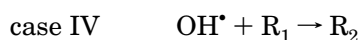
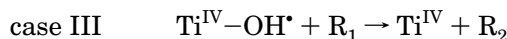
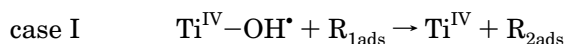
- (iv) Trapping of the hole and electron



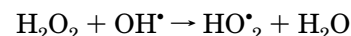
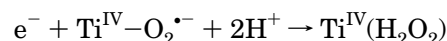
Attack of hydroxyl radical

(adsorbed or free) under different conditions

(adsorbed or free organic species)



Reactions of other radicals



Reduction of a metal ion (M^{n+}), if present,

by the electrons in the conduction band³⁴



3. Photolysis versus Photocatalysis

The role of a catalyst is to accelerate the rate of the reaction without being consumed in it. The photolytic reactions carried out in the absence of a photocatalyst exhibit very low efficiencies as compared to the reactions in the presence of a catalyst. The degradation of 2-chlorophenol and 3-chlorophenol in TiO_2 aqueous suspensions at wavelengths greater than 340 nm was studied. It was faster than direct photolysis at wavelengths greater than 290 nm. The dechlorination and dearomatization occurred more rapidly with TiO_2 than in the absence of TiO_2 .³⁵ Similarly, 1,10-dichlorodecane (D_2C_{10}) was found to be effectively photodegraded in aqueous suspensions of TiO_2 using a photoreactor equipped with a 300-nm lamp. Negligible direct photolysis was seen in the absence of TiO_2 .³⁶

Photolytic and photocatalytic interactions of aqueous chlorine with humic acid have also been investigated.³⁷ The rate of reaction for the removal of TOC (total organic carbon) was significantly higher for the photocatalytic pathway than for photolytic pathway (0.140 $mg\ L^{-1}\ min^{-1}$ for the photocatalytic reaction vs 7.85 $\times 10^{-2}\ mg\ L^{-1}\ min^{-1}$ for the photolytic reaction).

Table 1. Band-Gap Energies of Semiconductors Used for Photocatalytic Processes^a

| photocatalyst | band-gap energy (eV) | photocatalyst | band-gap energy (eV) |
|----------------------------------|----------------------|--------------------------------|----------------------|
| Si | 1.1 | TiO ₂ rutile | 3.02 |
| WSe ₂ | 1.2 | Fe ₂ O ₃ | 3.1 |
| α-Fe ₂ O ₃ | 2.2 | TiO ₂ anatase | 3.23 |
| CdS | 2.4 | ZnO | 3.2 |
| V ₂ O ₅ | 2.7 | SrTiO ₃ | 3.4 |
| WO ₃ | 2.8 | SnO ₂ | 3.5 |
| SiC | 3.0 | ZnS | 3.7 |

^a Adapted from Bhatkhande et al.³⁹

4. Photocatalytic Properties of Semiconductors

The properties of potential semiconducting materials used for this process should be such that the chemical element making up the material is capable of reversibly changing its valence state to accommodate a hole (in the case of a photoanode) without decomposing the semiconductor (such as $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ in nonstoichiometric TiO₂). The element should not have just one stable valence state in the semiconductor (as Cd²⁺ in CdS or Zn²⁺ in ZnO, both of which are decomposed by the formation of holes).³⁸

Also, the semiconductor must exhibit certain characteristics such as suitable band-gap energies, stability toward photocorrosion, nontoxic nature, low cost, and physical characteristics that enable them to act as catalysts.

Many materials such as TiO₂, ZnO, ZrO₂, CdS, MoS₂, Fe₂O₃, WO₃, and their various combinations have been examined as photocatalysts for the degradation of organic and inorganic pollutants. The band gaps and physical properties of some semiconductors used in photocatalysis are reported in Table 1.³⁹

A study on the photoelectrochemical activities of nanocrystalline TiO₂ film electrodes showed that the photocurrent (or photoactivity) for anatase-type TiO₂ was higher than that of rutile-type TiO₂ at longer wavelength and increased with decreasing wavelength (around 300 nm).⁴⁰

Some photocatalyst characteristics and their relevance in the photocatalytic process are discussed in the following subsections.

4.1. Catalyst Dose. Optimal catalyst dosing is necessary for efficient working of photocatalytic systems. The quantity of catalyst depends on the type and dimensions of reactor being used and varies with the kind of pollutant being degraded.

In a study by Eliet and Bidoglio,⁴¹ the optimum value of TiO₂ was found to be 2 g/L for 4-nitrophenol. This result was suggested from the findings that (a) aggregation of TiO₂ particles occurred at high concentrations, causing a decrease in the number of surface active sites, and (b) an increase in opacity and light scattering of TiO₂ particles occurred at high concentrations, leading to the decreased passage of irradiation through the sample.

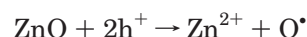
The successful photocatalytic degradation of polychlorinated dibenzo-*p*-dioxins (PCDDs) was carried out on TiO₂ films under UV (>300 nm) or solar light irradiation. The degradation rates increased with light intensity up to 2 mW/cm³ (300–400 nm) and TiO₂ coating weights up to 200 μg of TiO₂/cm².⁴² The rate of chlorophenol oxidation increased with increasing concentration of TiO₂ and reached a maximum level at a catalyst

concentration of 3 g/L. Thereafter, oxidation decreased to a constant value upon further increase in TiO₂.¹⁵

A 0.1 wt % concentration of TiO₂ was suggested by Prairie et al.⁴³ in pilot-scale studies carried out for the treatment of organics and heavy metals.

4.2. Stability/Reuse Properties. A photocatalyst should be resistive to photocorrosion, stable under different reaction conditions, and able to promote reactions efficiently upon repetitive use. TiO₂ is one catalyst that has been found to meet the above criteria, and so it has been widely used in photoreactions.

Yu et al.⁴⁴ evaluated the activity of TiO₂ in phenol degradation over TiO₂. Experiments were performed using the same TiO₂ catalyst in the reactor for over 120 h. At the end of the tests, the catalyst was recovered. There was no loss in the activity of the TiO₂ catalyst for 120-h run. In another study,⁴⁵ stability was monitored in terms of the dissolution of Zn²⁺ and Ti⁴⁺ ions from ZnO and TiO₂ catalysts, respectively. No traces of Ti⁴⁺ were found even after complete disappearance of phenol, indicating very good stability. A significant quantity of Zn²⁺ was detected for a ZnO suspension that was roughly equal to the quantity of removed phenol. The ZnO electrode was found to undergo anodic photocorrosion as follows

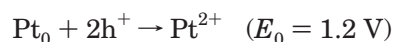


WO₃ was investigated as a photoanode for a photoelectrochemical cell and was found to be stable against photocorrosion. Although it was found to absorb a large portion of solar spectrum, its efficiency was very low.⁴⁶

The reuse of catalyst is a critical criterion for commercialization of this technology, as this is a major factor contributing to the operating costs of the system.

4.3. Modified Catalysts. Catalysts are used in various modified forms for the performance improvement. Some earlier studies in photocatalysis were performed on the loading of the photocatalyst TiO₂ with platinum metal. Addition of Pt dramatically improved the performance of the catalysts. Enhanced photocatalyst performance can be achieved by doping^{47–49} the catalyst with a suitable material (such as a metal ion) or using mixed catalysts.⁵⁰ Suspended or fixed-bed catalyst configurations also impart different performances in the process.

When TiO₂ catalyst particles were irradiated, the modified platinum (Pt) or palladium outside the TiO₂ particles functioned as a “transient” anode. The following oxidation reaction was proposed to explain this phenomenon⁴⁷



The trapping of holes or electrons by the metal ion prevents the recombination of e[−]–h⁺ pairs and helps maintain electroneutrality during the degradation of organic compounds.

A study was performed by Venezia et al.⁵¹ on chromium-doped polycrystalline titania used for dinitrogen photoreduction to NH₃ and for phenol photodegradation in the gas–solid and liquid–solid regimes, respectively. The role of Cr(III) ions used as a dopant for TiO₂ was mainly to improve charge separation of the photo-produced e[−]–h⁺ pairs by means of a permanent electric field.

It has been demonstrated⁴⁸ that the catalytic activity of TiO₂ can be increased by loading silver (Ag) in a

proportion of 1% (w/w) on the oxide surface. Using a silver-loaded photocatalyst, the photodegradation of chloroform was 44% as compared to 35% using pure catalyst. In contrast, for urea, 83% destruction by silver-loaded catalyst was achieved in 12 min of irradiation as compared to 16% without doping. However, after 6 h of irradiation, a silver ion concentration of 0.5 mg/L was detected in the TiO₂ suspensions. Upon reuse, a decrease in the photocatalytic activity was observed in both cases, but the decrease was lower in silver-loaded TiO₂.

A catalyst containing 12 wt % zirconia and 16 wt % silica in titania was observed to produce a better photocatalytic effect (about 3 times improved) than titania alone for the oxidation of ethylene. It was suggested⁵⁰ that these substances increased the activity by increasing the surface area. Increased thermal stability with respect to both densification and phase transformation also played a significant role.

The photodegradation of oil in water was carried out using slightly crystallized titanates prepared by the calcination of a mixture of KOH [Ba(OH)₂ or Ca(OH)₂] and TiO₂ slurry. The most active of all was a slightly crystallized precursor, and KOH calcined at 550 °C and modified calcined TiO₂ showed higher activities than pure TiO₂.⁵²

The feasibility of mixed semiconductors for the photodegradation of chlorinated organics in aqueous solutions has also been investigated. A higher degradation efficiency of 2-chlorophenol was observed at higher pH values. A combination of CdS and TiO₂ gave an enhanced rate of disappearance of 2-chlorophenol compared to that observed for the single photocatalyst. An increase in rate constant of between 1.2- and 2.5-fold in coupled semiconductors was observed relative to the single semiconductors.⁵³

A photoactive dye adsorbed (i.e., covalently attached) to a semiconductor electrode surface can sensitize the electrode to a higher-wavelength light. An effective photocatalyzed oxidation of hydroquinones by oxygen was carried out in the presence of phthalocyanine-coated TiO₂ powder in anatase form.⁵⁴

4.4. Suspended versus Supported Catalyst. One of the major design issues of photoreactor systems is the use of a suspended or supported catalyst configuration. The majority of experiments have used TiO₂ particles suspended in contaminated water, which makes it necessary to recover them after treatment. Supported catalyst configurations, on the other hand, eliminate the need for catalyst filtration but generally result in a significant reduction in system efficiency.

A 60–70% reduction in performance was reported⁵⁵ in aqueous systems for immobilized TiO₂ as compared to the unsupported catalyst.

In fixed-bed systems, the catalyst is anchored to an inert support. Many supports have been tested, including fiberglass beads; metal fibers; steel mesh; steel plates; aluminum; and many types of plastics and ceramics such as alumina, silicon carbide, silica, etc. Immobilized TiO₂ coated on sand in a flat-bed configuration was used for the photocatalytic oxidation of methylene blue, rhodamine B, methyl orange, and salicylic acid. The TiO₂-coated sand was repeatedly used for many experiments, and only in the case of methyl orange (sulfur compound) at highest concentration was a decrease in the activity of the catalyst (of 28%) seen.⁵⁶ TiO₂ catalysts supported on stainless steel plates were

tested for the photocatalytic degradation of formic acid in aqueous solutions. The metal-supported TiO₂ catalysts showed reaction activities comparable to those of the commonly glass-supported catalysts. During the photodegradation reaction, the oxidized surface of the metallic support was reduced and bleached. Partial participation of support in the process was likely indicated.⁴⁹

A field test of a solar photocatalytic process for the detoxification of water was conducted, in which BTEX (benzene, toluene, ethyl benzene, and xylene) compounds were found in fuel-contaminated groundwater. Pt–TiO₂ supported on silica gel was packed into a tubular photoreactor and used for single-pass operations.⁵⁷ Anatase immobilized on the surface of buoyant hollow glass microspheres was less effective than an anatase slurry in the photooxidation of aqueous solutions containing aromatic amino compounds.⁵⁸ However, unlike the other studies that showed slurries to be more effective, greater degradation was observed using TiO₂ on three silica-based supports than in the slurry (about 4 times more for silica support) for trichloroethylene destruction using solar energy.⁴²

5. Applications of Photocatalysis

Photocatalysis is mainly applicable to the oxidation of organic compounds and reduction of inorganic species. The oxidation–reduction behavior of species in contact with TiO₂ determines whether the material will be photooxidized or photoreduced. Mollers et al.⁵⁹ suggested that oxidation is the initial step that determines reduction. The redox reactions of this process have versatile applications especially for water treatment. TiO₂ photocatalysis has been reported⁶⁰ to kill microorganisms and was not found to produce trihalogenated methanes when used to treat drinking water. It was evaluated as an alternative disinfection method for use with small systems (less than 3300 people) because of concern over presence of trihalomethanes and other chlorinated byproducts in chlorinated drinking water.

Herrera-Melian et al.⁶¹ conducted an interesting study on the successful photodegradation of hazardous laboratory wastes of academic institutions combined with pretreatment using potassium permanganate. The authors reported that academic institutions generate small amounts of waste containing many hazardous chemicals. Furthermore, the composition of the waste changes with every new research project and experiment. Conventional treatment methods for such a versatile waste would also not be feasible from an economic point of view. Both photo-Fenton and photocatalytic treatment studies were carried out.

In another study,⁶² the combination of adsorption and heterogeneous photocatalysis was investigated for the removal of 2-chlorophenol. Organophilized clay mineral (hexadecyl pyridinium chloride modified montmorillonite, HDPM) was used as an adsorbent and Degussa P25 TiO₂ as a photocatalyst. It was reported that this combination could be an efficient and economical means of accumulating, removing, and oxidizing organic water contaminant.

Pretreatment (with activated sludge) followed by photocatalytic oxidation was found to be nonselective in removal of specific organics found in pulp bleaching effluents. The application of photocatalytic oxidation biotreatment was recommended as an alternative to

other physicochemical processes for the removal of biorefractory compounds. Chloride and COD, which were both present in high concentrations in the wastewater, had an inhibitory effect on the process.⁶³ It was demonstrated that toxic pollutants in industrial wastewater can be eliminated efficiently by photochemical methods using a combination of UV and heterogeneous photocatalysis and a combination of UV/H₂O₂ and ferric compounds. The combination of UV and photocatalysis decreased the COD of wastewater by around 60–70% in 1–4 h of treatment. In another study,¹⁴ COD of 2500 ppm in a shale dry distillation wastewater was found to be reduced by 62% after 1 h of illumination. Complete elimination of phenols was achieved by using calcium oxide to prevent a strong pH decrease. This was suggested as a low-cost alternative for wastewater treatment.

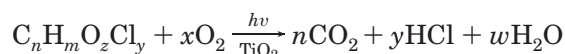
It has been observed that the photooxidative degradation of TiO₂-blended poly(vinyl chloride) thin films generates no dioxins. The illumination of such blends in aqueous environments was carried out by long-wavelength UV radiation and by solar exposure. This was observed to be a low-temperature process.⁶⁴

In the next subsections, we attempt, on the basis of the available literature, to highlight the necessary conditions and applications of photocatalysis to the degradation of organic compounds and heavy metals.

5.1. Photodegradation of Organic Compounds.

The degradation of organic compounds in the aqueous and gaseous phases has been an extensively studied subject since the infancy of this process. Work has been done on the removal of chlorinated hydrocarbons, nitro compounds, and aromatic hydrocarbons such as trichloroethylene, chloroform, and chlorophenols from water and wastewater.

The equation given below can be considered the basic reaction for the degradation of a chlorinated organic compound (C_nH_mO_zCl_y).⁶⁵ It can be seen that the products of the reaction are innocuous species.



Some of the factors that affect the rate of degradation in the photoreactors are discussed in the next four subsections.

5.1.1 Effect of Light Intensity and Wavelength.

The influence of the intensity and wavelength of the UV light was studied for the oxidation of halide ions by oxygen in TiO₂ suspensions. It was concluded⁶⁶ that only photons with wavelengths shorter than the absorption edge of TiO₂ (approximately 400 nm) resulted in reaction. A direct proportionality was found between the incident light flux and the conversion level. An initial quantum yield of approximately 2% was found for all pH values. Another study conducted for the removal of COD supported the occurrence of reaction at the same wavelength and indicated a linear decrease in reaction with irradiation time.⁴⁵

In a study on TiO₂ supported on a silica-based material for trichloroethylene destruction using solar energy, the supported photocatalysis displayed high light efficiency over a wide range of weather conditions. An apparent quantum yield of 40% was obtained in an experiment conducted in the late afternoon on a rainy day.⁴² Glatzmaier et al.^{67,68} studied the destruction of dioxin and polychlorinated biphenyls (PCBs) at high temperature. They concluded that concentrated solar

energy effectively destroyed many hazardous chemicals, including dioxins, PCBs, furans, chlorinated benzenes, and chlorinated methanes. The destruction of these compounds was significantly enhanced by the high-energy photons present in solar destruction processes unlike conventional incineration processes. Magrini et al.⁶⁹ reported that increases in radiation intensity also increased the decomposition rate for the organic contaminants.

5.1.2. Effect of Dissolved Oxygen. Molecular oxygen plays an important role in the photooxidation process.^{70–72} It is found to either hinder or support the reaction depending on the degradation pathway/mechanism of the destruction of pollutant.

The primary role for oxygen in the photodegradation process is to act as an electron sink for photogenerated carriers.⁷³

The effect of dissolved oxygen was studied by Hajime et al.⁷⁴ for the photolytic degradation of chlorinated hydrocarbons in groundwater. The degradation rates were elevated in the absence of dissolved oxygen. They suggested that dissolved oxygen acted as an “inner filter” or “scavenger”. That is, dissolved oxygen reduced the UV light intensity in the photoreactor because molecular oxygen has absorption bands at 185 and 254 nm, the former being stronger, so it absorbs light in this wavelength region. Photocatalytic mineralization of 2-chlorobiphenyl (2-CB) in aqueous TiO₂ suspensions was conducted under four different oxygen partial pressures in closed reactors. Pressure reductions from 21 to 2 kPa resulted in 35% less CO₂ formation after 5 h of irradiation. It was proposed⁷⁵ that molecular oxygen acted as an important reactant following the attack of a second hydroxyl radical during ring opening in the degradation of dioxyl byproducts. A higher oxygen pressure resulted in a higher initial rate of 2-CB transformation. The effect was more significant for 2-CB mineralization than for 2-CB transformation. At a pressure of 0.5 kPa, 75% of the 2-CB was transformed but only 1% was mineralized to CO₂ after 5 h of illumination. Involvement of molecular oxygen in the cleavage of aromatic ring was suggested.

5.1.3. Effect of pH. The rate of reaction for many compounds differs under acidic and alkaline conditions. The change in pH also affects the band edge of the photocatalyst. Different pH conditions result in the formation of different reaction products. Photooxidation of aqueous solutions and polluted groundwater containing aromatic amino compounds was undertaken. For experiments with synthetic solutions, TiO₂ catalyst and aniline, *p*-toluidene, and 2,4-xylene were taken. The catalyst was found to be more effective in acidic and slightly alkaline media. A similar study was also carried out for the purification of groundwater from an abandoned military base.⁵⁸ A pH of 3.5 was suggested as optimal for the degradation of phenol (with reduced anatase),⁴⁵ in contrast to another study on alkaline pH conditions, which concluded that alkaline conditions are necessary for the elimination of phenols and COD.¹⁴

The photocatalytic oxidation rates of nitrotoluenes (2-nitrotoluene and 3-nitrotoluene) and dinitrotoluenes (2,4-dinitrotoluene and 2,6-dinitrotoluene) in aqueous suspensions of Degussa P25 TiO₂ were found to be pH-independent. It was believed that these compounds did not exhibit any pH-dependent speciation. The reaction rate of mononitrotoluene was found to be 60–80% greater than that of dinitrotoluene.⁷⁶ It has been

demonstrated that CCl_4 can be degraded under both oxic and anoxic conditions. CHCl_3 , C_2Cl_4 , and C_2Cl_6 were detected as intermediates during photocatalysis at pH 2.8, whereas no intermediates were formed at pH 12.4.⁷⁷ In another study, the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) in illuminated aqueous suspensions of TiO_2 was demonstrated at pH 1–12. It was suggested that, at pH \sim 3, the initial step was chiefly direct hole oxidation, whereas below and (especially) above pH 3, the mechanism shifted progressively to a hydroxyl-radical-like reaction, following rate-limiting hole oxidation of surface hydroxyls. Different products were formed in the two pathways.⁷⁸ A study on the treatment of EDTA (ethylenediamine tetraacetic acid) and its metal complexes using photocatalysis performed by Madden et al.⁷⁹ showed that the degradation of EDTA was enhanced at lower pH (pH 4). The Pb–EDTA treatment showed Pb(II) deposition on the catalyst at pH 6 under aerobic conditions. Cu–EDTA showed effective complex transformation under anaerobic conditions at pH 6, whereas Ni–EDTA and Cd–EDTA exhibited slow complex transformations with no metal removal by deposition under aerobic conditions at pH 4.

5.1.4. Effect of Ions. The presence of ions either enhances or degrades the rate of reaction depending on the mechanism of reaction. Experimental results showed that dissolved manganese (Mn^{2+}) ions increase the rate of oxidation of chlorophenols. It was proposed that Mn^{2+} ions enhanced the oxidation rate by surface reaction increasing the number of photogenerated electrons and holes and inhibiting electron–hole recombination.⁸⁰ Similarly, a small quantity of Cu^{2+} ions (less than 0.1 mM) showed a catalytic effect in the degradation of phenol by trapping photogenerated electrons and thereby reducing e^- – h^+ recombination. However, large quantities of ions reduced the degradation.⁴⁵ A recirculation system of aqueous trichloroethylene solution through a packed-bed reactor with TiO_2 pellets has also been investigated for this process. The degradation rates were found to decrease in the presence of H_2O_2 but to markedly increase upon addition of $\text{S}_2\text{O}_8^{2-}$. A $\text{S}_2\text{O}_8^{2-}$ ion concentration of more than 0.01 mol/dm³ was assumed to completely suppress e^- – h^+ recombination and mineralized 50 ppm of trichloroethylene in 2 h of irradiation. $\text{S}_2\text{O}_8^{2-}$ caused photodegradation without TiO_2 ; however, trichloroethylene was converted into an intermediate that was slowly oxidized through Cl^{\bullet} . Trichloroethylene was found to always be mineralized by TiO_2 .⁸¹ In dilute (10–200 ppm) aqueous solutions, the chloromethanes CCl_4 , CHCl_3 , and CH_2Cl_2 were completely mineralized to CO_2 and HCl by TiO_2 . Chlorine ion inhibited the rate of degradation.⁸² The addition of oxyanion oxidants such as ClO_2^- , ClO_3^- , IO_4^- , $\text{S}_2\text{O}_8^{2-}$, and BrO_3^- increased the rate of photodegradation of 4-chlorophenol in the order $\text{ClO}_2^- > \text{IO}_4^- > \text{BrO}_3^- > \text{ClO}_3^-$. BrO_3^- appeared to increase the photoreactivity by scavenging conduction-band electrons and reducing charge-carrier recombination.⁸³ The effect of common inorganic anions on the rate of photocatalytic oxidation of salicylic acid, aniline, and ethanol over glass supported near UV-illuminated TiO_2 was investigated by Abdullah et al.⁸⁴ At a pH of nearly 4.0, the rate of oxidation decreased with increasing concentration of chlorides. Perchlorates and nitrates had very little effect. Sulfates or phosphates even at millimolar concentrations were found to be rapidly adsorbed by the

catalyst and to reduce the rate of oxidation by 20–70%. It was assumed that inorganic anions might compete with organic solute molecules for oxidation sites on the surface to form oxidizing inorganic radical ions.

5.2. Photodegradation of Heavy Metals. Metals found in industrial wastewater are toxic in some of their valence states. It is necessary to convert such metals to their nontoxic forms or remove the metals from the waste streams for the safe disposal. The application of photocatalysis for changing the hazardous ionic states of metals is remarkable. Prairie et al.⁸⁵ carried out a detailed study giving the conditions under which photocatalysis would be applicable to the treatment of metal- and organic-contaminated water. They concluded that Ag(I), Cr(VI), Hg(II), and Pt(II) were easily treated by photocatalytic reduction using 0.1 wt % TiO_2 whereas Cd(II), Cu(II), and Ni(II) could not be removed. The ability to remove metals was found to depend on the standard reduction potential of the metals for the reduction reaction. Potentials more positive than 0.4 V were required. Oxidants (i.e., metals or oxygen) were required for the destruction of organics, whereas reductants (organics, water) were required for the reduction of metals. It was suggested that the rates of oxidation (of organics) and reduction (of metals) were intrinsically interrelated. In addition, photocatalytic decontamination could be efficiently realized by applying the technology to water contaminated with the right mixtures of organic compounds and reducible toxic metals. In another study,⁴³ using solar-energy-based reactors, one-sun systems were found to be more efficient than those using concentrated solar radiation, and photocatalysis was suggested as a suitable alternative for handling hard-to-treat organometallic complexes.

Photodeposition of metal ions was reported by Tanaka et al.⁸⁶ on Pt-loaded TiO_2 . The Pb^{2+} concentration in the suspension decreased and catalyst became brown after some time. Similar experiments were carried out with Mn^{2+} , Tl^+ , and Co^{2+} . It was noted that the metal ions were effectively eliminated from solution, especially at low concentration, and that the deposition rate decreased in the order $\text{Pb}^{2+} > \text{Mn}^{2+} > \text{Tl}^+ > \text{Co}^{2+}$. Replacement of Pt-loaded TiO_2 with unloaded TiO_2 decreased the efficiency. The deposition of metal ions did not occur in the absence of TiO_2 . For Hg^{2+} , in the absence of TiO_2 , the metal ion concentration was reduced by 11.51% as compared to a 90% decrease in the presence of TiO_2 . It was also suggested that Hg^{2+} is reduced by electrons from the conduction band and water is oxidized by the holes. The presence of oxygen caused an increase in the reaction rate, and the presence of nitrogen caused the reverse. PbO_2 and Tl_2O_3 were identified as the compounds deposited on the catalyst. They were found to be oxidized by the positive holes of TiO_2 as follows



The recovery of the metal ions from deposited oxides was also studied to ensure the reuse of the catalyst. Evolution of oxygen was observed in the recovery reaction.

A brief description of some studies conducted on heavy metal removal through photocatalysis is provided in Table 2. In the subsections below, some of the studies

Table 2. Studies Conducted on the Removal of Metal Ions

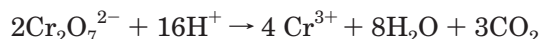
| process description | photocatalyst used | light source | parameters studied | comments | ref |
|--|---|--|--|--|-------------------------------|
| reduction of dichromate to Cr(III) | TiO ₂ rutile, anatase, reduced rutile; WO ₃ , Fe ₂ O ₃ , SrTiO ₃ | 1-kW xenon lamp, sunlight | catalyst and dichromate concentrations | WO ₃ found to be most active catalyst | Yoneyama et al. ⁴⁶ |
| photodeposition of Pb ²⁺ , Mn ²⁺ , Tl ⁺ , Co ²⁺ , Hg ²⁺ | TiO ₂ rutile, platinum-loaded TiO ₂ | 500-W super-high-pressure mercury lamp | presence and absence of oxygen, using platinum-loaded and -unloaded TiO ₂ | deposition rate increased in the order Pb ²⁺ > Mn ²⁺ > Tl ⁺ > Co ²⁺ , rate increased with oxygen bubbling, efficiency better with Pt–TiO ₂ | Tanaka et al. ⁸⁶ |
| Cr(VI) reduction | ZnO, chromium-doped ZnO, reduced ZnO | medium-pressure mercury vapor lamp (125 W), sunlight | irradiation time, initial Cr(VI) concentration, pH, temperature | reduction increased with increasing temperature and irradiation time, slightly decreased in the absence of oxygen, and decreased with increasing pH and decreasing initial concentration; Cr-doped and reduced ZnO performed better than undoped ZnO | Domenech et al. ⁹¹ |
| Cr(VI) reduction | TiO ₂ (Degussa P25) | 125-W high-pressure mercury vapor lamp | irradiation times, catalyst mass, initial Cr(VI) concentration, pH | presence of Fe(III) and Cr(III) increased reaction rate; reduction increased with increasing mass of catalyst and irradiation time and decreased slightly with decreasing initial concentration of Cr(VI) | Munoz et al. ⁸⁷ |
| Cr(VI) reduction | TiO ₂ (Degussa P25) | 400-W medium-pressure mercury UV lamp | pH, dissolved oxygen | thermodynamic aspects studied at pH 0 and 10; reduction faster in the absence of oxygen | Wen-Yuan et al. ⁸⁹ |
| Cr(VI) reduction | TiO ₂ (Degussa P25) | 365-nm black-blue fluorescent UV lamp | pH, TiO ₂ dose, light intensity, dissolved oxygen | reduction rates significantly higher for acidic than for alkaline solutions; oxygen had minimal effect in acidic conditions; ethanol enhanced rate of reduction | Ku and Jung ⁸⁸ |
| Cr(VI) reduction | ZnO | xenon lamp (1500 W/m ²) | presence of humic acid and dissolved oxygen | reduction enhanced in the presence of humic acid (which sensitized reduction); higher reduction under anoxic conditions | Selli et al. ²⁰ |
| Cr(VI) reduction | TiO ₂ (Degussa P25, Hombikat UV100) | 400-W medium-pressure mercury lamp | presence of salicylic acid | photocatalytic deactivation higher for Degussa P25 than for Hombikat UV100 | Colón et al. ¹¹⁶ |
| Cr(VI) reduction | TiO ₂ | 150-W medium-pressure mercury lamp | simultaneous oxidation of Luranzol S Kong dye; pH, pollutant concentration | reactions for both dye and Cr(VI) faster than at acidic than neutral pH | Schrank et al. ¹¹⁷ |
| Cr(VI) reduction | TiO ₂ (Degussa P25) | mercury lamp (Philips HPK, 125 W) | catalyst concentration, pH | acidic pH favorable for reduction; fouling of catalyst at pH > 4 | Gimknez et al. ¹¹⁸ |
| Cr(VI) reduction | TiO ₂ | medium-pressure 250- and 125-W mercury lamp, sunlight | presence of 4-chlorophenol | adsorption of Cr(VI) decreased with increasing pH; reduction rate higher in the presence of 4-chlorophenol | Fu et al. ¹¹⁹ |
| Hg(II) reduction | TiO ₂ (Degussa P25, Hombikat UV100) | 450-W Xe arc lamp | pH, catalyst mass, incident light intensity, amount of hole scavengers, chloride concentration | Degussa P25 found to be photocatalytically more active than Hombikat UV100 at low catalyst loadings and low light intensities | Wang et al. ¹²⁰ |
| Hg(II) reduction | TiO ₂ (Degussa P25) | 100-W mercury spotlight | solution basicity and temperature (pH 9 and 0 °C; pH 11 and 40 °C) | mercury more chemisorbed at pH 11 and 40 °C so more difficult to recover than at pH 9 and 0 °C | Lau et al. ⁹⁹ |
| removal of HgCl ₂ and CH ₃ HgCl | TiO ₂ (Degussa P25) | 1500-W xenon lamp | irradiation time and pH | HgCl ₂ removed easily under natural pH but CH ₃ HgCl required methanol (20% v v) for effective removal | Serpone et al. ⁹⁸ |
| removal of Hg(II) | TiO ₂ (Degussa P25) | UV lamp (18 W) | presence of citric acid | Hg(II) 99% removed | Bussi et al. ³² |
| Ag(I) removal from black-and-white photoprocessing waste | TiO ₂ (Degussa P25) | 100-W mercury spotlight, sunlight | presence of thiosulfate | effective removal with both sunlight and artificial light; thiosulfate in lower concentration enhanced reduction | Huang et al. ⁹⁷ |
| Ag(I) reduction | TiO ₂ (Degussa P25) | Philips HPK 125-W mercury lamp | initial silver concentration, temperature, radiant flux, | application suggested for treatment of very dilute solutions and separation of silver from copper in electrolytic baths | Herrmann et al. ⁹⁶ |
| Cu(II) photo-deposition, separation, and oxidation | TiO ₂ (Degussa P25) | 15-W Sylvania black light | pH, organics | reversible photoreduction deposition observed in pH range 1.84–6.60; reduction dependent on type of organic used as hole scavenger | Foster et al. ⁹⁵ |
| photoreduction of Cu(II) | TiO ₂ (Degussa P25) | fluorescent black light bulbs | different sacrificial donors | sodium formate was best donor; rate of reduction independent of initial concentration of Cu(II) and increased with TiO ₂ concentration; rate also increased gradually with temperature | Yamazaki et al. ⁹³ |
| Cu(II) reduction | ZnO | Philips HPK medium-pressure mercury vapor lamp, sunlight | irradiation time, catalyst mass, salt concentration, light intensity | reduction increased with increasing mass of catalyst up to 13 g/L; anoxic conditions increased deposition by 10% | Domenech et al. ⁹² |
| reduction of Cr(VI), Hg(II), Cd(II), Au(III), Pt(IV), Ag(I), Pd(II), Cu(II), Ni(II) | TiO ₂ | 100-W UV spotlight, Oriel 1000-W ozone-free Hg(Xe) lamp | different organics | Cr(VI), Hg(II), Au(III), Pt(IV), Ag(I), Pd(II) reduced easily but not Cd(II), Cu(II), Ni(II) | Prairie et al. ⁴³ |

on individual metals showing the optimum conditions for their reduction are emphasized.

5.2.1. Chromium. The photocatalytic reduction of dichromate to Cr(III) on n-type semiconducting powders

was reported by Yoneyama et al.⁴⁶ The utilization of solar energy for photodegradation was investigated on WO₃. The results obtained showed an effective (99%) removal for the dilute (0.5 mM) static solutions in 0.5

h. In addition, concentrated solutions of 62.5 mM were successfully treated (88%) on being agitated with a higher reaction time (9 h) but lower catalyst concentration (2 g in 10 mL of solution). The overall reaction proposed for the process was



Prairie et al.⁸⁵ concluded that Cr(VI) reduction was very sensitive to pH and most efficient below pH 3, giving Cr(III) in the solution. At pH 5, Cr(III) formed a stable precipitate on the catalyst, and the catalyst and water separated at this stage could be disposed safely as per regulatory limits. Some other investigations also support this view. Samples of wastes from metal surface treatment industries were used to test the photocatalytic procedure for Cr(VI) elimination in a real case.⁸⁷ The percentage of reduction was significantly greater at acidic pH than at neutral pH. It was also observed that the presence in these samples of certain species such as Fe(III) and Cr(III) at low concentrations increased the yield of Cr(VI) photoreduction. It was assumed that these cations acted by maintaining the pH during the process, preventing the alkalization by the hydrolysis of the solution. In another study,⁸⁸ the optimum pH for the adsorption of Cr(VI) was found to be in the range 3–6. The Cr(VI) adsorbed on the surface of TiO₂ particles was found to be reduced almost completely. The reaction rates were higher for acidic solutions than for alkaline solution.

The thermodynamic aspects of the photocatalytic reduction of Cr(VI) on TiO₂ were discussed and contrasted for pH 0 and pH 10 aqueous media by Wen-Yuan et al.⁸⁹ They concluded that the thermodynamic driving force for Cr(VI) reduction on TiO₂ in basic aqueous solutions was less than that in acidic media. They also found hole transfer to be thermodynamically more favorable than photocorrosion of TiO₂ in basic media. The interfacial energetics at acidic and alkaline pH were also compared (Figure 2).

A recent study conducted by Testa et al.⁹⁰ was carried out to obtain direct evidence of Cr(V) intermediacy in the heterogeneous photocatalytic reduction of Cr(VI) over TiO₂ in the presence and absence of EDTA by EPR spectroscopy. The formation of Cr(V) became rapidly inhibited in the absence of a hole scavenger. Addition of EDTA was found to efficiently suppress the electron-shuttle mechanism that inhibited Cr(VI) reduction. It was reported that Cr(V) and Cr(IV) were notably unstable species.

The photocatalytic reduction of Cr(VI) in an aqueous suspension of ZnO was studied.⁹¹ Equilibrium sorption studies showed that Cr(III) was completely adsorbed on ZnO whereas Cr(VI) adsorption was very low (22.5% in 5 min with agitation). Also, Cr(VI) adsorbed on ZnO was not photoreduced. Temperature studies showed that chromium was chemisorbed on ZnO. Solar irradiation of a ZnO suspension induced the photoreduction of Cr(VI), leading to a marked increase in adsorption. For dilute Cr(VI) solutions, the adsorption was almost 100% for 6 h of exposure, whereas for concentrated solutions, 70% of the Cr(VI) was deposited. Adsorption on TiO₂ in darkness was found minimal. The quantity of Cr(VI) eliminated increased with increasing irradiation time and decreased with decreasing initial Cr(VI) concentration. Chromium(III) hydroxide and Cr₂O₄²⁻ ions, respectively, were deposited on ZnO at a pH of 6.2 for low and

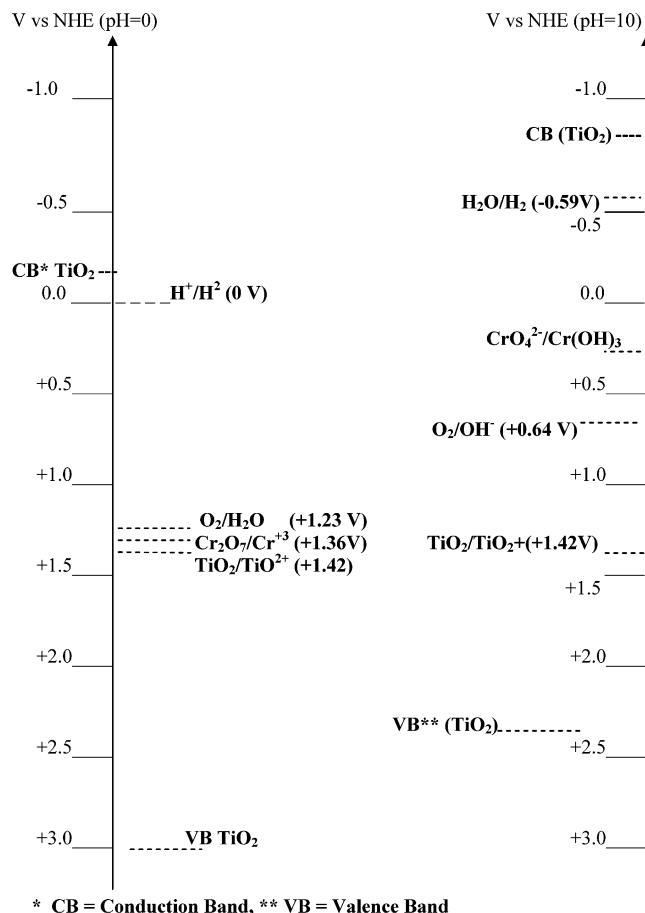


Figure 2. Surface-band energetics at TiO₂ and solution redox levels for pH 0 and 10 cases.

high initial Cr(VI) concentrations. It has been reported that oxygen competes with Cr(VI) for the photogenerated electrons in TiO₂,^{87,89} decreasing the yield of the Cr(VI) photoreduction considerably. The same effect was expected with ZnO, but instead, 5% lower reduction was obtained in the absence of oxygen for ZnO. A homogeneous reduction by H₂O₂ produced by oxygen photoreduction was assumed. The results under anoxic conditions showed a considerable increase in the quantity of Cr(III) produced and adsorbed.

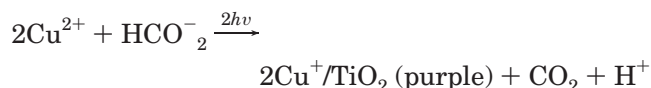
The presence of certain substances enhances the reduction rates of metals. Humic acid adsorbed on the photocatalyst surface sensitized Cr(VI) photoreduction and competitive reduction of oxygen molecules by absorbing a significant portion of solar radiation. H₂O₂, which formed as a result, was found to partially reduce Cr(VI) in the pH range of 7–9.²⁰

5.2.2. Copper. The reduction of Cu(II) ions in aqueous suspensions of ZnO under UV illumination was investigated by Javier et al.⁹² Irradiation time, salt concentration, semiconductor mass in the suspension, and light intensity were varied parameters. The amount of copper deposited was found to increase with increasing ZnO concentration, attaining a limiting value for a ZnO mass of 13 g/L. Suspensions containing more than this amount ensured a maximum light absorption by ZnO. The absence of oxygen increased the quantity of copper deposited to approximately 19%. In solar experiments, all of the copper was found to be deposited. The percentage deposited for 2 h of irradiation was 32%, 25%, and 16%, respectively, for 1, 2.5, and 5 mM initial concentrations of copper.

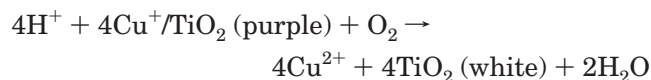
Photoreduction of Cu(II) ions was studied in the presence of sacrificial donors such as HCOONa, Na₂C₂O₄, and Na₂H₂EDTA. Formate was the best donor with respect to reduction rate, but an induction period was observed that increased with increasing concentration of Cu ions and the presence of sulfates, phosphates, and chlorides. The difference in the reduction rates in the oxalate and formate systems was explained in terms of electrostatic interactions between the Cu(II) complex and the TiO₂ surface and a negative shift in potential by oxalate coordination. It was concluded⁹³ that carboxylic acids such as formate, oxalate, EDTA, salicylic acid, and citric acid could be employed as hole-consuming sacrificial agents in photocatalysis for the decontamination heavy-metal-polluted water. The rate of reaction was found to be independent of the initial concentration of copper ions.

A similar study⁸⁵ in the presence of salicylic acid as a reductant showed that the process of photocatalysis using TiO₂ did not effectively removed Cu²⁺ ions. Another study⁹⁴ supported this view. The reduction of copper was found to be most difficult among the other metals studied. Only 17% removal was observed in the presence and absence of oxygen. The presence of methanol as a reductant, however, gave a better result than the presence of salicylic acid.

Particulate TiO₂ was used to remove and concentrate Cu(II) ions in aqueous solution through a cyclic process of photodeposition, separation, and oxidation. Illuminated nitrogen-purged solutions containing CuSO₄, excess sodium formate (pH 3.6), and TiO₂ formed a purple Cu–TiO₂ species. Cu(II) concentrations in the suspension were driven from 51 to about 0.018 µg/mL. Upon oxygen purging, the purple Cu–TiO₂ system reverted back to white, accompanied by a corresponding increase in the Cu(II) concentration in the solution. The net photoreaction as suggested by the author⁹⁵ is

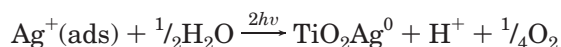
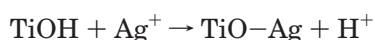


and the suggested net dark oxidation is



Eighty-six percent of the Cu(II) in the synthetic waste was concentrated to an organic-free solution having 7% of the initial value. The result was also found to be dependent on the organic used to scavenge the holes and independent of the copper salts used.

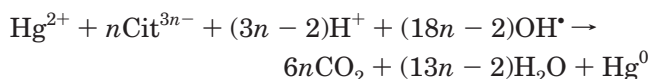
5.2.3. Silver. The effect of various parameters on the photoassisted reduction of silver ions on powder titanium dioxide was investigated.⁹⁷ The initial deposition rate was found to vary with the starting concentration of Ag⁺ ions according to a Langmuir–Hinshelwood mechanism. Also, the rate was almost independent of temperature around 300 K and was proportional to the radiant flux (300 nm < λ < 400 nm) of photons absorbable by TiO₂ at least up to a value of 7.6 × 10¹⁵ photons s⁻¹ cm⁻². The replacement of surface protons with silver ions was proposed to occur via



The silver ions were also found to be reduced by photogenerated electrons.

Treatability data on actual waste⁹⁷ show that titania-based photocatalysis can be used to remove silver from black-and-white photoprocessing waste. The silver ion was reduced to its metallic form, forming particles comparable in size to TiO₂. The mass of silver recovered approached 3 times the amount of titania. Thiosulfate played a role as a hole scavenger, thus increasing silver reduction rate, but hindered photocatalytic reactions when present at higher concentrations. An optimum TiO₂ loading of 0.1 wt % was suggested from the results.

5.2.4. Mercury. The removal of mercury from the hazardous waste of a chlor-alkali plant by a combined process of acid attack and photoreduction system was demonstrated. The acid attack of solid waste gave a liquid that was then treated by photocatalytic reduction by UV radiation in the presence of TiO₂ and an organic agent (citric acid). More than 99% of the mercury initially present in the solution was removed. The mechanism suggested for the process was



The pH changed from 7 to 4.5–5.0 because of the formation of weak organic acid intermediates during citric acid degradation. Competitive adsorption of the other metal ions present in the waste resulted in lower rates of mercury reduction. However, the presence of other metal ions such as iron increased the overall rate. Also, metals such as calcium, magnesium, and sodium remained in the solution after the process because of their higher reduction potentials.³²

The removal of mercury(II) chloride and methylmercury(II) chloride from aqueous media was investigated⁹⁸ in air-equilibrated suspensions of TiO₂ (2 g/L) irradiated by AM1 simulated sunlight. HgCl₂ was found to deposit effectively under natural-pH, air-equilibrated conditions, whereas the methylmercury(II) solution necessitated the addition of methanol (20%, v/v) as a hole scavenger. The process was more efficient in the absence of oxygen (90% removal of HgCl₂ in the absence of O₂ versus 60% in the presence of O₂). Recovery of 70% of the mercury was obtained by treatment of TiO₂ in aqua regia.

In another investigation, degradation of 100 ppm aqueous mercury chloride with a 100-W mercury spot-lamp in the presence of TiO₂ was carried out. Solution basicity and temperature were varied, and two sets of conditions were used: pH 9, 0 °C and pH 11, 40 °C. Concentrations below 20 ppb were achieved. A mercury mass balance revealed that more than 97% of the mercury was removed and deposited as mercury metal on the TiO₂ for pH 9 and 0 °C. The deposited mercury could be driven off by heating at 100 °C for 30 min under nitrogen flow.⁹⁹

6. Photocatalytic Reactors

Many photocatalytic reactor designs have been proposed for use with solar as well as artificial light utilization. In this section, we highlight the studies on various reactor designs and their treatment efficiencies.

When sun is exploited as a source of light in detoxification plants, expenses for the installation and consumption of artificial light sources can be saved. For

solar energy utilization, both concentrating and non-concentrating collectors have been used, each which has their particular advantages and disadvantages. The nonconcentrating systems have an advantage of collecting both direct and diffused light, whereas the concentrating systems have an advantage of a small reactor tube area, making the system easier to handle.⁵⁵ Malato et al.¹⁰⁰ tested two different reactor designs, namely, a medium-concentrating radiation system (parabolic trough collector reactor) and a low-concentrating radiation system (compound parabolic concentrator reactor), for the photocatalytic oxidation of 2,4-dichlorophenol (DCP) using TiO_2 suspensions at the pilot-plant scale. The advantages and disadvantages of the two types of photoreactors in DCP oxidation were compared. A strong potential of photocatalytic peroxydisulfate-assisted degradation at high DCP concentrations was demonstrated in both systems. The compound parabolic concentrator reactor was found to be better than the medium-concentrating reactor under cloudy conditions only, whereas on a clear day, the performances of the two reactors did not differ much.

A comparison has also been made among thin-film fixed-bed (TFF) reactors, parabolic trough (PTR) collectors, and plexiglass double-skin sheet (PDSS) reactors. The PDSS and TFF reactors were found to be useful in utilizing total global UV radiation and had low investment costs and simple construction, whereas the PTR used only direct UV irradiation (maximum of ~50% of global UV sunlight) and entailed high investment costs.¹⁰¹

A one-sun parabolic concentrator system was fabricated at a cost of \$160/m². It was suggested¹⁰² by preliminary findings that reducing mainly unit catalyst costs could reduce the overall treatment cost whereas further improvement in unit reactor costs would have little impact on overall treatment.

A new photocatalytic reactor¹⁰³ for water purification under solar light was proposed for the degradation of phenol. A rotating-drum reactor coated with Pt-loaded TiO_2 on the outer surface of the glass drum was used. The reactor was designed so as to receive solar light and oxygen from the atmosphere effectively. Phenol with an initial concentration of 22.0 mg/dm³ was decomposed within 60 min and completely mineralized through intermediate products within 100 min. The initial degradation rate of phenol was 1.635 mg m⁻² min⁻¹, and the mineralization rate was 0.18 mg m⁻² min⁻¹ under solar light.

Sodium benzene sulfonate as a model surfactant was decomposed in aqueous TiO_2 dispersions under highly concentrated solar light illumination (geometric concentration = 70 suns) to examine the photocatalytic characteristics of a parabolic round concentrator reactor to in degrading pollutants without visible light absorption. The authors¹⁰⁴ of this study suggested that light-concentrating systems had the important advantage that, for the same light-harvesting area, the reactor volume could be smaller than in nonconcentrating systems. The optimum TiO_2 loading was found to be 9 g/L for this reactor.

An aerated cascade photoreactor based on a nonconcentrating suspension photoreactor was demonstrated,¹⁰⁵ suggesting the advantages of a cascade (increased mass transfer) and use of oxygen from the air as an oxidizing agent in a bubble column. This configuration was found to outperform the thin-film fixed-bed reactor with a

3–13 times higher degradation efficiency for the model compound dichloroacetic acid. The treatments of biologically pretreated wastewater from a textile factory and car washing unit were successfully carried out with artificial and sunlight. It was suggested from these results that nonbiodegradable compounds in this wastewater could be decomposed photocatalytically.

Ray¹⁰⁶ proposed a new reactor design that addressed two parameters, namely, the light distribution inside the reactor and the high specific surface area of the catalyst. A reactor with several hollow tubes employed as a means of light delivery to the catalyst present on the outside surface of the tubes. A reactor designed and constructed on the basis of the modeling results, was reported to show promising results.

Dionysiou et al.¹⁰⁷ evaluated the photocatalytic degradation of phenol, chlorinated phenols, and lindane in a continuous-flow TiO_2 rotating-disk photocatalytic reactor (RDPR). The specifications of the RDPR were a hydraulic residence time of 0.25 day and a disk angular velocity of 12 rpm. It was concluded that, at low molar feed concentrations (0.038 mM/L), the removal efficiencies for phenol and chlorinated phenols were on the order of 86% or higher, whereas the removal efficiency for lindane at a feed concentration of 0.016 mM/L was on the order of 63%.

Funken et al.¹⁰⁸ worked on the solar photocatalytic detoxification of nonbiodegradable chlorinated hydrocarbon solvents (NBCSs) in different concentrating and nonconcentrating devices using TiO_2 as the photocatalyst either fixed on the inner surface of the reaction tubes or in a slurry. They suggested that the reaction was most effective using a TiO_2 concentration of 200 mg/L as a slurry in a compound-parabolic-concentrator reactor. The concentrating-parabolic-trough reactor had a poor activity because of its minor irradiated reactor surface. It was concluded that the degradation results were very promising and could possibly lead to commercial applications of this technology.

7. Economic Analysis of Photocatalytic Systems

A number of studies have been conducted on the technical improvement of the solar detoxification process. Of these, some have involved calculations of the projected costs of such systems in comparison with those of the conventional treatment technologies used. Also, more efficient systems have been designed that ultimately aimed for an overall increase in efficiency and decrease in cost.

The cost of a typical detoxification system is broadly divided into nonrecurring capital costs and recurring operation and maintenance (O&M) costs. The capital costs are the costs entailed in the basic installation of the system, including the costs of its individual components. The O&M costs are the costs of running the system. The capital costs can be improved by designing more efficient systems. One-sun systems have been shown to be better in this regard, as they absorb both the diffuse and direct components of solar radiation.

The O&M costs depend on a number of factors such as the type and concentration of the pollutant; the rate constant of the reaction; the desired level of treatment; and most importantly, the optimization of catalyst dose, its mode of use (fixed bed or slurry), and its reuse which will determine the pre- and posttreatment costs.

Goswami et al.¹⁰⁹ have made a good comparison for a flat-plate (slurry) system with 100% and 0% catalyst

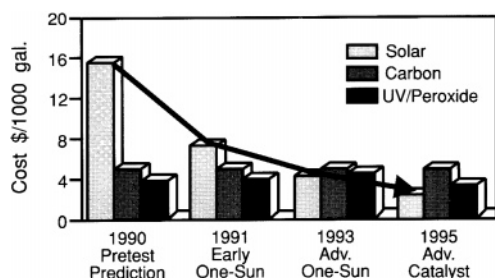


Figure 3. Current and projected cost estimates for the solar photocatalytic process, compared to granulated activated carbon and UV/peroxide oxidation systems.

loss and a flat-plate reactor (fixed type), finding the costs of treatment to be \$27.57, \$12.81, and \$13.69 per 1000 L of water, respectively, for the three cases. Despite the lower capital costs of the flat-plate slurry system with 100% catalyst loss, the overall cost was increased because of the high O&M costs, which would make this system disadvantageous in the long run.

Anderson et al.¹¹⁰ suggested that the largest gains (perhaps 5–100 times) for a designed fixed-bed parabolic-trough reactor could be made through catalyst improvements, whereas gains from system cost reductions (3–4 times) and from process optimization (1.5–2 times) would likely be smaller. Cost projections indicated that the commercial water detoxification process offered significant reductions in processing costs over competing technologies such as granulated activated carbon and UV lamp/peroxide treatment systems.

A cost estimate was, in fact, reported (Figure 3) for the projected costs of solar photocatalytic process compared to granulated activated carbon and UV/peroxide oxidation systems.¹¹¹

For a 500-m² facility, the estimated total cost for photocatalytic degradation was reported to be competitive with those of conventional technologies and was estimated to be ca. \$0.7 \$/m³ by Vidal et al.¹¹² for a low-cost compound parabolic concentrator (CPC) for the destruction of 500 mg/L of selected pesticides to maximum permitted levels (0.1 mg/L) and the four-log inactivation of *Efaecalis* bacteria.

Crittenden et al.⁵⁷ conducted a field test of a solar photocatalytic process for detoxification of water containing BTEX (benzene, toluene, ethyl benzene, and xylene) pollutants. The treatment cost was estimated to be \$5.52 per 1000 gal, and the authors reported that such costs are competitive with those of conventional treatment technologies. The analysis was said to be preliminary and to require long-term testing to determine the actual costs of pretreatment and catalyst life.

Similar results were reported by Turchi et al.¹¹³ for three different solar operating configurations explored for the treatment of 100000 gal/day of groundwater contaminated with trichloroethylene. They concluded that the current projected costs for solar water detoxification systems were comparable with those for conventional treatment technologies such as carbon adsorption and electric lamp-powered, ultraviolet light/hydrogen peroxide systems.

In another study,¹¹⁴ the solar photocatalytic treatment of BTEX-contaminated groundwater was demonstrated onsite. The performance and costs of a solar system were determined. Costs for a solar system at the site were found to be high (\$18–26 per 1 m² or \$70–

100 per 1000 gal), and it was observed that this was primarily due to interference from other water constituents.

Ollis et al.⁶⁵ gave a preliminary comparison of process economics between ultraviolet ozonation and activated carbon adsorption using a reference of integrated water treatment for the removal of PCBs. Their calculations indicated that, for all intermediate and larger sizes of reactors, the costs of photocatalytic systems are comparable to those of activated carbon systems.

In 1998, Vidal¹¹⁵ reported cost estimates for solar-driven photocatalysis involving parabolic-trough concentrators at a small scale, finding a cost of \$10.90 per 1000 gal for the solar trough-slung reactor system with a throughput of 100000 gal/day used at the experimental site. For comparison, the estimated treatment costs were \$6.20/1000 gal with a granulated activated carbon adsorption system and \$4.40/1000 gal with a lamp-powered UV/hydrogen peroxide system. The author concluded that, although treatment costs for solar water detoxification systems were higher at that time than those for conventional technologies, potentially greater cost reductions were being investigated.

8. Conclusion

To summarize this review, the following conclusions can be made:

- (i) Photocatalysis can be used for the treatment of industrial wastewater for the removal of metal ions and nonbiodegradable organics.
- (ii) This technique can be used effectively for the purification and disinfection of drinking water.
- (iii) No studies seem to have been made on the hazard potential and end use of the photocatalysts.
- (iv) Various designs of photocatalytic reactors, using both solar and artificial light, have been proposed. The solar-based reactors should be selected according to the climatic conditions of the location and economic feasibility of the reactor.
- (v) The present treatment costs of photocatalytic systems are slightly higher than those of conventional techniques, but the efforts being made in the design of more efficient systems with improved catalyst usage will establish this technology to be a cleaner and cost-effective alternative.

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