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Chemical Oxidation Technologies: Ultraviolet Light/Hydrogen Peroxide, Fenton's Reagent, and Titanium Dioxide-Assisted Photocatalysis

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ABSTRACT

The application status and potential of three chemical oxidation treatment methods which generate powerful oxidants (hydroxyl radicals): ultraviolet light (UV)/hydrogen peroxide (H_2O_2) process, Fenton's reagent treatment, and titanium dioxide (TiO_2)-assisted photocatalytic degradation, are described and discussed. These oxidation methods are known to effectively degrade and, in several cases, mineralize contaminants ranging from inorganic compounds (such as cyanides) to chlorinated aliphatic compounds and complex aromatic compounds in reaction times on the order of a few minutes to a few hours. Of the three oxidation systems discussed, the technology for the UV/ H_2O_2 process is the most advanced, with numerous successful full-scale treatment units already in existence. Applications of both the Fenton's reagent and TiO_2 -assisted photodegradation processes are currently being developed, with the concepts proven in numerous laboratory-scale studies for a wide range of contaminants. However, both of these processes have only been studied at the pilot/field scale to a limited extent. The application of Fenton's reagent as a pretreatment step prior to biological treatment for industrial wastes and contaminated soils appears promising. Improved system configuration and quantum efficiency of photoreactors are likely to improve the economics of TiO_2 -assisted photodegradation for groundwater treatment, especially with the use of solar illumination.

INTRODUCTION

Chemical oxidation technologies are useful in the oxidative degradation or transformation of a wide range of pollutants for the treatment of drinking water, groundwater, wastewater, and contaminated soils. Chemical oxidation methods are especially applicable for (1) the treatment of hazardous organics present at low concentrations such as in contaminated groundwaters, (2) use as a pretreatment step before biological treatment of low-volume, high-strength wastewaters, (3) the treatment of wastewaters with constituents that are resistant to biodegradation methods or upset biological treatment reactors, such as cyanides and complexed metals, and (4) use as a post-treatment step following biological treatment to reduce aquatic toxicity [1]. Chemical oxidation methods can also be combined with other treatment technologies to achieve optimum and cost-effective treatment.

Three chemical oxidation processes, the ultraviolet light (UV)/hydrogen peroxide (H_2O_2) process, Fenton's reagent treatment, and titanium dioxide (TiO_2)-assisted photocatalytic degradation, are described and discussed herein with regard to their application status, further potential, and their advantages/disadvantages. Oxidation by permanganate, chlorine dioxide, ozonation, and combined ozonation, UV, and H_2O_2 are alternative chemical oxidation methods.

UV/HYDROGEN PEROXIDE OXIDATION SYSTEMS

Hydrogen Peroxide

H_2O_2 is a strong oxidant (standard potential 1.80 V and 0.87 V @ pH 0 and 14, respectively) [2] and its application in the treatment of various inorganic and organic pollutants is well-established. Numerous applications of H_2O_2 in the removal of inorganic pollutants, including prevention of odors of sulfides from wastewater collection and treatment units, removal of sulfites, hypochlorites, nitrites, cyanides, and chlorine are available and are summarized in Table 1 [2]. H_2O_2 is also useful in the treatment of the gaseous pollutants sulfur oxides and nitrogen oxides by conversion to the corresponding acids [Table 1]. Other related uses include the bleaching of pulp and paper and organic syntheses. A few examples of the industrial applications of H_2O_2 [2] are:

1. Detoxification of wastewater and concentrates containing cyanide by oxidation to cyanate;
2. Purification of iron- and manganese-containing groundwater by conversion of the heavy metals to insoluble hydroxides/oxides which can be removed by precipitation/clarification;
3. Treatment of photochemical effluents containing sulfites and silver by conversion to sulfate and the precipitated silver complex, respectively;
4. Degradation of formaldehyde in air emissions by washing with H_2O_2 and ammonia;
5. Prevention of odors by conversion of sulfides, thioethers, disulfides, sulfites, and thiosulfates to elemental sulfur or sulfate in the washing solution;
6. Treatment of sulfur and nitrogen oxides present in air emissions from coking, sulfuric acid production, pickling, and other chemical plant processes by conversion to the corresponding acids; and
7. Removal of excess chlorite and hypochlorite in wastewater, air, or in bleached textiles and pulps by reduction to chloride salts.

H_2O_2 also has applications in the surface treatment industry involving cleaning, decorating, protecting, and etching metals [3]. For example, surface treatment baths used for bleaching of aluminum often use sulfochromic acid containing toxic hexavalent chromium. H_2O_2 -based cleaning baths can offer a non-toxic alternative for surface treatment. H_2O_2 is also useful in the conversion of oxidized copper to copper sulfate for surface cleaning of copper and copper alloys, and in the regeneration of cupric chloride for etching of printed circuits [3].

H_2O_2 can also supply oxygen, by disassociation into oxygen and water, to microorganisms in biological treatment facilities and in the bioremediation of contaminated sites. It can be used as a disinfecting agent in the control of undesirable biofilm growth. Since oxygen concentration is generally rate-limiting during the *in situ* biodegradation of organic contaminants, several applications using injection of H_2O_2 into the subsurface have been successfully attempted to enhance biodegradation activity [4-6]. H_2O_2 can be decomposed into water and oxygen by enzymatic and

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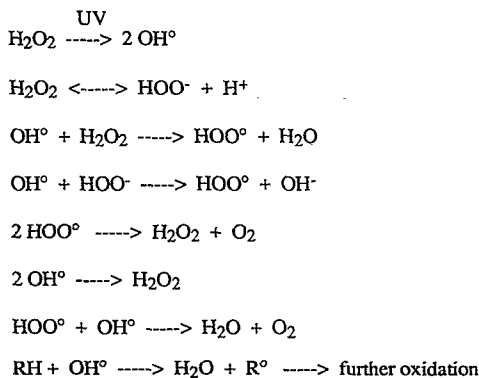
nonenzymatic routes. Viable and nonviable microorganism cells possessing enzymes, such as peroxidases and catalase, can decompose H₂O₂. Iron salts and also light can decompose H₂O₂ and generate one mole of oxygen from two moles of H₂O₂. H₂O₂ is typically injected at concentrations in the range of 50-200 ppm for *in situ* applications with high concentrations in excess of 500 ppm being used to control microbial growth [7].

Treatment with H₂O₂ can reduce the toxicity and improve biodegradability of organics which are inhibitory to biological treatment. Examples of organics that can be oxidized by H₂O₂ include nitrobenzene, aniline, cresols, monochlorophenols, dichlorophenols, and trichlorophenol [1]. Table 1 also includes applications of H₂O₂ for removal of organic contaminants, including removal of formaldehyde, phenols, and fat, oil, grease, and suspended solids in wastewaters [2]. Factors affecting H₂O₂ treatment include pH, temperature, contact time, application rate, and reactivity of compounds [8]. In general, inorganics react faster than organics with H₂O₂ and reaction of trace organics are the slowest due to mass transfer limitations [8].

Oxidation by H₂O₂ alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g., cyanides), because of low rates of reactions at reasonable H₂O₂ concentrations. Transition metal salts, such as iron salts, and UV light can activate H₂O₂ to form hydroxyl radicals which are strong oxidants. Oxidation processes utilizing activation of H₂O₂ by iron salts, termed Fenton's reagent, are discussed in the following section. Oxidation processes utilizing UV and/or ozone as co-oxidants are discussed below. In general, oxidation processes which are based on the generation of hydroxyl radical intermediates are termed Advanced Oxidation Processes (AOP). Hydroxyl radicals (oxidation potential: 2.8 V) are stronger oxidants than ozone and H₂O₂. Hydroxyl radicals nonspecifically oxidize target compounds at high reaction rates on the order of 10⁹ M⁻¹s⁻¹ [9]. The efficiency of oxidation can be reduced by scavengers of hydroxyl radicals. For example, carbonate and bicarbonate ions have reaction rates of 1.5 × 10⁷ M⁻¹s⁻¹ and 4.2 × 10⁸ M⁻¹s⁻¹, respectively, with hydroxyl radicals [10].

UV/H₂O₂ Systems

UV/H₂O₂ oxidation involves the single-step dissociation of H₂O₂ to form two hydroxyl radicals (OH[•]). Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals (R[•]), which are highly reactive and can be further oxidized. The various reactions which occur during UV/H₂O₂ oxidation are as follows:



Degradation of the organics can also take place directly by activation caused by UV, which improves the ability of the organics to be oxidized either by H₂O₂ or by the generated hydroxyl radicals. The activation of the organic compounds can involve direct oxidation by UV or the formation of organic radicals or other reactive intermediates. UV wavelengths of 200-280 nm lead to disassociation of H₂O₂, with mercury lamps emitting at 254 nm being the most commonly used. If the concentrations

of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2 , water, and, in the case of substituted organics, inorganic salt if the treatment is continued.

UV/ H_2O_2 systems can effectively oxidize recalcitrant organics such as trichloroethylene (TCE), tetrachloroethylene (PCE; perchloroethylene), butanol, chloroform, methyl isobutyl ketone, 4-methyl-2-pentanol, methyl ethyl ketone, and carbon tetrachloride [1]. Additionally, laboratory-scale UV/ H_2O_2 systems were used to demonstrate the oxidation of acetate [11], the degradation of formic, acetic, and propionic acids [12], the disappearance of methanol and various phenolic compounds [13], several chlorinated aliphatic compounds [14], substituted phenols [15] and 2,4-dinitrotoluene [16], the degradation of benzene [17], the oxidation of chlorophenols [18], the oxidation of several phenolic compounds [19], and the degradation of 4-chloronitrobenzene [20], 1,2-dichlorobenzene [21], atrazine [22], 4-bromodiphenylether [23], phenol [24], the insecticide malathion [25] and the pesticides metoxuron and carbetamide [26]. Information on known UV/ H_2O_2 processes are summarized in Table 2.

Partial removal of methanol, phenol, *p*-cresol, allyl alcohol, benzene, dimethylphthalate, and toluene was reported with efficiencies ranging from 25% to 60% using UV/ H_2O_2 [13]. The complete dechlorination of several chlorinated aliphatic compounds was demonstrated [14]. 98% of benzene could be degraded by UV/ H_2O_2 to intermediate organics, which could also be degraded by supplemental H_2O_2 addition and continued treatment [17]. Dimethylaminomethyl-substituted phenols (DMP)- and isophorone-contaminated water were successfully treated [15]. Removal efficiencies of 85-100% of mono-, di- and trichlorophenols were achieved in a 3-h reaction period [18]. Sundstrom et al. [19] showed degradation of benzene, toluene, chlorobenzene, phenol, 2-chlorophenol, 2,4,6-trichlorophenol, dimethylphthalate, and diethylphthalate. The phthalates showed the lowest rates of reactions of all the compounds tested. Intermediates generated from phenolic compounds could also be degraded with continued treatment [19]. UV/ H_2O_2 oxidation resulted in nearly double the rate of degradation of 1,2-dichlorobenzene than that obtained with UV light alone in a laboratory-scale reactor [21]. A mechanistic model for the UV/ H_2O_2 oxidation of butyl chloride was proposed [27]. The effects of molar ratio of H_2O_2 to butyl chloride, hydraulic retention time, UV intensity, pH, inorganic carbon, and humic substances on the removal of butyl chloride were investigated experimentally and mathematically. Atrazine was not mineralized by UV/ H_2O_2 oxidation and cyanuric acid was the final product [22].

UV/ H_2O_2 was also used to remove naturally present organics from distilled and tap water [28], reduce total organic carbon (TOC) in boiler feedwater [29], treat explosives-containing wastewaters [30], degrade tannery waste effluents and keratin solutions [31], treat textile plant wastewaters [32], paper and pulp bleaching wastewaters [33] and a cutting oil wastewater [34]. 88% and 98% reduction in TOC was achieved by UV/ H_2O_2 treatment of organics in tap and distilled water, respectively [28]. 90% reduction of TOC of tannery waste was achieved in a pilot system using UV irradiation for 2 min [31]. Prat et al. [33] demonstrated that only 70% of color was removed in bleaching wastewaters. They concluded that only partial decolorization could be obtained with UV/ H_2O_2 treatment and that the equipment and operating costs would not be economically competitive.

There are about forty full-scale treatment systems in operation using the *Perox-Pure* (trademark, Peroxidation Systems, Inc.) oxidation system, which is a UV/ H_2O_2 oxidation process using high intensity UV lamps [35]. The *Perox-Pure* system is applicable for the treatment of about 64 different organics and for the removal of biological oxygen demand (BOD), chemical oxygen demand (COD), color, and TOC [36]. Four case studies of UV/ H_2O_2 oxidation were presented for the treatment of chlorinated solvent-contaminated groundwaters [36]. Reported costs ranged from \$1.37 to \$58.51/1000 gal of groundwater. Yost [37] presented two case studies, a pilot system and the other a full-scale operation, of the application of the *Perox-Pure* system. Annual cost projections for a full scale unit were reported to be \$2.59/1000 gal of groundwater, at 600 gal/minute (gpm), contaminated with aromatic compounds; capital investment for three 200-gpm *Perox-Pure* systems were estimated at \$515,000 [37]. Five case studies of the treatment of groundwater contaminated with chlorinated aliphatic and aromatic compounds, at flow rates ranging from 15 to 350 gpm, were presented [38]. In each case, the economics of the UV/ H_2O_2 process were more competitive than those of alternative technologies of air stripping and activated carbon adsorption. Also, effluent criteria were met without any air emissions. The UV/ H_2O_2 systems can also be used in the gas-phase treatment of pollutants

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Mechanism and Kinetics

UV/H₂O₂ degradation of aliphatic acids led to the formation of lower molecular weight acids, alkanes, and CO₂ [12]. 2,4-dinitrotoluene was degraded by side-chain oxidation to form 1,3-dinitrobenzene, which was hydroxylated to form hydroxynitrobenzene derivatives [16; Figure 1]. Further reactions of ring cleavage yielded carboxylic acids and aldehydes, which upon continued oxidation were eventually converted to CO₂, water, and nitric acid. In the UV/H₂O₂ oxidation of chlorophenols, chlorinated and dechlorinated catechols and quinones were formed [18,42]. Benzene was oxidized to several intermediates, four of which were identified as phenol, catechol, hydroquinone, and resorcinol; all intermediates were degraded with continued treatment [17]. The degradation of 4-bromodiphenylether yielded several intermediates via dehalogenation, cleavage of the ether bond to form phenol and benzene, ring-opening reactions to form carboxylic acids, and mineralization reactions [23]. Compounds that are similar to humic acids in structure and resistant to photodegradation may also be formed from polymerization reactions [23].

Treatment times for complete degradation of halogenated aliphatic compounds in the UV/H₂O₂ systems are on the order of a few minutes and reactions follow a pseudo first-order reaction rate. A

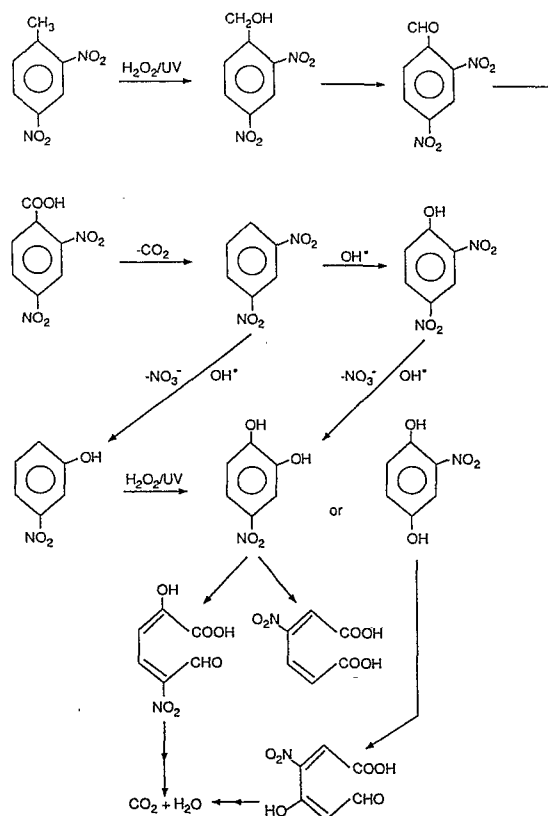


FIGURE 1

Mechanism of UV/H₂O₂ Oxidation of 2,4-Dinitrotoluene [adapted from Ho, 1986; Ref. 16]; "Reprinted with permission from **Environmental Science and Technology**, Copyright 1986, American Chemical Society."

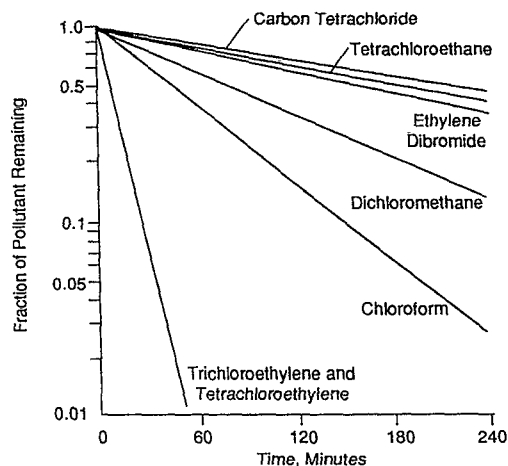


FIGURE 2

Comparison of UV/H₂O₂ Oxidation of Halogenated Aliphatics at 20°C [adapted from Sundstrom et al., 1986; Ref. 14]; "Reprinted with permission from **Hazardous Waste & Hazardous Materials**, Copyright 1986, Mary Ann Liebert, Inc."

first-order rate constant of 0.0903 min⁻¹ was reported for TCE at 58 ppm [14]. TCE at an initial concentration of 50 ppm was degraded to less than 1 ppm in 50 min at 20°C and in 10 min at 40°C [14]. The effect of the temperature may also have been due to the increased intensity caused by the warming of the lamp [14]. The rate of degradation was also affected by the chemical structure of the contaminant; H₂O₂ concentration; the UV light intensity; and, to a lesser extent, solution pH. Increasing rates of reaction were in the following order for chlorinated aliphatic compounds: carbon tetrachloride < tetrachloroethane and ethylene bromide < dichloromethane < chloroform < PCE < TCE [14; Figure 2]; i.e., chlorinated alkenes were more rapidly degraded than alkanes. Benzene degradation also followed a pseudo first-order reaction rate for the first 10-20 min of the reaction, with 99% of benzene being degraded in 90 minutes of treatment [17]. Increases in the initial H₂O₂ concentration (up to a certain extent) and UV light intensity increased the rate and extent of oxidation [17,19; Figure 3]. Increases in the H₂O₂ concentration yielded increased hydroxyl radicals for more efficient degradation. However, at high H₂O₂ concentrations, excess H₂O₂ reacts with hydroxyl radicals to form water and oxygen [34]. The rate of reaction increased only slightly with increasing pH in the range of 5.5-7.9 [14].

Process Improvements

Recent modifications in the type of UV lamps used have improved the efficiency and cost-effectiveness of direct UV oxidation.

Earlier processes used low-pressure mercury vapor lamps, which are used in disinfection systems having a bulk of their output at 254 nm. Modified high intensity UV lamps, which possess higher energy outputs and higher electrical efficiencies, are less temperature-sensitive, have lower capital costs, and produce a broad band spectrum output, have been used to improve the process efficiency [35,43]. The broader spectrum output allows for the oxidation or activation of a wider range of compounds and generated intermediates than the low intensity lamps. Other advantages of the high intensity lamp include compactness of design (6 lamps treating 400 gpm of contaminated groundwater in a 2 ft x 8 ft unit) and rapid reaction rates with treatment times on the order of a few minutes, which allow for degradation of volatile compounds that would otherwise be stripped away during longer reaction periods [35].

Another advance in UV lamp technology is the addition of dopants to mercury vapor lamps,

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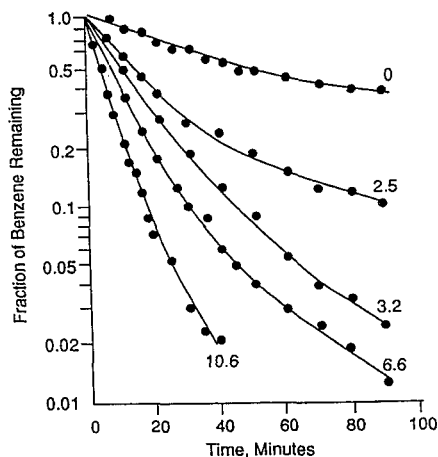


FIGURE 3

Effect of Initial Molar Ratio of H_2O_2 to Benzene on UV/ H_2O_2 Decomposition of Benzene at $25^\circ C$ and pH 6.8. Initial benzene = 0.2 mM [adapted from Sundstrom et al., 1989; Ref. 19]; "Reprinted from *Environmental Progress*, 8(1), D.W. Sundstrom, B.A. Weir, and H.E. Klei, 'Destruction of Aromatic Pollutants by UV Light Catalyzed Oxidation with Hydrogen Peroxide', 6-11, (1989); Reproduced by permission of the American Institute of Chemical Engineers, 1989 AIChE. All rights reserved."

which increases the intensity of the output at several wavelengths other than 254 nm [41]. These UV lamps modified with dopants, termed metal halide lamps, can degrade organic contaminants with or without H_2O_2 , although their efficiency is improved when combined with H_2O_2 [41].

A further improvement is the use of modified lamps which generate a UV continuum, i.e., UV wavelengths covering absorption wavelengths of all organics present [41]. These modified lamps have the advantage of treating mixtures of several different kinds of organic contaminants. A UV continuum can be generated by pulsed xenon and custom built flashlamps [41]. Petroleum hydrocarbons; polynuclear aromatic hydrocarbons (PAHs), such as naphthalene and pyrene; unsaturated and saturated halogenated aliphatic compounds, such as TCE, carbon tetrachloride, and chloroform; pesticides; cyanides; PCBs; dioxins; nitrites; and trinitrotoluene (TNT) were all reportedly degraded using a pulsing UV continuum [41]. Cost estimates of \$0.59 for the conventional UV/ H_2O_2 process and \$0.33 for pulsed UV photolysis were reported to treat 1000 gal of benzene- and TCE-contaminated groundwater.

Lipowicz [44] treated high-strength industrial wastes in a total processing time of 15-30 min by a three-stage process using sequential treatment by oxidation in a cavitation chamber, catalyzed H_2O_2 oxidation, and UV/ H_2O_2 oxidation. All three steps achieved oxidation by generated radical species, mainly hydroxyl radicals. Reported costs were \$7.50/1000 gal of bottling-plant wastewater (COD: 7,000 mg/L) and \$17.50/1000 gal of sludge (COD: 13,000 mg/L) [44].

Safarzadeh-Amiri et al. [43] used a novel UV reduction process to degrade refractory chlorinated compounds. The process generated the powerful reductants, hydrated electrons, from the UV irradiation of a proprietary additive. The hydrated electrons were believed to progressively dechlorinate halogenated alkanes, which are slower to degrade in UV oxidation processes.

Advantages/Disadvantages

The UV/ H_2O_2 systems are superior to alternative technologies, such as stripping followed by activated carbon adsorption, which simply transfer contaminants from one phase to another because the UV/ H_2O_2 process can completely oxidize the contaminants to innocuous products. These systems

have the ability to treat a wide variety of contaminants. In some cases, they are also reported to be more cost-effective, as evidenced by implementation of several successful full-scale operations. These systems also have the advantage of being mobile and being able to be installed in a short time frame (less than one year) for the treatment of contaminated water at different sites [37]. However, these systems are not applicable for the treatment of contaminated soils because UV light does not penetrate soil particles and also because of the presence of other energy sinks in the soil that reduce efficiency. Surfactants are required to transfer the contaminants from within soil matrices to the surface and to mobilize the contaminants into solution prior to UV/H₂O₂ oxidation for this process to be effective.

Certain inorganic compounds, such as calcium and iron salts, may precipitate during UV treatment and coat the lamp tubes, thereby reducing UV light penetration [35]. For this reason, pretreatment or softening of the influent may be required. Suspended solids and some inorganic and organic species exhibiting color have a negative effect on the performance of the UV/H₂O₂ systems and consequently increase operational costs [35]. Interference due to colored compounds may have been the cause of the incomplete (70%) removal of color from bleaching wastewaters in the work of Prat et al. [33]. Pretreatment involving filtration and clarification for removal of suspended solids and turbidity may improve efficiency. In the case of interfering inorganic and organic compounds, other treatment options may need to be combined with the UV/H₂O₂ system for effective treatment.

In some situations, pH control may be required to prevent precipitation of metal salts during the oxidation process and to avoid a loss in efficiency due to the precipitates [35]. Generally, metal hydroxide precipitation is avoided for pH less than 6. Alkaline pH can adversely affect the reaction rate, possibly due to the base-catalyzed decomposition of H₂O₂ [17].

UV/H₂O₂ systems have primarily been used to treat low levels of pollutants in the ppm range typical of groundwater concentrations and may not be applicable for the treatment of high-strength wastes. Initial treatment by UV/H₂O₂, followed by the use of alternative technologies, is a possible approach for highly concentrated wastes. Gray et al. [34] pointed out that the treatment of high-strength wastes would require more efficient UV lamps with better hydroxyl radical generation efficiency. Their initial attempts at testing a laboratory-scale system to treat an industrial cutting oil wastewater containing several organics were marginally successful, although complete degradation was not reported.

UV Irradiation, H₂O₂, and Ozone Processes

AOPs using combinations of UV irradiation, H₂O₂, and ozone have also been investigated in depth and are capable of generating hydroxyl radicals at high rates sufficient to make treatment processes practical [45]. Commercial applications of UV, H₂O₂, and ozone processes [45] are increasingly being used and should be considered as competing technologies with the UV/H₂O₂ process. A brief description of these alternative processes are described below.

Application of UV, H₂O₂, and ozone processes in the treatment of a variety of industrial wastewaters and contaminated groundwaters were reported [46-48]. AOPs are being used both for complete treatment and as a pretreatment or polishing step with other treatment technologies. Processes which employ ozone/H₂O₂, UV/ozone and UV/ozone/H₂O₂ combinations can also generate hydroxyl radicals by complex mechanisms involving perhydroxyl radicals and superoxide ions. Several pesticides (pentachlorophenol (PCP), malathion, Baygon, DDT and Vapam) [49], TNT [50], halogenated aliphatic compounds (chloroform, bromodichloromethane, PCE) [51], and aromatics (nitrobenzene, benzoic acid, 3-chlorobenzoic acid, and anisole) [52] have all reportedly been oxidized by UV/ozone systems [17]. In complex wastewaters, inhibition of some mechanisms may be possible, in which case the UV/ozone/H₂O₂ systems are superior [45] because these systems involve several mechanisms for generating oxidative radicals. UV/ozone/H₂O₂ systems are affected to a lower extent by colored and turbid wastewaters, and are also applicable over a wider pH range than UV/H₂O₂ systems [45].

Aieta et al. [53] reported the results of a field-scale evaluation of an AOP employing H₂O₂ and ozone. The effects of the H₂O₂ to ozone ratio, ozone dosage, and contact time on the treatment efficiency were investigated. A concentration ratio of H₂O₂ to ozone of 0.34:1, an ozone dosage of 9 ppm, and a contact time of 15 min were determined to achieve approximately 90% removal of TCE and

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PCE in a 40-L pilot-scale reactor. Treatment cost estimates of \$0.094/1000 gal of TCE- and PCE-contaminated water were reported to be more competitive than alternative technologies of liquid-phase activated carbon adsorption and air-stripping with gas-phase activated carbon adsorption. Garland [54] and Peyton [55] reported that during the treatment of 6 gpm of TCE-contaminated groundwater by UV/ozone/H₂O₂, precipitation in the reaction chamber, coating of the UV lamps, and mass transfer of ozone into the reactor were some of the operational problems encountered. In the same process, treatment by ozone/H₂O₂ was claimed to be considerably more important in the treatment mechanism than UV/H₂O₂ based on reaction rate constants of 0.14 and 0.011 min⁻¹ for TCE during treatment by ozone/H₂O₂ and UV/H₂O₂, respectively [55].

Guittonneau et al. [20] determined that the ozone/UV system was more efficient than the UV/H₂O₂ system for the oxidation of 4-chloronitrobenzene for a given oxidant dose because of the higher rate of hydroxyl radical generation by ozone photodecomposition. A UV/ozone/H₂O₂ system was superior to UV/H₂O₂ treatment for COD removal in treating a 650 gpm wastewater stream [45]. The UV/ozone/H₂O₂ system reduced COD by about 80% in 20 min; ozone/UV removed only 50% of COD in 30 min and H₂O₂/ozone removed 69% in 30 min [45]. A cost of \$2.15/1000 gal of wastewater was reported for a UV/ozone/H₂O₂ system [45]. A cost of \$2.11/1000 gal for the treatment of water containing chlorinated organics, PCBs and pesticides from 1 ppm to less than 10 ppb was reported for a 100 gpm UV/ozone/H₂O₂ system [56]. Ozone and ozone/UV processes were superior to UV/H₂O₂ for nitrobenzene removal [57]. Removal rates of nitrobenzene of 1.21 × 10⁻⁶, 1.61 × 10⁻⁶, and 0.76 × 10⁻⁶ M/min were reported using ozone, ozone/UV, and UV/H₂O₂, respectively. However, the rates of removal of trihalomethane precursors were approximately the same in all three processes [57].

However, in cases where UV/H₂O₂ systems are sufficient to cause the desired oxidation, H₂O₂ may be more economical than ozone. Although the cost per pound of H₂O₂ (\$0.75-1.50) is slightly higher than that of ozone (\$0.60-1.10), ozone, a sparingly soluble and unstable gas, requires on-site generation and storage, which increases equipment and operating costs. On the other hand, H₂O₂ is totally miscible in water and does not require any special equipment for storage. Additionally, an ozone contacting device is required and the efficiency is limited by mass transfer of ozone into the liquid phase. The low solubility and low mass transfer rate of ozone are especially limiting for the large-scale degradation of industrial wastes. Such large-scale treatment is more effective when UV/H₂O₂ systems are used.

FENTON'S REAGENT

Fenton's reagent is a mixture of H₂O₂ and ferrous iron, which generates hydroxyl radicals according to the reaction:



In the presence of substrates, such as target contaminants, the hydroxyl radicals generated are capable of detoxifying the contaminants via oxidation. The hydroxyl radicals can be generated by small amounts of iron, using concentrations as low as 0.05 mM, and also using other transition metals instead of iron. Numerous competing reactions, which involve Fe²⁺, Fe³⁺, H₂O₂, hydroxyl radicals, superoxide radicals, and radicals derived from the substrate, are also possible during Fenton's reagent treatment [58].

Several hazardous pollutants can be oxidized by the hydroxyl radicals generated using Fenton's reagent or Fenton-like reactions. Research studies using Fenton's reagent have demonstrated the oxidation of the following compounds present as pure compounds in solution: phenol [59], chlorophenols [60], 2,4-dichlorophenol and dinitro-*o*-cresol [61], hydroxymethanesulfonic acid [62], formaldehyde [63], PAHs [64], chlorobenzene [65], PCBs [66], and nitrophenols and nitrobenzene [67]. Synthesis of phenol from benzene was studied by Tzedakis et al. [68]. Additional literature reports of oxidation of compounds by Fenton's reagent or Fenton-like reactions include hydrazine and benzene [69,70]. Studies on Fenton's reagent treatment are summarized in Table 3.

Sudoh et al. [59] used H_2O_2 , generated from the electroreduction of oxygen, and iron to completely degrade phenol in the range 260-2600 ppm as COD at pH 3. Barbeni et al. [60] demonstrated complete mineralization of various chlorophenols. Complete degradation of 500 ppm of formaldehyde to formic acid and CO_2 was demonstrated [63]. Partial mineralization of various PAHs was demonstrated to varying extents up to about 17.5%, with conversion to more polar products [64]. Chlorobenzene was completely degraded, but not mineralized [65]. 2-Chlorobiphenyl was degraded from 10 μM to 1 μM [66].

Several instances of the use of Fenton's reagent or similar reactions in wastewater treatment are cited in the literature [71-73]. Walton et al. [73] showed a 90% reduction of thiosulfates and sulfides in a few minutes by conversion to sulfur or sulfates. Treatment of wastewaters containing sodium dodecylbenzene sulfonate [74], *p*-toluenesulfonic acid and *p*-nitrophenol [75], and azodyes [76] using Fenton's reagent was also reported. Reduction in COD and BOD using Fenton's reagent or Fenton-like reactions have also been documented [72,77-79]. Approximately 91% removal of BOD in a hydrolyzed protein waste was achieved by H_2O_2 and iron salt [78]. Brett and Gurnham [77] used H_2O_2 and dichromate with wet air oxidation to reduce the COD of glucose. Oxidation by H_2O_2 and chromium was possible at neutral pH and improved the COD removal from 2% to 74%. Fenton's reagent was also used as an intermediate step between two biological steps to treat landfill leachate containing phenols and other organic compounds [79]. Following initial biological treatment the leachate consisted of equal amounts of compounds with molecular weights above and below 1000. Chemical oxidation resulted in changing the distribution of compounds with molecular weights less than 1000 to about 80%, which improved the biodegradability in the final step [79].

More recently, Kuo [80] used Fenton's reagent to decolorize simulated dye wastewaters. An average decolorization of over 97% was obtained with concomitant COD removal of about 90% in 30 minutes or less. The most effective pH for treating dye wastewater was 3.5 and below. Different dosages of H_2O_2 and ferrous iron were required for different types of dyes. Complexes of ferric iron and hydroxide ions could also coagulate the dyes. The results of the simulated wastewaters were confirmed with actual wastewaters obtained from dyeing mills. H_2O_2 and iron were used to treat wastewater containing phenol and/or formaldehyde produced in phenol and coke in gas plants and coal distillation plants, and in the production of phenol/formaldehyde resins [2]. Approximately 8 moles of H_2O_2 for phenol degradation and an additional 2 moles for formaldehyde degradation were required in a reaction time of 30-60 min and the process was only practical for concentrations of phenol up to 5000 ppm, before H_2O_2 costs became uneconomical. The products of oxidation were CO_2 , and oxalic and other carbonic acids [2].

A few instances of pretreatment of phenolic compounds using Fenton's reagent prior to biological treatment have also been reported. Fenton's reagent significantly reduced the toxicity and improved the biodegradability of two phenolic wastewaters [61] and enhanced the biodegradability of PCP by aerobic mixed cultures [81]. Biodegradation of PCP was improved from 5% to 33% using a selected microbial consortium and from 2.5% to 20% using activated sludge by pretreatment with Fenton's reagent. The chemical pretreatment also improved the biodegradability, from 30% to 100%, of PCP by activated sludge microorganisms [82], the biodegradability of TCE from 32% to 73% [83], and also the biodegradability of *o*-cresol and 2,4-dinitrophenol by anaerobic bacteria, as indicated by a 50% reduction in toxicity [84,85]. UV radiation used with Fenton's reagent also improved the extent of degradation of 4-nitrophenol [86].

Fenton's reagent has also been proposed as a soil decontamination technology. Aged sandy soils contaminated with town gas waste containing a mixture of PAHs were successfully tested with Fenton's reagent using a 10% H_2O_2 solution over a reaction period of 16 hours [64]. This chemical oxidation was proposed both for pretreatment of refractory PAHs before biological treatment as well as posttreatment following biological treatment for residual PAHs. Pilot-scale testing of the concept of an integrated system using Fenton's reagent and biological treatment for PAH-contaminated soils was recently reported [87]. Watts et al. [58] demonstrated the complete mineralization of PCP by Fenton's reagent in contaminant-spiked silica sand in a laboratory-scale system. PCP treatment was also shown in two natural soils, with the physical and chemical properties of the soil affecting the efficacy of treatment. The most effective treatment, as measured by the highest ratio of PCP degradation to lowest H_2O_2 consumption, was obtained with contaminated silica at pH 3 [58].

Fenton
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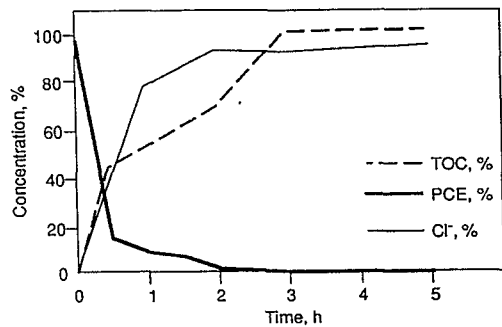


FIGURE 4
Perchloroethylene Degradation by Fenton's Reagent with Time. The initial PCE concentration was 1000 mg/kg sand. Complete mineralization of PCE was evidenced by the generation of CO₂ (TOC) and Cl⁻. The CO₂ and Cl⁻ concentration are expressed as the equivalent amount of PCE [adapted from Leung et al., 1992; Ref. 88]; "Reprinted with permission from the *Journal of Environmental Quality*, Copyright 1992, American Society of Agronomy."

Fenton's reagent completely mineralized PCE in a contaminant-spiked silica sand matrix [88; Figure 4] and removed octachlorodibenzo-*p*-dioxin (OCDD) from four types of dioxin spiked soils [89]. No degradation products could be detected in the case of OCDD treatment [89]. The treatment efficiencies ranged from 75% to 96% removal and the loss of OCDD was inversely related to the soil organic carbon content. Elevated temperatures and higher H₂O₂ concentrations improved dioxin removal; removal at 80°C was 85% compared to 15% removal at 20°C using 35% H₂O₂ and there was almost no removal using 3.5% H₂O₂ at 20°C [89]. The treatment of soil contaminated with PCP, trifluralin, hexadecane, and dieldrin using 12% H₂O₂ with and without iron addition at pH 3 was demonstrated in laboratory-scale spiked-soil systems [90]. PCP and trifluralin degradation rates were lower in soils with higher organic content but soil organic carbon had no effect on the degradation of hexadecane and dieldrin. PCP degradation rate constants were approximately 0.0042, 0.0039, and 0.0002 min⁻¹, respectively, in soils when 400 mg/L, 240 mg/L, or no iron were used. However, the degradation efficiency (the ratio of contaminant degradation rate constant to the H₂O₂ degradation rate constant) was highest for treatment with no iron addition, suggesting that naturally occurring iron in the form of oxides in the soil are sufficient to catalyze degradation. This was confirmed by using various iron minerals with silica sand and demonstrating PCP degradation [90].

Fenton's reagent was also used to degrade oil and fuel hydrocarbon-contaminated soils from a spill site [91]. Laboratory studies demonstrated that the total petroleum hydrocarbons (TPH) levels in the soil could be reduced from 2000 mg/kg to below the regulatory limit of 100 mg/kg in 7 days using 12% H₂O₂ with and without iron addition. The optimum pH values were 2 and 3; the treatment was complete without any iron addition at these pH values. Addition of 2, 7, and 35% H₂O₂ was also tested; when 2 and 7% H₂O₂ were used, three H₂O₂ treatments were required as compared to only two treatments at higher H₂O₂ concentrations. Cost estimates for using 2 and 7% H₂O₂ were \$7.23 and 25.32/yd³ of soil and were more economical than that for higher H₂O₂ concentrations. Thus, the optimum conditions determined were: pH 3, no iron addition, 2 or 7% H₂O₂. These conditions were subsequently used for pilot testing of the process using 1.25 yd³ of soil in 55-gallon drums over a reaction period of one to three days. The cost of treatment was estimated at \$14.50/yd³ of soil. No degradation products were observed; however, the possibility of contaminant polymerization and bound residue formation was noted [91].

Mechanism and Kinetics

The chemistry of the action of Fenton's reagent is similar to that of the UV/H₂O₂ oxidation process to some extent because both processes involve the generation of hydroxyl radicals which are

responsible for contaminant oxidation. As discussed above, however, the UV/H₂O₂ oxidation process had additional mechanisms by which oxidation of contaminants may occur.

Depending upon the nature of the substrate contaminant, different reactions may occur following initial oxidation by hydroxyl radicals. In the case of chlorobenzene, chlorobenzoquinone is formed primarily as an intermediate along with some dichlorobiphenyl [65]. Chlorophenols can be further oxidized by hydroxyl radicals to form chlorinated and nonchlorinated diols [65]. In the case of benzo(a)pyrene, about 25% was recovered as CO₂ and the rest recovered as oxidized products which could be further oxidized by continued treatment [64]. Hydroxylation by Fenton's reagent was reported for benzene conversion to phenol, among numerous other products [68] and for PCBs [66]. PCE was converted to dichloroacetic acid followed by further dechlorination and decarboxylation to yield CO₂ [88].

In soil treatment, pentachlorophenol degradation was substantiated by reduction in TOC of the soil slurry filtrate [90]. Petroleum hydrocarbons were also degraded in soils without the detection of degradation products [91]. The polymerization of these contaminants as a result of H₂O₂ oxidation forming soil-bound residues is a distinct possibility [91]. Hydroxylation of aromatic pollutants followed by further oxidation yielding CO₂ is likely when high concentrations of H₂O₂ are used; however, low concentrations in the range of 100 to 1000 mg/L H₂O₂ can promote polymerization reactions [91]. Thus, in soil matrices, which involve complex reactions for H₂O₂ consumption, polymerization may be favored over mineralization and not necessarily result in innocuous endproducts.

Most reactions have been conducted for time periods ranging from 5 min to 2 h for compounds in solution, to a few hours to days in soils. For example, 24 h were required to completely degrade 250 mg/kg of PCP present in soils at pH 3 [58] and 75 min were required for complete dechlorination of monochlorophenols at 3×10^{-4} M [60]. Formaldehyde was degraded from 500 ppm to 1 ppm in 2 h treatment with Fenton's reagent [63]. A stoichiometry of 5 moles of H₂O₂ per mole of chlorobenzene was reported for complete degradation [65] while 12 moles H₂O₂ were required per mole of dichlorophenol [61].

Advantages/Disadvantages

Fenton's reagent processes are particularly advantageous in situations where alternative technologies are not effective. For example, traditional biological treatment processes are not effective in the decolorization of dye wastewaters because many commercial dyes are toxic to the microorganisms involved, whereas Fenton's reagent can effectively decolorize dye wastewaters [80]. Other examples of the usefulness of Fenton's reagent include the degradation of higher molecular weight PAHs, and PCE, both of which are refractory towards biological degradation. Additionally, Fenton's reagent has an advantage over UV/H₂O₂ methods; colored organic compounds which interfere with the UV/H₂O₂ process by UV light absorption can be successfully degraded by Fenton's reagent.

The optimum pH range for effective treatment by Fenton's reagent is in the acidic range of 2 to 4, which implies that a pretreatment step may be needed for pH adjustment. This treatment technology may not be applicable to alkaline soils and sludges with strong buffering capacities. However, a reaction similar to Fenton's reaction is also possible at basic pH values, involving oxidation by H₂O₂ in the presence of a small amount of the complex salt sodium-iron (III)-ethylenediamine-tetraacetate-trihydrate [2]. Bull and Zeff [45] indicated that another disadvantage of Fenton's treatment is the requirement for ferrous iron, resulting in the production of iron sludge which requires proper disposal.

Capital equipment costs for application of Fenton's reagent can be expected to be very low compared to the UV/H₂O₂ oxidation process. The primary factor contributing to the chemical costs of Fenton's reagent is the cost of H₂O₂ (\$1.72/gallon for 50 wt % aqueous solution) [58]. For this reason, it may be important to optimize the amount of H₂O₂ required, especially in the treatment of contaminated soils [58]. Note, however, that for site clean-up, the H₂O₂ costs were determined to be only about 5% of the total costs, which included costs of excavation, labor, pH adjustment, sampling, and analysis [91]. Fenton's reagent is most likely to be effective in on-site treatment applications (e.g., in a slurry reactor or in land treatment units) rather than *in situ* because the reaction would

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Process Improvement

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Technology Summary

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because the reaction would

require thorough mixing of the contaminants and the co-substrates. The possibility exists that iron which is naturally present in soils and groundwater catalyzes Fenton's reaction when H₂O₂ is added *in situ*. However, because the optimum pH for oxidation of organics by Fenton's reaction is in the acidic range, significant reaction rates may not occur in groundwater and *in situ* remediation cases involving H₂O₂ injection without pH modification.

Process Improvements

UV irradiation can enhance the degradative activity of Fenton's reagent as demonstrated for the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) [92,93]. UV-assisted Fenton's reaction can yield an increased concentration of hydroxyl radicals by generation from the photolysis of aquated Fe³⁺. The reaction rate constants of hydroxyl radicals generated by photoassisted Fenton's reagent with various chlorinated contaminants were reported [94]. Degradation of the herbicides (concentration 0.1 mM) using the Fenton-like reaction of Fe³⁺ and H₂O₂, in which Fe³⁺ acts as a true catalyst, was incomplete (less than 70%) even at high H₂O₂ concentrations of up to 500 mM [92]. However, the use of UV irradiation in addition to Fe³⁺/H₂O₂ led to the complete mineralization of 2,4-D [92,93]. Also, transformations of 2,4-D and 2,4,5-T were 2.7 and 1.6 times faster, respectively, in UV irradiated reactions than in reactions conducted with Fe³⁺/H₂O₂ alone [92]. Mineralization was complete in less than 2 h and the H₂O₂ required was reduced to 5 moles of H₂O₂ per mole of substrate using UV irradiation [92]. Degradation during UV irradiation was thought to be primarily due to the photolysis/decarboxylation of Fe³⁺ complexes of degradation intermediates [93].

Technology Status

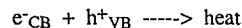
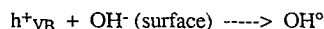
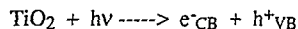
Fenton's reagent treatment has been primarily studied at the laboratory scale level with limited applications in a field setting. However, two successful reports of the application of Fenton's reagent in the pretreatment of contaminated soils at the pilot scale are available [87,91]. Fenton's reagent was tested as a pretreatment step to degrade PAHs present in coal tar-contaminated soils prior to biological treatment. Sixteen field plots (4 × 12 ft) containing soils to a depth of 6-8 in. were tested. The combination of chemical oxidation and biological treatment reduced the treatment time period by nearly 50% to about four weeks [87]. The process is likely to be extended to full-scale treatment in the next phase of the project. Also, 22.5 yd³ of soil were treated using Fenton's reagent [91].

Bench-scale treatability studies are needed to evaluate the usefulness and optimum conditions necessary for successful application of Fenton's reagent, especially in the treatment of contaminated soils. Since the physical and chemical properties of soils, environmental conditions, such as pH, and concentrations of the substrate and oxidants can greatly affect the rate of oxidation and the product distribution, the effects of these parameters need to be investigated to effectively apply Fenton's treatment.

TiO₂-ASSISTED PHOTOCATALYSIS

Oxidative degradation of pollutants by photocatalysis using semiconductor particles, such as TiO₂, has been the subject of numerous recent studies. The principle behind semi-conductor assisted photocatalysis in an aqueous phase containing organic pollutants and semi-conductor particles involves the photoexcitation of the semi-conductor particles by UV light causing the energy state of the electrons to change from "the valence band of the solid to the conduction band" [95,96]. This results in the formation of electrons and holes at the surface of the semi-conductor particle which can either recombine, producing thermal energy, or interact with other molecules [96]. The surface containing electrons and holes generate hydroxyl and other radicals formed by the oxidation of oxygen, water, or hydroxide ions [95]. Superoxide and perhydroxyl radicals are other radicals formed from the reactions of electrons with adsorbed oxygen [97]. The generated radicals can then oxidize the pollutants at the solid-liquid interface. Direct oxidation of the pollutant may also be possible by photo-generated holes and may proceed in competition with hydroxyl radical oxidation, as proposed for benzene oxidation

[98], although Okamoto et al. [99] did not report the existence of this pathway for phenol. Oxidation by holes was suggested for some acids, such as trichloroacetic acid and oxalic acid, which are formed as intermediates from the oxidation of chlorinated ethanes by hydroxyl radicals [100]. The photogeneration of radical species can be represented by the following reactions [101]:



where $h\nu$ represents UV radiation, h^+_{VB} represents valence-band holes, e^-_{CB} represents conduction-band electrons, and $\text{O}_2^{\bullet-}$ represents superoxide ion. H_2O_2 , which can also be generated from the superoxide ion by various mechanisms, can also be a source for hydroxyl radicals by further reacting with electrons or superoxide ions and by photolytic disassociation [102]. In the presence of species that can be reduced, such as metals and oxygen, oxidation of the organics was enhanced [96]. The recombination of electrons and holes was reportedly the main factor in limiting oxidation rates of organic substrates [96]. Kormann et al. [103] determined that the reaction of surface-bound hydroxyl radicals with the adsorbed organic compound was the rate determining step. TiO_2 was shown to act as a true catalyst with no significant changes in the activity after repeated use [104]. The principles and mechanisms of photocatalysis were described in detail by Schiavello [105].

Numerous reports of pollutant degradation with mineralization to inorganic products in several cases have been reported:

- Aliphatic acids:
acetic acid and chloroacetic acids [106]
- Alkanes:
pentane, heptane, isooctane, paraffin, and polyethylene [98]
dodecane, dodecyl sulfate, 1-bromododecane, 1-decanol, and decanoic acid [107]
- Aromatic compounds:
1,3-diphenylisobenzofuran [108]
p-dichlorobenzene [109]
benzene [98,110]
benzoic acid, naphthalene, and fluorescein [111]
phenol [98,111-114]
dimethyl phthalate, diethyl phthalate, dibutyl phthalate, and bis
(2-ethylhexyl)-phthalate [115]
di-n-butyl-ortho-phthalate [116]
- Chlorinated and brominated aliphatic compounds:
TCE, PCE, and dichloroethane [104,117-119]
trichloromethane (chloroform), carbon tetrachloride, and dichloromethane
[103,104,119-123]
1,1- and 1,2-dibromoethane [124]
di-, tri-, and tetrachloro- derivatives of methane, ethane, and ethylene [125]
- Chlorophenols:
2-, 3- and 4-chlorophenol [111,126-129]
2,4,5-trichlorophenol [130]
2,4-dichlorophenol and other di- and trichlorophenols [95,128,131]
- Colored organic compounds:
methyl violet [132]
methylene blue, Rhodamine B, methyl orange, and salicylic acid [133]
organic dyes [134]

pathway for phenol. Oxidation of oxalic acid, which are formed by hydroxyl radicals [100]. The reactions [101]:

es, e^-_{CB} represents conduction-band electrons can also be generated from the hydroxyl radicals by further reacting [102]. In the presence of species which are enhanced [96]. The rate of reaction in limiting oxidation rates of the oxidation of surface-bound hydroxyl species. TiO_2 was shown to act as a photocatalyst [104]. The principles and mechanisms of photocatalysis [105].

and decanoic acid [107]

bis

chloromethane

ethylene [125]

28,131]

acid [133]

brown or black wastewater from pulp and paper mills [135]
mercurochrome dye [136]

- Cyanide [137,138]
- DDT [139]
- Fluorinated aromatic compounds:
2-, 3-, and 4-fluorophenol, and 2,4- and 3,4-difluorophenol [140]
- Gas-Phase pollutants:
toluene [141]
acetone, 1-butanol, butyraldehyde, formaldehyde, and *m*-xylene [142]
TCE [143-145]
- Herbicides:
2,4,5-trichlorophenoxyacetic acid [130]
molinate [146]
bentazon [147]
atrazine, simazine, trietazine, prometon, and prometryn [148]
- Methyl alcohol [109]
- Methyl vinyl ketone [131,149]
- Nitroaromatics and amines:
proline, theophylline [150]
n-pentylamine, piperidine, pyridine, phenylalanine, desipramine, thiothiazine, penicillamine, isosorbide dinitrate, 4-nitrocatechol, 2,4-dinitrophenol, cyclophosphamide, 5-fluorouracil, atrazine, ethylene diaminetetracetic acid, and tetrabutylammonium phosphate [150,151]
nitrophenols [152]
benzamide and 4-hydroxybenzamide [153,154]
- Organophosphorus compounds:
trimethyl phosphate, trimethylphosphite, and *o,o*-dimethyl ammonium phosphodithioate [155]
dimethyl-2,2-dichlorovinyl phosphate (DDVP) and dimethyl-2,2,3-trichloro-1-hydroxyethyl phosphonate (DEP) [156]
4-nitrophenyl diethylphosphate, diethyl-*p*-nitrophenyl diethylphosphate, *O,O*-dimethyl-*S*-(1,2-dicarbethoxyethyl)-phosphorodithioate (Malathion), 4-nitrophenylethylphenyl phosphinate [157]
phenyl-, butyl-, and benzyl-phosphonic acids [158]
- Pesticides
permethrin [159]
metoxuron and carbetamide [26]
- PCP [131,160,161]
- Polychlorinated dioxins and polychlorinated biphenyls (PCBs) [161-163]
3,4-dichlorobiphenyl [164]
- Solvents:
2-ethoxy- and 2-butoxyethanol [165]
- Surfactants:
dodecylbenzene sulfonate [166,167]
nonylphenol ethoxylate and other anionic, cationic, and nonionic surfactants [168-173]
- Urea [123]

Studies on TiO_2 -assisted photodegradation are summarized in Table 4. Most of the above laboratory-scale studies have demonstrated complete degradation and, in several cases, mineralization of the target compound present as a single component in aqueous suspensions. A typical

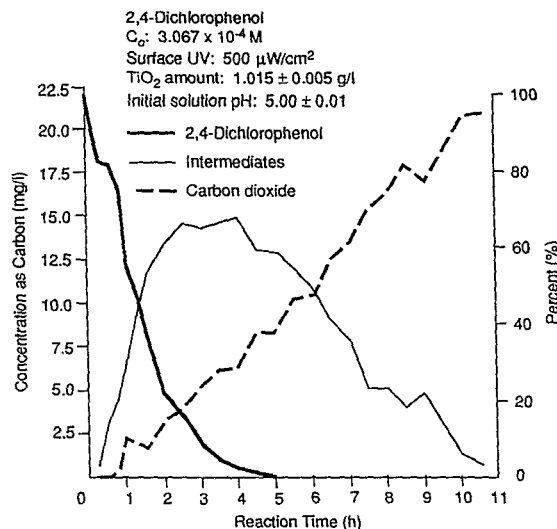


FIGURE 5

The Carbon Distribution of the Photocatalytic Decomposition of 2,4-Dichlorophenol in the Presence of TiO_2 at pH 5 [adapted from Ku and Hsieh, 1992; Ref. 95]; "Reprinted from *Water Research*, 26(11), Y. Ku and C.-B. Hsieh, 'Photocatalytic Decomposition of 2,4-Dichlorophenol in Aqueous TiO_2 Suspensions', 1451-1456, (1992), with kind permission from Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, UK."

representation of the formation of intermediates and CO_2 from contaminant degradation is shown in Figure 5 [95]. However, 2,3-dichlorophenol and 2,3,5-trichlorophenol seemed to undergo only partial mineralization while 2,4,6-trichlorophenol was not mineralized [128]. Additionally, atrazine and other related s-triazine herbicides were also not completely mineralized and cyanuric acid was the final product [148]. The complete degradation of Aroclor 1254, a mixture of PCBs, was also demonstrated [162]. The decolorization of pulp and paper mill wastewater was also demonstrated by photooxidation although ZnO was superior to TiO_2 as a photocatalyst [135]. The determination of organic carbon in water by quantitative conversion of organic compounds to CO_2 using TiO_2 -assisted photocatalysis was proposed [174].

TiO_2 -assisted photocatalysis may also be useful in the removal of certain heavy metals including mercury and silver via their reduction followed by deposition at the catalyst surface [96,175,176]. Mercury and methylmercury salts at concentrations of 100 ppm could be removed from solution by photooxidation in less than 30 min [176]. A laboratory-scale TiO_2 -catalyzed process was used to remove and concentrate copper ions in aqueous solutions [177].

Although photolytic degradation can be conducted with several semi-conductors, e.g., zinc oxide and cadmium sulfide, TiO_2 has been widely studied at concentrations ranging from 1 to 5 g/L and is known to be the most efficient catalyst [160,163]. TiO_2 is also more stable, insoluble, non-toxic, and inexpensive compared to other catalysts [133,162]. The advantage of cadmium sulfide is that it can be activated by visible light whereas TiO_2 can only be activated by UV light [178]. The physicochemical properties of TiO_2 , which are dependent on the method of preparation, can affect the photocatalytic properties [179].

Photocatalytic degradation can be accomplished by artificial light or sunlight (by light in the UV range) [104,156,166,180] eliminating the need for xenon or UV lamps, with comparable rates of degradation. TiO_2 -assisted photocatalysis may also be useful in the treatment of contaminated soils [181] and contaminants present in air emissions [142-145].

Mechanism and Kinetics

Oxygen and water are essential for the photocatalyzed degradation and mineralization of the organic pollutants [113,126,160]. Chlorobenzene was oxidized to 2- and 4-chlorophenol, which on dechlorination formed the corresponding benzoquinones and hydroquinones [117]. However, condensation products, such as 4,4'-dichloro-1,1'-biphenyl, were also formed from chlorobenzene. Several additional intermediate products including dichlorophenols were formed from dichlorobenzene. No ring cleavage products were detected.

However, several researchers later demonstrated the complete mineralization of phenolic and complex aromatic compounds. 2- and 3-Chlorophenol were mineralized to innocuous products [129]. The chlorophenols were hydroxylated at the *para* position to yield the corresponding chlorohydroquinone [128,129]. Upon further hydroxylation, chlorohydroquinone formed hydroxyhydroquinone, which decomposed to carboxylic acids and carbonyl compounds, with CO₂ and inorganic chloride as the other products [129]. The degradation of chlorophenols proceeded by addition of hydroxyl radical at the *para* position [128].

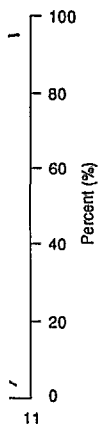
The complete mineralization of PCP [160], and dioxins and biphenyls [163] was demonstrated. The formation of inorganic products, carbonate, nitrate, ammonium, and phosphate ions, was reported from various nitroaromatic compounds and amines [150,151]. TCE was mineralized with dichloroacetaldehyde as an intermediate [121]. Several chlorinated byproducts were formed from the degradation of TCE and PCE [182]. At pH 7, less than 4% of TCE degraded was recovered as dichloroacetaldehyde and dichloroacetic acid with traces of trichloroacetaldehyde and trichloroacetic acid formed. At pH 8, less than 15% of PCE degraded was recovered as dichloroacetic and trichloroacetic acids. Two pathways were proposed for the degradation of TCE and PCE [182]: (i) an oxidative pathway in which the contaminant was oxidized by hydroxyl radicals forming hydroxylated chloroalkene radicals, which were further oxidized yielding trichlorinated byproducts, CO₂, and inorganic chloride by several steps; and (ii) a reductive pathway in which the contaminant was reduced by electrons to form dichlorinated byproducts (Figure 6). In the degradation of chlorinated ethanes, C-centered radicals, generated from the C-H bond cleavage by hydroxyl radicals, and peroxy radicals, generated from oxygen addition, were proposed as the key radical intermediates [100]. Chlorinated acids, HCl, and CO₂ were formed as the principal intermediates with some formation of aldehydes and formic acid as well. Further photodegradation of the intermediates led to complete mineralization [100]. The photodegradation of surfactants proceeds by initial cleavage of the aromatic group, followed by the degradation of the alkyl or ethoxylate groups [170]. The degradation of triazine herbicides to cyanuric acid and inorganic chloride and nitrate proceeded by alkyl chain oxidation, dealkylation, dehalogenation, and hydroxylation reactions [183].

TiO₂-assisted photooxidation of pollutants follows Langmuir-Hinshelwood kinetics [97,184], wherein the initial rate of disappearance of the pollutant can be described by its concentration and its adsorption and reaction characteristics as follows:

$$-\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (1)$$

where C is the concentration of the pollutant in solution, k is the rate constant, K is the adsorption equilibrium constant of the pollutant on the TiO₂ surface, and t is the time involved. The kinetics of oxidation of several organics were studied by Matthews [97,184,185]. The adsorption equilibrium constant may inversely vary with the substrate concentration, as shown for phenol [186]. The rates of disappearance and mineralization of different pollutants were reported by several researchers. For example, between 21 and 46 minutes were required for 50% mineralization of colored organics present at 10 μM [133]. Using solar illumination, 50 ppm of chloroform could be completely mineralized in a period of 3 h [104]. The mineralization of 2-chlorophenol and 4-chlorophenol required about 24 h [126,129], whereas complete disappearance of 2-chlorophenol occurred in 6 h [129].

The following order of chlorinated aliphatic compounds with decreasing rates was reported:



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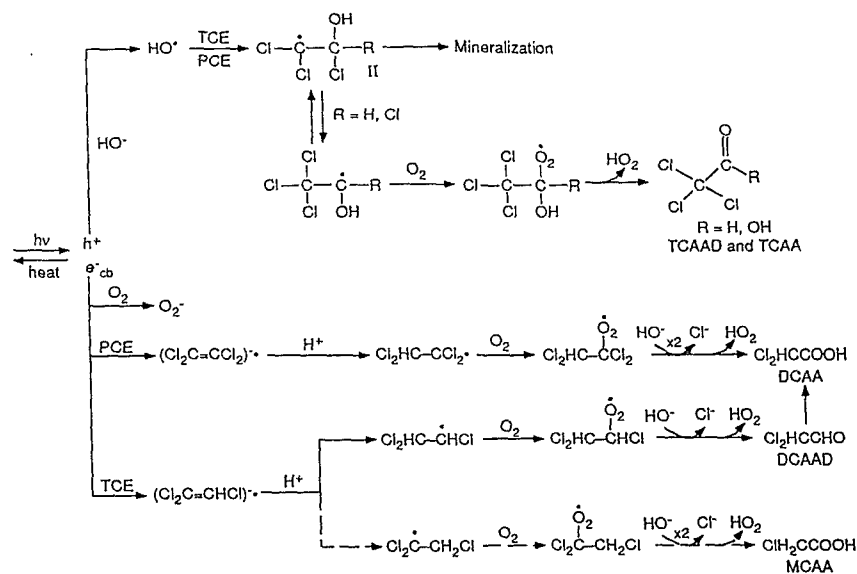


FIGURE 6
Proposed Routes for the TiO₂-Mediated Photodegradation of TCE and PCE and Byproduct Production [adapted from Glaze et al., 1993; Ref. 182]; "Reprinted with permission from **Environmental Science and Technology**, Copyright 1993, American Chemical Society."

dichloroacetaldehyde > TCE > PCE > dichloroacetic acid, dichloromethane > trichloromethane > 1,2-dichloroethane, monochloroacetic acid, tetrachloromethane > trichloroacetic acid [117]. In general, compounds of similar saturation with a higher degree of chlorination had lower rates of degradation and ethylenes were degraded faster than ethanes with the same degree of chlorination [125]. The degradation rate of chlorophenols decreased in the order: monochlorophenol > dichlorophenol > trichlorophenol [128]. For different monochlorophenols, the rate decreased in the order: 4-chlorophenol > 3-chlorophenol > 2-chlorophenol. For dichlorophenols, the rate decreased in the order: 2,6-dichlorophenol, 2,5-dichlorophenol > 3,4-dichlorophenol, 2,4-dichlorophenol > 2,3-dichlorophenol [128]. The kinetics may be different during the treatment of mixtures of contaminants. 4-Chlorophenol exhibited apparent zero-order kinetics but its degradation was first order when present in an equimolar mixture of 2,4-dichlorophenol and 2,4,5-trichlorophenol; however, the extent of degradation of 4-chlorophenol was comparable when present as a single component and in the mixture [187].

Although the time required for complete degradation of some compounds may be similar, the time required for complete mineralization may be markedly different. For example, approximately 30-40 min are required to completely remove both PCE and benzene. However, while quantitative CO₂ production from PCE occurs in the same time-frame, approximately 150 min are required for CO₂ production from benzene [188]. This is most likely due to the formation of stable intermediates in the case of benzene [188]. Only about 100 min were required for complete disappearance of benzamide; however, 150 h of irradiation were needed for complete mineralization to inorganic nitrate [153].

The rate of degradation is also influenced by several other factors, such as pH, TiO₂ concentration, temperature, dissolved oxygen, light intensity, and dissolved anions and cations. The optimum TiO₂ concentration was determined to be 1.4 g/L for 3 × 10⁻⁴ M of 2,4-dichlorophenol [95]. Higher TiO₂ concentrations result in lower rates probably because of lower light penetration in the presence of increased solid catalyst. The pH effect is slight and may vary for different organics [95]. The rate of degradation of chloroform was not significantly affected by pH in the range of 4 to 11; the rate was slightly higher at higher pH values with the optimum at pH 9 and the rate was 50% of the maximum at pH 3. However, in the presence of 5 mM chloride, the pH dependence was more

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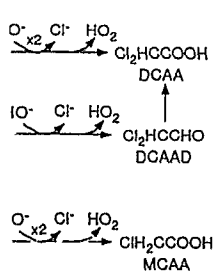
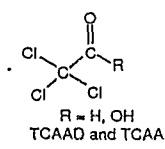
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The reaction rate dependence of salicylic acid, a model compound, on temperature could be described by Arrhenius kinetics; an activation energy of 11±0.8 kJ/mol was reported with a temperature increase of 54°C required to double the rate constant [111]. Dissolved oxygen concentration increased the rate of degradation of chlorophenols [101] and phenol [128]; the rate at a dissolved oxygen concentration of 5 ppm was approximately 40% of that at 27 ppm [128].

Ollis et al. [188] summarized the effect of light intensity on the rate of reaction. At low illumination levels, the rate is directly proportional to the intensity; at intermediate illumination levels, the rate varies as the square root of the intensity; and at high illumination levels, the rate is independent of the intensity and is constant when the mass transfer limit is encountered. However, the quantum efficiency of degradation (the proportion of the extent of degradation to the number of photons required) is constant at low illumination levels, is inversely proportional to the square root of the intensity at intermediate levels [103], and is inversely proportional to the intensity at high levels.

Various cations and anions affect the rate of photodegradation. Concentrations of 1 mM Co²⁺, 0.2 mM Al³⁺, and 0.5 mM Zn²⁺ reduced the reaction rate of chloroform by 50%, 70%, and 60%, respectively [103]. In contrast, Fe³⁺ ions increased the rate of phenol oxidation [189], 5 × 10⁻⁴ M Fe³⁺ improved the rate of phenol oxidation [190], and 0.49 mM of Ag, Hg, Cu, Pt, and Cd each significantly enhanced the photooxidation of salicylic acid in the absence of oxygen [96]. The degradation rates of toluene were enhanced in the presence of 10⁻⁵ M Cu²⁺, Fe³⁺, and Mn²⁺ at pH 3, with decreased rates at higher concentrations and higher pH values; whereas, Ni²⁺ and Zn²⁺ had no significant effect on the rate [191]. Under optimum conditions of pH 3 and 10⁻⁵ M Cu²⁺, a two-fold increase in the initial reaction rate was observed; increased reaction rates were attributed to homogeneous mechanisms and not to reactions at the catalyst surface. The beneficial effect of Fe³⁺ may be because it can act as an electron scavenger and can generate additional hydroxyl radicals by Fenton's reaction [190]. Addition of metals to contaminated waters to enhance photodegradation is not an attractive option because the enhancement is not significant enough to outweigh the costs of pH adjustment and metal addition followed by removal [191]. Organic-contaminated waters also containing high concentrations of metals may need to be pretreated for metal removal for effective photodegradation [191]. Another possible effect of added metal ions that has not been studied in detail is the possible change in reaction mechanism yielding a different product distribution, as known to occur during photooxidation of methanol in the presence of Na⁺ [192].

Advantages/Disadvantages

The primary advantages of semi-conductor-assisted photodegradation as a treatment process involves its ability to degrade a wide range of pollutants with rapid rates of reaction under moderate reaction conditions. The ability to mineralize pollutants completely to CO₂ makes it an attractive treatment option, especially in cases where alternative treatment technologies are ineffective (e.g., when the pollutants are refractory towards biological degradation). TiO₂-assisted photocatalysis has an advantage over the UV/H₂O₂ oxidation process in the degradation of colored organics as these compounds do not interfere with TiO₂-assisted photocatalytic reactions. While UV/H₂O₂ oxidation is accomplished most readily using wavelengths in the 200-280 nm range, TiO₂-assisted photooxidation can be accomplished with higher wavelengths since TiO₂ has an absorption maximum at approximately 340 nm [134]. Thus, TiO₂-assisted photocatalysis can be accomplished with solar radiation or simulated sunlight at wavelengths greater than 340 nm, albeit with a lower overall efficiency. TiO₂-assisted photocatalysis may also be applicable in the treatment of water contaminated with both organics and heavy metals [96].

Although, in most cases, half-lives of mineralization of pollutants are on the order of a few hours, substantial irradiation times are required for some pollutants and TiO₂-assisted photodegradation may not be economical in such cases. For e.g., cyanide, 2,7-dichlorobenzo-*p*-dioxin, and benzamide require about 30, 90, and 150 h of irradiation time, respectively [138,153,163]. In most studies, the pollutants have only been tested as single compounds at low concentrations ranging from ppb to low ppm levels, typical of those encountered during treatment of

groundwater and drinking water. Few studies have evaluated the efficacy of TiO₂-assisted photodegradation in the treatment of mixtures of contaminants and actual wastewaters. The process is unlikely to be used in the treatment of high-strength industrial wastewaters or for the large-scale direct clean-up of contaminated soils. Loss of efficiency due to competing substrates in the case of mixtures, interference by dissolved anions and cations, which cause significant reductions in rates of photodegradation, and light interference by high concentrations of soils are likely problems in industrial wastewaters and soils. However, soils spiked with 2-chlorophenol, dioxin, and atrazine could be treated using soil slurries up to 60 g/L [181]. The economics of application for soil decontamination are not known.

Glaze et al. [182] pointed out that during oxidation of TCE and PCE, several chlorinated byproducts were formed, at least one of which, dichloroacetic acid, is a known carcinogen and has greater toxicity than either TCE or PCE. However, several researchers have shown quantitative conversion of chlorinated organics to innocuous endproducts such as inorganic chloride and CO₂ [104,117,121]. Also, PCP and 2,4-dichlorophenol were completely detoxified (as judged by toxicity to activated sludge microorganisms) by photolytic oxidation; however, the toxicity increased during the treatment most likely due to the formation of intermediate compounds more toxic than the parent compound [131]. Since toxic byproducts are formed during the treatment process, the effluent from such a process needs to be carefully analyzed for residual compounds and toxicity as incomplete treatment may cause more of a treatment problem.

Process Improvements

The TiO₂ catalyst can also be used as a stationary phase attached to a support medium, such as silica gel or fiberglass [133,193,194], glass beads [195], or in ceramic membranes [196] instead of suspended particles, thereby avoiding the need for a separation step followed by resuspension of the particles in a treatment process [133]. Coating TiO₂ on the interior surface of glass tubes [97,151] was also used as a method of catalyst support. Immobilization of the catalyst can, however, lead to reactant mass transfer limitations in the apparent rates of reaction and, which is indicated by the dependence of the rate constants on the flow rate of the reactant solution in immobilized systems [188,197], as demonstrated for salicylic acid [111] and chlorophenols [102]. For example, the degradation rate of phenol obtained with a suspension of TiO₂ was approximately 2.6-fold faster than that obtained with TiO₂ immobilized on sand [186]. In reactors using TiO₂ suspensions, the mass transfer rates are large in comparison with the intrinsic reaction rates and the apparent reaction rates are controlled by the intrinsic reaction rate parameters [198].

The TiO₂-assisted photodegradation of TCE and PCE was significantly enhanced by amendment with H₂O₂ [118]. Augmentation with 136 mg/L H₂O₂ decreased the reaction time for disappearance of TCE from 75 min to about 20 min [118]. The enhancement was believed to be due to the presence of increased hydroxyl radicals [118], which could either be derived from the photolysis of H₂O₂ or from the increased reactions of holes with hydroxide ions as a result of decreased hole-electron recombination due to the abstraction of surface electrons by H₂O₂ [188]. H₂O₂ could also increase oxygen concentrations which can enhance degradation [188]. Harada et al. [156] also showed that 1.2×10^{-2} M H₂O₂ shortened the half lives of the pesticides DDVP and DEP by 10- and 2-fold to 9 and 17.5 min, respectively. Similar enhancements were demonstrated for the photodegradation of chloral hydrate [199], phenol [200], and chlorophenols [101]. H₂O₂ also significantly reduced the half-lives of degradation of various chlorinated methanes, ethanes, and ethylenes; the highest reduction by 25.5-fold was for 1,2-dichloroethylene, whereas, the half-lives of chloroform, carbon tetrachloride, and 1,1,1-trichloroethane were not affected by H₂O₂ [125]. In contrast, 0.01 and 0.1 mM H₂O₂ reduced the yield of CO₂ from the degradation of di-n-butyl-ortho-phthalate by approximately 71% and 46%, respectively [116]. However, the highest enhancement of photodegradation was achieved when H₂O₂ and Fe³⁺ ions were used with TiO₂ [116], as also demonstrated for phenol [189].

The catalytic activity of TiO₂ can also be improved by loading metals, such as silver or platinum, on the catalyst surface. Kondo and Jardim [123] loaded silver at 1% (w/w) on TiO₂ and improved the removal of chloroform from 35% (obtained using unloaded TiO₂) to 44% and the

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removal of urea from 16% to 83%. Similarly, platinum loading improved the degradation rates of DDVP and DEP by factors of 4.5 and 6, respectively [156], times that of cyanide [137], and that of chlorinated aliphatic compounds [125]. The drawback of this enhancement is the transfer of the loaded silver into solution at 0.5 ppm, which is 10 times higher than its regulatory limit and is an added pollution problem [123]; the dissolution of platinum was not reported.

Inorganic oxidants also increase the rate of photocatalytic degradation and influence the reaction mechanism. Peroxydisulfate and periodate can react with the photogenerated electrons and, thereby, prevent the recombination of electrons and holes and generate other oxidizing intermediates which can participate in oxidative degradation [101,201]. Enhancements in rates of degradation would be more useful for compounds with low rates of degradation and were reported for 2-chlorophenol, 2,7-dichlorodibenzodioxin, and atrazine [201]. For example, disappearance of 4 ppm of the dioxin was complete in 30 and 60 min using 0.1 M periodate and peroxydisulfate, respectively; whereas 87.5% disappearance required about 120 min using photodegradation by TiO₂ alone. These inorganic oxidants were reported to have the advantages of being nontoxic and also producing only nontoxic products, such as sulfate and iodide [201].

Technology Status

Most studies on TiO₂-assisted photocatalysis have been conducted at the laboratory-scale with reaction volumes ranging from 20 mL to 5.5 L. Laboratory-scale studies [104,111,180,194] have been scaled up to the pilot plant stage using large parabolic troughs and heliostats to concentrate the sunlight [202]. Large-scale tests conducted at flow rates ranging from 20 to 100 L/min in a reactor volume of 250 L [96] demonstrated the effectiveness of the process to treat low levels of TCE and PCE (up to 10 ppm); however, it was concluded that a very large surface area of the solar collectors would be required and the process would be impractical to treat chlorinated methanes and ethanes, which are more difficult to degrade [96].

Mehos and Clyne [203] reported the successful completion of field tests of TiO₂-assisted solar detoxification of groundwaters containing TCE and other volatile organic compounds. The system used consisted of two strings of solar parabolic troughs, each 120 ft long, had a maximum flow rate of 30 gpm, and used 1700 ft² of solar concentrators. Concentrations of TCE were reduced from 200 ppb to less than 5 ppb in about 6 min. Process modifications were used to increase efficiency and reduce system costs. A system which does not use concentrated sunlight and yields a larger reactor area than the system with parabolic trough concentrators was found to result in superior TCE degradation rates both in laboratory and field tests. These process improvements resulted in lowering the cost of the process by nearly 50% to \$8/1000 gal of contaminated water, estimated for a flow rate of 100,000 gal/d. Although the current cost of the system is still higher than the costs of alternative treatment technologies of activated carbon adsorption (\$6/1000 gal) and UV/H₂O₂ treatment (\$4/1000 gal), further improvements in the future were believed to lower the costs below those of the alternative technologies. The solar detoxification process was reportedly being used to treat groundwater contaminated with spilled jet fuels [203].

SUMMARY AND CONCLUSIONS

UV/H₂O₂ systems can effectively oxidize numerous compounds ranging from chlorinated aliphatic compounds to several aromatic compounds. There are two primary mechanisms by which UV/H₂O₂ oxidation occurs: oxidation by hydroxyl radicals generated from H₂O₂ by UV irradiation and direct activation or oxidation of contaminants by UV light. The contaminants can be completely detoxified to innocuous inorganic compounds. Treatment times for complete degradation of halogenated aliphatic compounds in the UV/H₂O₂ systems are on the order of several minutes.

There are numerous full-scale treatment systems in operation using the *Perox-Pure* (trademark, Peroxidation Systems, Inc.) oxidation system, which is a UV/H₂O₂ oxidation process using high intensity UV lamps. Pulsed lamps, which generate a wide range of UV wavelengths, are a significant improvement in the UV photodegradation technology. Petroleum hydrocarbons, PAHs, unsaturated and saturated halogenated aliphatic compounds, pesticides, cyanides, PCBs, dioxins, nitrites, nitrates,

and TNT reportedly have all been degraded using pulsing UV lamps. UV/ozone/H₂O₂ systems should also be considered as they may be superior and more cost-effective than UV/H₂O₂ systems in some cases, such as with degradation of complex mixtures of contaminants. Reported cost estimates for the treatment of contaminated groundwater ranged from \$0.59 to \$2.59/1000 gal for the conventional UV/H₂O₂ process and \$0.33/1000 gal for pulsed UV photolysis. These systems are not applicable for the treatment of contaminated soils. The application of these systems is primarily limited to the treatment of groundwater containing low levels of contaminants. Suspended solids and some inorganic and organic species exhibiting color have an adverse effect on the performance of the UV/H₂O₂ systems and require additional processes for effective treatment.

Fenton's reagent is a mixture of H₂O₂ and ferrous iron, which produces hydroxyl radicals with the ability to effectively oxidize numerous aromatic compounds such as phenols, chlorinated phenols, and PAHs. To date, the degradation of chlorinated aliphatic compounds has only been studied to a limited extent. Reactions have been completed in time periods ranging from 5 min to 2 h for compounds in solution and up to several hours and days in soils. Degradation of organic compounds occurs primarily by hydroxylation reactions. Fenton's reagent has been applied in the treatment of wastewater containing phenol and formaldehyde at an industrial scale. Research examples of pretreatment using Fenton's reagent for phenolic compounds prior to biological treatment are also known. Fenton's reagent was also proposed as a soil decontamination technology, but most studies to date have investigated contaminant-spiked soils and not soils from actual contaminated sites. As a result, the effect of aging of the contaminants on the soils has not been addressed. The treatment of hydrocarbon-contaminated soils and pretreatment prior to bioremediation of PAH-contaminated soils by Fenton's reagent were reported using soils from contaminated sites.

Fenton's reagent is particularly advantageous in situations where alternative technologies are not effective (e.g., in the decolorization of dye wastewaters and in the degradation of higher molecular weight PAHs and PCE). Capital equipment costs for application of Fenton's reagent can be expected to be very low compared to the UV/H₂O₂ oxidation process. This technology has been field-tested for soil clean-up only to a limited extent. The studies conducted to date have primarily been performed at the laboratory-scale level and more field demonstrations are needed before Fenton's reagent treatment gains acceptance as a full-scale soil clean-up technology.

The principle behind TiO₂-assisted photocatalysis involves the photoexcitation of TiO₂ particles by UV light causing the formation of electrons and holes, which can generate hydroxyl and other radicals formed by the oxidation of oxygen, water or hydroxide ions. The generated radicals can then oxidize the pollutants. Direct oxidation of the contaminant by photo-generated holes or reduction by electrons is also possible. Numerous inorganic and organic pollutants have been effectively degraded and, in several cases, completely mineralized using TiO₂-assisted photocatalysis in laboratory-scale systems. However, most studies have investigated pollutants present as single compounds at low concentrations and not actual wastewaters. The pollutants investigated include several chlorinated aliphatic compounds, phenols, chlorinated and fluorinated aromatic compounds (such as chlorophenols, chlorobenzenes, PCBs, and dioxins), surfactants, nitroaromatics and amines, organophosphorus insecticides, colored organics, and PAHs.

TiO₂-assisted photocatalytic degradation can also be accomplished using solar illumination and is most likely to be developed into a process for compounds (such as TCE) with high rates of degradation. However, the process may be unsuitable for contaminants which are slower to degrade, such as chlorinated methanes and ethanes, compared to TCE because of the need for large collector surface area for solar-driven processes. Based on longer half-lives of degradation, a large number of aromatic compounds may also be unsuitable target compounds for TiO₂-assisted photodegradation in current systems. Successful field tests of TiO₂-assisted solar detoxification of groundwaters containing TCE and other volatile organic compounds have been recently demonstrated. A pilot-scale system which does not use concentrated sunlight, and thereby, eliminates the costs associated with solar collectors, was found to yield superior TCE degradation rates. The cost of the process is estimated to be about \$8/1000 gal of contaminated water. Systems which do not use concentrated sunlight and yield high rates of degradation are likely to be extended to the treatment of compounds which have low rates of degradation in current systems. The economics of TiO₂-assisted photodegradation using UV lamps for large-scale systems are not known; it is possible that solar

illuminated system may not be applicable or loss of efficiency significantly reduced. It has not been determined.

For the pollutants contained in (2) groundwater.

Gaseous inorganic compounds, sulfides and volatile organic compounds containing organic H₂O₂ scrubbing as acids. UV irradiation phase reactions system and Fenton degradation is considered.

Groundwater unsaturated and (and alkenes), a contaminants are to the ppb level compounds are accomplished through application of technology because of the. However, the advances in treatment is not aliphatic compounds efficient. In a hydroxybenzanthrone, but more tested [154].

High concentrations of complex mixtures with characteristics are phenols, chlorinated and nitroaromatics. Periods combined make the application technically infeasible. The technology of them competitive wastewater cost using high concentration factor contribute economically pretreatment processes, particulate degradation by

Pesticides found in soil can be used for Fenton's reagent.

UV/ozone/H₂O₂ systems are more likely to find application. Additionally, TiO₂-assisted photodegradation may not be applicable for the treatment of industrial wastewaters because of interference of illumination or loss of efficiency due to dissolved anions and cations and competing substrates, which can significantly reduce rates of photodegradation. The process economics for soil decontamination have not been determined.

For the purpose of a comparison of the applicability of the three chemical oxidation processes, pollutants can be broadly classified as occurring in the following four media: (1) air, (2) groundwater, (3) industrial wastewater, and (4) soil, sludges and sediments.

Gaseous pollutants present in air emissions from various chemical plants are primarily inorganic compounds such as nitrogen and sulfur oxides and odor-causing compounds such as sulfides and various sulfur-containing compounds. Stripping operations generate emissions containing organic compounds. Nitrogen and sulfur oxide compounds can be adequately treated with H₂O₂ scrubbing of the emissions resulting in recovery of the oxidized pollutants in aqueous solutions as acids. UV irradiation is applicable for the treatment of gaseous organic compounds because vapor phase reactions are a feasible mechanism by which degradation can occur. However, the UV/H₂O₂ system and Fenton's reagent are not applicable; TiO₂-assisted photodegradation for vapor phase degradation is conceivable and has been demonstrated in a few laboratory studies.

Groundwater contamination is caused most commonly by pollutants such as chlorinated unsaturated and saturated aliphatic compounds (e.g., TCE, PCE, and various other chlorinated alkanes and alkenes), and some aromatic compounds (e.g., gasoline and diesel hydrocarbons). These contaminants are usually present at low concentrations in the low ppm range requiring treatment down to the ppb levels. Low concentrations of dissolved salts and low concentrations of other organic compounds are typical of contaminated groundwater. The treatment of groundwater can be readily accomplished by UV/H₂O₂ systems as evidenced by numerous full-scale units in operation. The application of the TiO₂-assisted photocatalytic process in groundwater treatment appears promising because of the numerous reports of complete mineralization of a wide range of contaminants. However, the process may be unsuitable for contaminants with low degradation rates and further advances in technology are needed to improve its economic competitiveness. Fenton's reagent treatment is not likely to be used for groundwater treatment because the degradation of chlorinated aliphatic compounds has been attempted only to a limited extent and UV/H₂O₂ systems are more efficient. In a direct comparison of the three systems for the degradation of benzamide and 4-hydroxybenzamide in water, the two photolytic processes were concluded to be comparable to each other, but more efficient and more nonspecific than Fenton's reagent treatment under the conditions tested [154].

High concentrations of organic compounds, a range of mixtures from a few components to complex mixtures, high BOD values, and high-dissolved salt concentrations are all typical characteristics of industrial wastewaters. A few pollutants commonly present in industrial wastewaters are phenols, chlorinated aromatic compounds, colored organic compounds, pesticides, surfactants, and nitroaromatics. The requirement for higher illumination intensities and longer treatment time periods combined with possible interferences due to suspended solids and dissolved salts will likely make the application of the UV/H₂O₂ and the TiO₂-assisted photodegradation processes economically or technically impractical for the treatment of high-strength industrial wastes. Further advances in the technology of these two processes or the use of combinations of technologies may, however, make them competitive. On the other hand, Fenton's reagent treatment appears to be least affected by other wastewater constituents. Additionally, high concentrations of organic compounds can be treated by using high concentrations of H₂O₂ without any major increase in the capital costs. Since the primary factor contributing to the chemical costs of Fenton's reagent is the cost of H₂O₂, the process will be economically feasible only up to a particular H₂O₂ concentration. Therefore, Fenton's reagent pretreatment prior to biological treatment may be the most cost-effective alternative for industrial wastes, particularly in cases where the wastes contain contaminants which are resistant to biological degradation but are amenable to Fenton's reagent treatment.

Pesticides, PCP, PCBs, PAHs, dioxins, and petroleum hydrocarbons are typical pollutants found in soil contamination situations at a wide range of ppm concentrations. The primary application niche for Fenton's reagent is most likely to be in the clean-up of contaminated soils because of its

Photoexcitation of TiO₂ particles generate hydroxyl and other reactive generated radicals can then generate holes or reduction by have been effectively degraded photocatalysis in laboratory-scale as single compounds at low and include several chlorinated natic compounds (such as nitroaromatics and amines,

and using solar illumination and as TCE) with high rates of which are slower to degrade, of the need for large collector degradation, a large number of 2-assisted photodegradation in oxification of groundwaters y demonstrated. A pilot-scale ates the costs associated with . The cost of the process is hich do not use concentrated o the treatment of compounds onomics of TiO₂-assisted own; it is possible that solar

demonstrated ability to degrade many of the refractory aromatic compounds which are common soil contaminants and because the photodegradative processes are not directly applicable for soil treatment. Fenton's reagent is likely to be applied in on-site treatment systems such as land treatment or slurry reactors. Fenton's reagent pretreatment followed by biological treatment may be the most cost-effective treatment option. The treatment of sludges and sediments, although conceivable, has not been attempted using Fenton's reagent.

Of the three oxidation systems discussed, the technology for the UV/H₂O₂ oxidation process is the most advanced with numerous successful full-scale applications already in existence for groundwater treatment. Applications of both the Fenton's reagent and TiO₂-assisted photodegradation processes are currently being developed with the concept proven in numerous laboratory-scale studies for a wide range of contaminants. However, both of these processes have only been studied at the pilot/field scale to a limited extent. The application of Fenton's reagent as a pretreatment step prior to biological treatment for industrial wastes and contaminated soils appears promising. Process improvements such as improved system configuration and improved quantum efficiency are likely to improve the applicability and economics of TiO₂-assisted photodegradation for groundwater treatment, especially with the use of solar illumination.

NOTATION

AOP	Advanced oxidation process
BOD	Biological oxygen demand
C	Concentration of organic compound
CO ₂	Carbon dioxide
COD	Chemical oxygen demand
2,4-D	2,4-dichlorophenoxyacetic acid
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
DDVP	Dimethyl-2,2-dichlorovinyl phosphate
DEP	Dimethyl-2,2,3-trichloro-1-hydroxyethyl phosphonate
DMP	Dimethylaminomethyl-substituted phenols
e ⁻ _{CB}	Conduction-band electrons
EDTA	Ethylenediaminetetraacetic acid
Fe ₂ O ₃	Ferric oxide
FeSO ₄	Ferrous sulfate
h ⁺ _{VB}	Valence-band holes
H ₂ O ₂	Hydrogen peroxide
k	Rate constant (in the Langmuir-Hinshelwood adsorption isotherm)
K	Adsorption capacity of the organic compound on the catalyst surface (in the Langmuir-Hinshelwood adsorption isotherm)
O ₂ ⁻	Superoxide ion
OCDD	Octachlorodibenzo- <i>p</i> -dioxin
PCBs	Polychlorinated biphenyls
PCE	Perchloroethylene, Tetrachloroethylene
PCP	Pentachlorophenol
pH	Negative logarithm of hydrogen ion concentration
t	Time
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
TCE	Trichloroethylene
TiO ₂	Titanium dioxide
TNT	Trinitrotoluene
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons
UV	Ultraviolet
g/L	grams per liter
gpm	gallons per minute
h	hour

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ly applicable for soil treatment.
ch as land treatment or slurry
tment may be the most cost-
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uantum efficiency are likely to
tion for groundwater treatment,

kJ/mol	KiloJoules per mole
mg/L	milligrams per liter
mg/kg	milligrams per kilogram
min	minute
mM	millimoles per liter
mol	mole
mW/cm ²	milliWatts per square centimeter
nm	nanometer
ppb	parts per billion
ppm	parts per million
V	Volt
W	Watt
w/w	weight per weight
yd ³	cubic yard
μM	micromoles per liter

TABLE 1
Applications of H₂O₂ (Adapted from Degussa Corp., Ref. 2)

Application	Main Industries	Basic Chemical Equations	Problems Solved by H ₂ O ₂
Odor and Corrosion Control	Sewage treatment plants, pulp and paper mills, textile mills, food processing plants	$\text{SO}_4^{2-} \xrightarrow{\text{bacteria}} \text{H}_2\text{S}$ $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2 \text{H}_2\text{O}$	Health hazard (H ₂ S), concrete deterioration
Oxygen Supply	Sewage treatment plants, food processing plants	$2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$	Peak loads overburdening biological waste treatment; anaerobic conditions in holding tanks and lagoons
Removal of Sulfite (SO ₃ ²⁻)	Oil refineries, photo finishing, paper mills, metal finishers, plating shops	$\text{SO}_3^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$ $\text{HSO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$	High oxygen demand, fish toxicity
Removal of Hypochlorite (OCl ⁻)	Chlorine producers, chlorine processors, wastewater treatment	$\text{OCl}^- + \text{H}_2\text{O}_2 \rightarrow \text{Cl}^- + \text{H}_2\text{O} + \text{O}_2$	Corrosion, formation of chlorinated compounds, fish toxicity
Removal of Nitrite (NO ₂ ⁻)	Hardening shops, metal surface treatment, plating shops	$\text{NO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O}$	High oxygen demand, nitrosamine formation
Removal of Cyanide (CN ⁻)	Hardening shops, mining, plating shops, steel mills, coking plants, waste incinerator plants, and pyrolysis plants	$\text{CN}^- + \text{H}_2\text{O}_2 \rightarrow \text{OCN}^- + \text{H}_2\text{O}$ $\text{OCN}^- + 2 \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{CO}_3^{2-}$	Extreme toxicity
Treatment of Photoprocessing Effluent	Film and paper (copy) processors	$\text{SO}_3^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$ $\text{S}_2\text{O}_3^{2-} + 4 \text{H}_2\text{O}_2 \rightarrow 2 \text{SO}_4^{2-} + 2 \text{H}^+ + 3 \text{H}_2\text{O}$ (silver precipitates)	High oxygen demand, silver losses
Oxidation of Fe ²⁺ to Fe ³⁺	Iron and steel mills, galvanizing plants, mineral water bottlers	$2 \text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2 \text{H}^+ \rightarrow 2 \text{Fe}^{3+} + 2 \text{H}_2\text{O}$	pH lowering, iron precipitation
Removal of Formaldehyde (CH ₂ O)	CH ₂ O processing: resin plants, disinfection, etc.	$2 \text{CH}_2\text{O} + \text{H}_2\text{O}_2 + 2 \text{OH}^- \rightarrow 2 \text{HCOO}^- + \text{H}_2 + 2 \text{H}_2\text{O}$	Toxicity
Removal of Phenols	Refineries, coke and gas plants, resin plants, disinfection operations, aviation	Depends on stoichiometry and type of phenol	Toxicity
Removal of Sulfides (S ²⁻)	Leather producers, refineries, tanneries, metallurgical processes, textile mills	$\text{S}^{2-} + 4 \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 4 \text{H}_2\text{O}$	Toxicity, oxygen demand, odors
Removal of Sulfur Dioxide (SO ₂)	Power plants, ore processing, sulfuric acid production	$\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$	Acid rain, emission limits
Removal of Nitrogen Oxides (NO _x)	Power plants, nitric acid users, and producers	$2 \text{NO} + 3 \text{H}_2\text{O}_2 \rightarrow 2 \text{HNO}_3 + 2 \text{H}_2\text{O}$ $2 \text{NO}_2 + \text{H}_2\text{O}_2 \rightarrow 2 \text{HNO}_3$	Toxicity, acid rain
Removal of Chlorine (Cl ₂)	Chlorine producers, chlorine processors	$\text{Cl}_2 + \text{H}_2\text{O}_2 \rightarrow 2 \text{HCl} + \text{O}_2$	Toxicity
Removal of Hydrogen Sulfide (H ₂ S)	Sewage treatment plants, sulfide users	$\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2 \text{H}_2\text{O}$	Extreme toxicity, odors, corrosion
Aseptic Packaging	Food processing plants		Producing and maintaining sterile conditions
De-inking (Recycling of Wastepaper)	Recycling mills		Yellowing and low brightness of recycled pulp
Replacement of Chlorine and Chlorine Dioxide in Pulp Bleaching	Pulp and paper mills		Chlorinated compounds in effluent, low brightness, long bleaching sequences
Removal of Fat, Oil, Grease, and Suspended Solids	Food processing, pulp and paper mills, and textile mills	$2 \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ (as fine bubbles)	Meeting COD, COD, and other discharge limits

1 isotherm)
catalyst surface (in the

TABLE 2
Summary of Ultraviolet Light/H₂O₂ Treatment

Contaminant	Initial Concentration	Degradation or Mineralization Rate/ Reaction time	Degradation/Mineralization Efficiency or Final Concentration	Products	Conditions/ Comments	Reference
Malathion	150 ppm	Initial degradation rate: 0.36 μmol/L-s	100% degradation in 100 min	Not reported	Reactor volume: 1.62 L, 125 W mercury lamp, photon flux: 2.04 x 10 ⁻⁶ Einstein/s, H ₂ O ₂ : 0.19 M, temperature: 25°C, pH: 3.6	Aires et al., 1992 [25]
Dimethylaminomethyl-substituted phenols (DMP) Isophorone	50 ppm 50	60 min	0.05 ppm using 125 ppm H ₂ O ₂ 0.05 ppm using 250 ppm H ₂ O ₂	Not reported	UV irradiation @ 254 nm, average intensity: 1200 μW/cm ²	Borup and Middlebrooks, 1986 [15]
Atrazine	50 ppm	12 min	90% degradation	Endproduct: cyanuric acid	Reactor volume: 500 mL, medium pressure mercury lamp, intensity: 0.7 W/L @ 254 nm, H ₂ O ₂ : 0.06 g/L, pH: 4.7	Chan et al., 1992 [22]
Tannery wastewaters	COD: 3600 mg/L	8 min, 2 min of UV irradiation	90% reduction in COD	Not reported	Pilot scale system, flow rate: 0.2 gpm, 550 W mercury vapor lamp, H ₂ O ₂ : 500 mg/L, metal ion catalyst: 20 mg/L, pH: 12	Chang and Zateiko, 1981 [31]
Groundwater contaminated with: 1,1,1-Trichloroethane, TCE, 1,1-Dichloroethylene, PCE, 1,1-Dichloroethane, Benzene, and Ethylbenzene	20,000 ppb 5000 2000 500 250 500 500	Not reported	200 ppb 5 6 4 20 1 30	Not reported	Flow rate: 22 gpm, Cost: \$3.23/m ³ of groundwater	Cheuvront et al., 1990 [38]
Groundwater contaminated with: Toluene, Total xylenes, Naphthalene, s-Butyl benzene, 1,3,5-Trimethyl benzene, Ethylbenzene, Benzene, 1,2,4-Trimethyl Benzene, Bromoform, Chloroform, n-Butyl Benzene, n-Propyl Benzene, Methylene chloride, and 1,2-Dichloroethane	7000 ppb 3500 900 900 600 500 5000 300 250 200 175 78 20 10	Not reported	100 ppb 100 100 100 100 5 0.7 100 5 5 100 50 5 5	Not reported	Flow rate: 125 gpm, Cost: \$0.67/m ³ of groundwater	Cheuvront et al., 1990 [38]
Groundwater contaminated with: TCE, and PCE	70 ppb 30	Not reported	1 ppb 1	Not reported	Flow rate: 100 gpm, Cost: \$50,000 a year	Cheuvront et al., 1990 [38]
Groundwater contaminated with: Vinyl chloride, 1,1-Dichloroethylene, trans 1,2-Dichloroethylene, cis 1,2-Dichloroethylene, TCE, Toluene, PCE, and 1,1,1-Trichloroethane	500 ppb 50 90 16000 45000 1500 100 275	Not reported	1 1 2 40 50 2 1 150	Not reported	Flow rate: 15 gpm, Cost: \$50,000 a year	Cheuvront et al., 1990 [38]
Groundwater contaminated with: TCE, PCE, trans 1,2-Dichloroethylene, 1,2-Dichloroethane, 1,1,1-Trichloroethane, Methylene chloride, cis 1,2-Dichloroethylene, and Chloroform	100 ppb 50 10 10 20 5 5 150	Not reported	5 4 10 1 20 5 5 100	Not reported	Flow rate: 350 gpm, Cost: \$0.39/m ³ of groundwater	Cheuvront et al., 1990 [38]

Groundwater contaminated with:
Benzene,
Toluene,
Chlorobenzene,
Ethyl benzene, and
Xylenes

TCE, and
Dichloroethylene

Groundwater contaminated with:
Methylene chloride,
1,1,1-Trichloroethane, and
other contaminants

Hydrazine,
EDTA, and
iron

EDA,
EDTA, and
Copper

Ethylene glycol

Trimsol (industrial cutting oil: hydrocarbons, glycols, chloromethyl phenol and a sulfonated compound)

4-Chloronitrobenzene

Case Study 1:
Tetrachloroethylene,
1,1-Dichloroethylene, and
Trichloroethylene

Case Study 2:
Trichloroethylene, and
1,2-Dichloroethylene

Case Study 3:
Chloroform,
1,2-Dichloroethane, and
Methylene chloride

Case Study 4:
Methylene chloride,
Chloroform,
Carbon Tetrachloride
Freon
1,1,1-Trichloroethane,
1,1-Dichloroethylene,
Trichloroethylene,
Toluene,
Tetrachloroethylene,
1,1-Dichloroethane, and
Vinyl chloride

TABLE 2
Summary of Ultraviolet Light/H₂O₂ Treatment

Conditions/ Comments	Reference
Reactor volume: 1.62 L, 125 W mercury lamp, photon flux: 2.04 x 10 ⁶ Einstein/s, H ₂ O ₂ : 0.19 M, temperature: 25°C, pH: 3.6	Aires et al., 1992 [25]
UV irradiation @ 254 nm, average intensity: 1200 μW/cm ²	Borup and Middlebrooks, 1986 [15]
Reactor volume: 500 mL, medium pressure mercury lamp, intensity: 0.7 W/L @ 254 nm, H ₂ O ₂ : 0.06 g/L, pH: 4.7	Chan et al., 1992 [22]
Pilot scale system, flow rate: 0.2 gpm, 550 W mercury vapor lamp, H ₂ O ₂ : 500 mg/L, metal ion catalyst: 20 mg/L, pH: 12	Chang and Zaleiko, 1981 [31]
Flow rate: 22 gpm, Cost: \$3.23/m ³ of groundwater	Chevront et al., 1990 [38]
Flow rate: 125 gpm, Cost: \$0.67/m ³ of groundwater	Chevront et al., 1990 [38]
Flow rate: 100 gpm, Cost: \$50,000 a year	Chevront et al., 1990 [38]
Flow rate: 15 gpm, Cost: \$50,000 a year	Chevront et al., 1990 [38]
Flow rate: 350 gpm, Cost: \$0.39/m ³ of groundwater	Chevront et al., 1990 [38]

Groundwater contaminated with: Benzene, Toluene, Chlorobenzene, Ethyl benzene, and Xylenes	7.6 ppm 24.0 8.8 3.3 46.0	Not reported	100% degradation, all concentrations below detection limit	Not reported	Full scale treatment system	Froelich, 1992 [35]
TCE, and Dichloroethylene	Not reported	Not reported	Not reported	Not reported	Full scale treatment system with improved reactor design and UV output efficiency, flow rate: 150 gpm, capital costs: \$100,000 and operating costs: \$0.25/1000 gal, corresponding costs were \$150,000 and \$0.97/1000 gal with older design	Froelich, 1992 [35]
Groundwater contaminated with: Methylene chloride, 1,1,1-Trichloroethane, and other contaminants	903 ppb 60	Not reported	11 ppb 6	Not reported	Full scale system	Froelich, 1992 [35]
Hydrazine, EDTA, and Iron	150 ppm 450 15	Not reported	< 0.1 ppm < 10 15	Not reported	Full scale system, pH was maintained below 4 to prevent precipitation of metals and loss of efficiency	Froelich, 1992 [35]
EDA, EDTA, and Copper	1400 ppm 50 ppm 5 ppm	Not reported	< 100 ppm < 10 5	Not reported	Full scale system, pH was maintained below 4 to prevent precipitation of metals and loss of efficiency	Froelich, 1992 [35]
Ethylene glycol	1 wt %	210 min @ 10 wt % H ₂ O ₂ , 70 min @ 30 wt % H ₂ O ₂	100% degradation	Intermediate: formic acid, endproduct: CO ₂	Annular recirculation reactor, volume: 3.5 L, H ₂ O ₂ : 10 and 30 wt %, pH drops from 7.5 to 2.5	Gray et al., 1992 [34]
Trimsol (industrial cutting oil: hydrocarbons, glycols, chloromethyl phenol and a sulfonated compound)	15 g in 2.5 L water	350 min	Reduction in the TOC at a rate of 4 ppm/min over the first 60 min	Not reported	Annular recirculation reactor, volume: 3.5 L, H ₂ O ₂ : 30 wt %, temperature: 40°C, pH drops from 8.3 to 2.2 but maintained between 9 and 10 for subsequent experiments using buffer	Gray et al., 1992 [34]
4-Chloronitrobenzene	90 μM	40 min 60-80 min	100% degradation 100% inorganic chloride formation	Inorganic chloride, nitrate, CO ₂	Reactor volume: 4 L, low pressure mercury vapor lamp, H ₂ O ₂ : 1 mM, temperature: 16°C, pH: 7.5, batch recirculation flow rate: 60 L/h continuous flow rate: 60 L/h, H ₂ O ₂ : 0.12 mM	Guittonneau et al., 1990 [20]
Case Study 1: Tetrachloroethylene, 1,1-Dichloroethylene, and Trichloroethylene	704 μg/L 263 54	2.5 min	100% degradation	Not reported	UV dose: 160 W/L, H ₂ O ₂ dose: 7 mg/L- min, pH: 7.5	Huger et al., 1987 [36]
Case Study 2: Trichloroethylene, and 1,2-Dichloroethylene	1924 μg/L 198	4 min	100% degradation	Not reported	UV dose: 160 W/L, H ₂ O ₂ dose: 10 mg/L- min, pH: 7.1	
Case Study 3: Chloroform, 1,2-Dichloroethane, and Methylene chloride	8200 μg/L 16000 2060	45 min	100% degradation	Not reported	UV dose: 160 W/L, H ₂ O ₂ dose: 150 mg/L- min, pH: 8.1	
Case Study 4: Methylene chloride, Chloroform, Carbon Tetrachloride Freon 1,1,1-Trichloroethane, 1,1-Dichloroethylene, Trichloroethylene, Toluene, Tetrachloroethylene, 1,1-Dichloroethane, and Vinyl chloride	4254 mg/L 1843 1217 674 195 167 75 49 29 20 15	45 min	100% degradation	Not reported	UV dose: 590 W/L, H ₂ O ₂ dose: 300 mg/L- min, pH: 7.6	

TABLE 2
Summary of Ultraviolet Light/H₂O₂ Treatment

2,4-Dinitrotoluene	75.8 ppm 204.9	30 min 90	100% degradation in both cases; trace or no aromatic intermediates detected after 30 min @ 75.8 ppm of dinitrotoluene	Intermediates: 1,3-dinitrobenzene, hydroxynitrobenzene, carboxylic acids, and aldehydes, endproducts: CO ₂ , water, and nitric acid	450 W Medium pressure mercury vapor lamp, various H ₂ O ₂ concentrations used, best results with 13, 26, and 52 moles of H ₂ O ₂ /mole of dinitrotoluene, temperature: 27-35°C	Ho, 1986 [16]
Phenol	1 mM	15 min	100% degradation and 100% reduction in COD and TOC	Inorganic products	Reactor volume: 1 L, 400 W high-pressure mercury vapor lamp, H ₂ O ₂ : 14 mM, temperature: 30°C	Kawaguchi, 1992 [24]
Dissolved organic impurities in distilled, and tap water	TOC of distilled water: 46 ± 13 ppb TOC of tap water: 3117 to 3765 ppb	4 h	88% TOC reduction 98%	12% of residual nonpolar organics	Reaction volume: 500 or 5000 mL, 450 W medium-pressure UV lamp, H ₂ O ₂ : 1%, temperature: 40-45°C	Malaiyandi et al., 1980 [28]
Methanol Allyl alcohol Benzene Toluene, <i>p</i> -Cresol Phenol Dimethylphthalate	10.75 ppm 13.5 5.85 9.0 17.5 14.0 14.35	180 min 180 240 300 300 180 300	Disappearance: 38.5% 41.8 58.6 45.4 60.3 49.7 25.4	Not reported	125 W Lamp, 17 x 10 ⁻³ mole quanta/h, H ₂ O ₂ used and pH: 0.53 M 5.3 0.49 5.9 0.57 6.3 0.62 6.5 0.51 5.2 0.42 5.9 0.45 6.7 temperature: 20-25°C	Mansour, 1985 [13]
Meioxuron Carbetamide	20 ppm 20	150 min	> 90% disappearance	Hydroxylated and ring-cleavage products, initial product: hydroxycarbetamide	125 W high pressure mercury vapor lamp, H ₂ O ₂ : 0.17 ppm, temperature: 20-25°C	Mansour et al., 1992 [26]
2-Chlorophenol 2,4-Dichlorophenol 2,4,6-Trichlorophenol	12.6 ppm 11.3 10.0	3 h	Disappearance: 80% 95 100 13, 2, and 15% disappearance by direct photolysis	Catechol and chlorobenzoquinone from 2-chlorophenol, chlorohydroquinone and hydroquinone from 2,4-dichlorophenol, and 4,6-dichlorocatechol from 2,4,6-trichlorophenol	125 W Mercury medium pressure lamp, H ₂ O ₂ : 55 ppm	Moza et al., 1988 [18]
Aliphatic acids: acetic acid propionic acid	0.304 M 0.404 M	15 h 15 h	96.3% disappearance, CO ₂ yield: 104% 97.3% disappearance	methane, formic acid, glycolic acid, tartaric acid, and CO ₂ , methane, ethane, acetic acid, formic acid, lactic acid, B-hydroxypropionic acid, malonic acid, glycolic acid, and CO ₂	60 W low-pressure mercury lamp, H ₂ O ₂ : 1.34 or 1.27 M, temperature: 20°C	Ogata et al., 1981 [12]
1,2-Dichlorobenzene	25 ppm	180 min	55% @ 100 W intensity	Not reported	Reactor volume: 4.6 L, 100 W medium pressure mercury vapor lamp, H ₂ O ₂ /dichlorobenzene mole ratio: 7, improved rate of disappearance at 450 W intensity	Pinto and Rickabaugh, 1991 [21]
Pulp and paper bleaching wastewaters	3288 mg P/L of color; 1721 ppm COD	3 h	70% color removal	Not reported	Annular photoreactor, medium pressure mercury vapor lamp, H ₂ O ₂ : 0.339 M, pH: 11	Prat et al., 1988 [33]
TCE PCE Tetrachloroethane Dichloromethane Chloroform Carbon tetrachloride Ethylene dibromide	58 ppm	50 min @ 20°C and 10 min @ 40°C	1 ppm, 1st order rate constant: 0.0903 min ⁻¹ 0.0921 0.00374 0.00856 0.0166 0.00331 0.00387 (all rates @ 20°C) 100% conversion to chloride in each case	Chloride	Reactor volume: 1.5 L, Quartz low pressure mercury vapor lamp, intensity: 2.5 W @ 254 nm, 55% of lamp immersed in water, H ₂ O ₂ /TCE ratio: 4.5, stoichiometric amount of H ₂ O ₂ used for compounds other than TCE	Sundstrom et al., 1986 [14]

Benzene Chlorobenzene Toluene Phenol 2-Chlorophenol 2,4-Dichlorophenol Dimethylphthalate Diethylphthalate
Benzene
Effluent containing trichlorophenol, 3,3'-dichlorobenzidine, and 2,4-dichloro-4-nitroaniline
Groundwater contaminated with chlorinated solvents: PCE, 1,1-Dichloroethylene, Freon-TF, and TCE
Contaminant
2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 3,4-Dichlorophenol 2,4,5-Trichlorophenol
2,4-Dichlorophenol Dinitro- <i>o</i> -cresol Industrial wastewater 1 Industrial wastewater 1
Search in hydrolyzed prot waste
Phenol, and Formaldehyde-containing wastewater

TABLE 2
Summary of Ultraviolet Light/H₂O₂ Treatment

cr.	450 W Medium pressure mercury vapor lamp, various H ₂ O ₂ concentrations used, best results with 13, 26, and 52 moles of H ₂ O ₂ /mole of dinitrotoluene, temperature: 27-35°C	Ho, 1986 [16]
lar	Reactor volume: 1 L, 400 W high-pressure mercury vapor lamp, H ₂ O ₂ : 14 mM, temperature: 30°C	Kawaguchi, 1992 [24]
it	Reaction volume: 500 or 5000 mL, 450 W medium-pressure UV lamp, H ₂ O ₂ : 1%, temperature: 40-45°C	Malaiyandi et al., 1980 [28]
m	125 W Lamp, 17 x 10 ⁻³ mole quanta/h, H ₂ O ₂ used and pH: 0.53 M 5.3 0.49 5.9 0.57 6.3 0.62 6.5 0.51 5.2 0.42 5.9 0.45 6.7 temperature: 20-25°C	Mansour, 1985 [13]
d	125 W high pressure mercury vapor lamp, H ₂ O ₂ : 0.17 ppm, temperature: 20-25°C	Mansour et al., 1992 [26]
c	125 W Mercury medium pressure lamp, H ₂ O ₂ : 55 ppm	Moza et al., 1988 [18]
lic	60 W low-pressure mercury lamp, H ₂ O ₂ : 1.34 or 1.27 M, temperature: 20°C	Ogata et al., 1981 [12]
	Reactor volume: 4.6 L, 100 W medium pressure mercury vapor lamp, H ₂ O ₂ /dichlorobenzene mole ratio: 7, improved rate of disappearance at 450 W intensity	Pinto and Rickabaugh, 1991 [21]
	Annular photoreactor, medium pressure mercury vapor lamp, H ₂ O ₂ : 0.339 M, pH: 11	Prat et al., 1988 [33]
	Reactor volume: 1.5 L, Quartz low pressure mercury vapor lamp, intensity: 2.5 W @ 254 nm, 55% of lamp immersed in water, H ₂ O ₂ /TCE ratio: 4.5, stoichiometric amount of H ₂ O ₂ used for compounds other than TCE	Sundstrom et al., 1986 [14]

Benzene Chlorobenzene Toluene Phenol 2-Chlorophenol 2,4-Dichlorophenol 2,4,6-Trichlorophenol Dimethylphthalate Diethylphthalate	0.2 mM each	From >90% to complete disappearance	1st order reaction rate: 0.085 min ⁻¹ 0.063 0.094 0.082 0.050 0.081 0.100 0.045 0.047	Organic intermediates, which could also be degraded with continued treatment & up to 4 h)	Recirculation reactor, volume: 330 mL, low pressure UV lamp, intensity: 5.3 W @ 254 nm, H ₂ O ₂ /pollutant molar ratio: 7, lamp surface temperature: 40°C, solution temperature: 25°C, pH: 6.8	Sundstrom et al., 1989 [19]
Benzene	0.2 mM	90 min, highest rate @ molar ratio of 10.6, First order rate constant of 0.1636 min ⁻¹ , pH 6.8	99%	Intermediates: phenol, catechol, hydroquinone, resorcinol and other unidentified compounds	Recirculation reactor, volume: 285 mL, flow rate: 1.8 gpm, low pressure UV germicidal lamp, 5.3 W @ 254 nm, H ₂ O ₂ /benzene molar ratio: 6.6, temperature: 25°C, pH: 6.8	Weir et al., 1987 [17]
Effluent containing trichlorophenol, 3,3'-dichlorobenzidine, and 2,4-dichloro-4-nitroaniline	0.6 ppm 1.4 1.0	Retention time 30 min 2 min	10 ppb 10 ppb 0.01 ppm Estimated effluents of optimized system were: 0.30, 1.0, and 0.25 ppm, respectively	Not reported	UV dosage: 2.31 KW/gallon, H ₂ O ₂ addition rate: 340 mg/L-min, Optimized test parameters were: H ₂ O ₂ 0.00084 lbs/gal, UV dosage: 0.75 KW/gallon, flow rate: 400 gpm (avg.)	Yost, 1989 [37]
Groundwater contaminated with chlorinated solvents: PCE, 1,1-Dichloroethylene, Freon-TF, and TCE	704 ppb 263 71 54	2.5 min	Not detected Not detected 75 ppb Not detected	Not reported	flow rate: 400 gpm (avg.), UV dosage 160 W/L, H ₂ O ₂ : 7 mg/min, pH: 7.5	Yost, 1989 [37]

TABLE 3
Summary of Fenton's Reagent Treatment

Contaminant	Initial Concentration	Degradation or Mineralization Rate/ Reaction time	Degradation/ Mineralization Efficiency or Final Concentration	Products	Conditions/ Comments	Reference
2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 3,4-Dichlorophenol 2,4,5-Trichlorophenol	3 x 10 ⁻⁴ M	Half-lives of degradation 6.5 min 14.5 12.5 6.3 12 ~ 75 min for complete dechlorination of monochlorophenols	100% degradation	Hydroxylated intermediates	Reaction volume: 80 mL, H ₂ O ₂ : 5 x 10 ⁻³ M, perchloric acid: 5 x 10 ⁻³ M, Fe ²⁺ : 5 x 10 ⁻⁵ M, temperature: 25°C, highest rate of 3,4-dichlorophenol of 4.5 x 10 ⁻⁶ M/min degradation at 2 x 10 ⁻⁴ M Fe ²⁺ , highest rate of 4-chlorophenol degradation of 8 x 10 ⁻⁶ M/min using Fe ³⁺ and Fe ²⁺ at 5 x 10 ⁻⁵ M each	Barbeni et al., 1987 [60]
2,4-Dichlorophenol Dinitro- <i>o</i> -cresol Industrial wastewater 1 Industrial wastewater 1	COD (mg/L): 758 335 1277 6365	4 h	Reduction in toxicity (approx.): 8-fold 11 80 12	Not reported (reduction in COD and TOC)	Molar ratio of H ₂ O ₂ to 2,4-dichlorophenol: 4:1, added in hourly steps, Ferrous sulfate: 10-100 mg/L, pH: 3.5, treatment quantified by reduction in toxicity and increase in biodegradability	Bowers et al., 1989 [61]
Starch in hydrolyzed protein waste	BOD: 30,000 mg/L	30 min	91% BOD removal	Not reported	H ₂ O ₂ : 50 mg/L, ferrous sulfate: 5 mg/L	Burbank and Chen, 1975 [78]
Phenol, and Formaldehyde-containing wastewater	Up to 5000 ppm of phenol	30 to 60 min	100% degradation	CO ₂ , carbonic acids, mainly oxalic acid	Not known	Degussa Corp., undated [2]

TABLE 3
Summary of Fenton's Reagent Treatment

Benzo(a)pyrene Naphthalene Fluorene Anthracene Phenanthrene	Not reported	3 h	~15% and ~2%, a small % and ~30%, ~10% and ~20%, a small % and ~99%, ~17.5% and a small % radioactivity recovered as CO ₂ and recovered as methylene chloride extractable organics from radiolabeled contaminant, respectively, 43% of benzo(a)pyrene recovered as CO ₂ using 10% H ₂ O ₂	Methylene chloride extractable polar organics, CO ₂	Reaction volume: 10 mL, H ₂ O ₂ : 5%, ferrous sulfate: 10 mM	Kelley et al., 1990 [64]
Pretreatment of Polynuclear aromatic hydrocarbons (PAHs) in contaminated soils prior to biodegradation, radiolabeled benzo(a)pyrene spiked sandy soils		3 h	25%, 12%, and 50% radioactivity recovered as CO ₂ , nonpolar, and polar hydrocarbons from radiolabeled benzo(a)pyrene < 400 mg/kg	Polar and nonpolar organics, CO ₂	H ₂ O ₂ : 10%	Kelley et al., 1990 [64]
PAH-contaminated soils	175,000 mg/kg of dry soil	16 h Fenton's reagent treatment on 4 consecutive days	20 mg/kg	Not reported	H ₂ O ₂ : 10%, ferrous sulfate: 20 mM, optimal temperature: 20°C, pH: 4.5	
Simulated dye wastewaters prepared with disperse, reactive, direct, acid, and basic dyes, wastewaters contained 2.5 g/L sodium sulfate except wastewater prepared with reactive dye which contained 8 g/L of sodium sulfate and 4 g/L of sodium carbonate Dye wastewaters from mills	300 ppm dye concentration	5 min for the wastewater containing the disperse dye, 30 min for others	90% removal of COD, transparency above 25 cm, 97% decolorization	Not reported	Reaction volume: 300 mL, H ₂ O ₂ : 584, 292, 875, 292, and 292 ppm and ferrous sulfate: 250, 83, 500, 500, and 333 ppm for the wastewaters containing reactive, direct, acid, basic and disperse dyes, respectively, temperature: 50°C, similar results for dye wastewaters	Kuo, 1992 [80]
Pentachlorophenol (PCP) pretreatment prior to biodegradation by mixed aerobic cultures	266 ppm	4 h	2.97% PCP removal	Chloride at less than stoichiometric quantities	Reaction volume: 1 L, molar ratio of H ₂ O ₂ to PCP: 1:1, Fe ²⁺ as ferrous sulfate: 50 mg/L, temperature: 20°C, pH: 3.5, Fenton's reagent improved biodegradation of PCP from 3% to 33% using selected microbial consortium and 2.5% to 20% using activated sludge	Lee and Carberry, 1992 [81]
Perchloroethylene (PCE) spiked on silica sand	1000 mg/kg of soil	3 h, pseudo 1st order rate constants of PCE and H ₂ O ₂ were 1.65 ± 0.475 h ⁻¹ and 0.206 ± 0.036 h ⁻¹ , respectively	100% mineralization	Dichloroacetic acid, formic acid, CO ₂	3.5 g of silica sand in 40 mL reaction volume, H ₂ O ₂ : 2.1 M, ferrous sulfate: 5 mM, temperature: 20°C, pH: 3	Leung et al., 1992 [88]
2-Nitrophenol 4-Nitrophenol 2,4-Dinitrophenol Nitrobenzene	100 µM for all	Half lives of degradation: 60 min 23 13 360	Not reported	Hydroxylated aromatic intermediates	Batch reaction volume: 50 mL, ratio of H ₂ O ₂ to pollutant: 18:1, FeCl ₂ : 0.35 µM, pH: 4.5, 5.25, 5.0, and 5.9, respectively	Lipczynska-Kochany, 1991 [67]
Hydroxymethanesulfonic acid	0.01 M	1st order rate constant: 10 ⁻⁴ s ⁻¹	Not reported	Sulfate	H ₂ O ₂ : 0.1 M, Fe ²⁺ : 1 mM, temperature: 25°C, pH: 3	Martin et al., 1989 [62]
Formaldehyde in waste solution containing formic acid and methanol as other constituents	500 ppm	2 h	< 1 ppm	Formic acid, CO ₂	Batch reaction volume: 250 mL, molar ratio of H ₂ O ₂ to formaldehyde: 6:1, Fenton-like reaction with Fe ³⁺ used as true catalyst at 200 mg/L, temperature: 25°C	Murphy et al., 1989 [63]
2,4-Dichlorophenoxyacetic acid 2,4,5-Trichlorophenoxyacetic acid	0.1 mM 0.1	2 h 2	100% mineralization	Dechlorinated products	Reaction volume: 100 mL, H ₂ O ₂ : 10 mM, Fe ³⁺ : 1 mM, Temperature: 21°C, pH: 2.7, four 200 W fluorescent lights, light intensity: 0.035 mW/cm ² (290-385 nm) and 1.25 mW/cm ² (400-700 nm)	Pignatello, 1992 [92]

Pretreatment of pentachlorophenol (PCP) spiked on soils prior to biodegradation by activated sludge
Chlorobenzene
Polychlorinated biphenyls: 2-Chlorobiphenyl Aroclor 1242
PAH-contaminated soils
Phenol
2,4-Dichlorophenoxyacetic acid
Pentachlorophenol, Trifluralin, Hexadecane, and Dieldrin spiked on soils
Thiosulfate/Sulfide laden wastewater
Pretreatment of: <i>o</i> -Cresol, and 2,4-Dinitrophenol prior to biodegradation by mixed aerobic cultures
Pentachlorophenol (PCP) spiked on soils

TABLE 3
Summary of Fenton's Reagent Treatment

Reaction volume: 10 mL, H ₂ O ₂ : 5%, ferrous sulfate: 10 mM	Kelley et al., 1990 [64]
H ₂ O ₂ : 10%	Kelley et al., 1990 [64]
H ₂ O ₂ : 10%, ferrous sulfate: 20 mM, optimal temperature: 20°C, pH: 4.5	
Reaction volume: 100 mL, H ₂ O ₂ : 584, 292, 75, 292, and 292 ppm and ferrous sulfate: 250, 83, 300, 500, and 333 ppm for the wastewaters containing reactive, direct, acid, basic and disperse dyes, respectively, temperature: 0°C, similar results for dye wastewaters	Kuo, 1992 [80]
Reaction volume: 1 L, molar ratio of H ₂ O ₂ to PCP: 1:1, Fe ²⁺ as ferrous sulfate: 50 mg/L, temperature: 20°C, pH: 3.5, Fenton's reagent improved biodegradation of PCP from 5% to 33% using selected microbial consortium and 5% to 20% using activated sludge	Lec and Carberry, 1992 [81]
5 g of silica sand in 40 mL reaction volume, H ₂ O ₂ : 2.1 M, ferrous sulfate: 5 mM, temperature: 20°C, pH: 3	Leung et al., 1992 [88]
Batch reaction volume: 50 mL, ratio of H ₂ O ₂ to flutant: 18:1, FeCl ₂ : 0.35 mM, pH: 4.5, 5.25, 5.0, and 5.9, respectively	Lipczyńska-Kochany, 1991 [67]
H ₂ O ₂ : 0.1 M, Fe ²⁺ : 1 mM, temperature: 25°C, pH: 3	Martin et al., 1989 [62]
Batch reaction volume: 250 L, molar ratio of H ₂ O ₂ to formaldehyde: 6:1, Fenton's reaction with Fe ³⁺ used true catalyst at 200 mg/L, temperature: 25°C	Murphy et al., 1989 [63]
Reaction volume: 100 mL, H ₂ O ₂ : 10 mM, Fe ³⁺ : 1 nM, Temperature: 21°C, pH: 2.7, four 200 W fluorescent lights, light intensity: 0.035 mW/cm ² (290-385 nm) and 1.25 mW/cm ² (400-700 nm)	Pignatello, 1992 [92]

Pretreatment of pentachlorophenol (PCP) spiked on soils prior to biodegradation by activated sludge	~125 ppm	~700 h for combined chemical and biological treatment	100% disappearance due to chemical treatment and biodegradation compared to ~30% disappearance due to biodegradation alone	Chloride	Soil columns: 90 cm length and 4.1 cm diameter, dosages of H ₂ O ₂ : 0.18 mM and ferrous sulfate: 0.01 mM onto soil columns	Ravikumar and Guroi, 1991 [82]
Chlorobenzene	1.6 mM	2 h	100% degradation, but not mineralization of chlorobenzene and aromatic intermediates	Chlorophenols, dichlorobiphenyls, and phenolic polymers in the absence of oxygen, chlorobenzoquinone also formed in the presence of oxygen, chlorinated and nonchlorinated diols formed from chlorophenols	Reaction volume: 500 mL, molar ratio of H ₂ O ₂ to chlorobenzene: 5:1, H ₂ O ₂ added at 5 mM/h, Fe ²⁺ : 5 mM, temperature: 25°C, pH: 3.0	Sedlak and Andren, 1991 [65]
Polychlorinated biphenyls: 2-Chlorobiphenyl Aroclor 1242	0.01 mM 0.1 ppm	20 min	1 µM	Various hydroxylated products from 2-chlorobiphenyl	Reaction volume: 100 mL, H ₂ O ₂ : 0.2 mM, Fe ²⁺ : 0.8 mM, pH: 3, 4.2 or 7.2	Sedlak and Andren, 1991 [66]
PAH-contaminated soils	7000 mg/kg of soil	4 weeks for combined Fenton's and biological treatment compared to 8 weeks for biological treatment	67 - 72% of total PAHs removed, 50% more total PAHs removed compared to biological treatment alone	Not reported	Bench scale slurry or pan tests and field scale land treatment tests, field plots 2 ft x 12 ft, sandy loam soils, bench tests: 100 g/L soil with 2.5% H ₂ O ₂ (volume of 100% H ₂ O ₂ /mL-slurry) and 10 mM ferrous sulfate added over 16 h, simulated land treatment using 1 to 2 kg of soil in glass pans	Srivastava et al., 1991 [87]
Phenol	1-12 mM	100% degradation	Not reported	Intermediates: hydroquinone, catechol, p-quinone, muconic acid, maleic acid, oxalic acid, endproduct: CO ₂	Fe ²⁺ : 0.2-50.0 mM, Temperature: 5-45°C, pH: 1-4, oxygen sparging rate: 1.50-1.63 cm ³ /sec, electrogeneration of H ₂ O ₂ , cathode potential: 0.2-1.0 V	Sudoh et al., 1986 [59]
2,4-Dichlorophenoxyacetic acid	0.1 mM	16 h for Fenton's reaction (dark reaction) followed by less than 1 h for photolysis	100% mineralization	intermediate: oxalic acid, endproducts: inorganic chloride and CO ₂	Reaction volume: 100 mL, H ₂ O ₂ : 10 mM, Fe ³⁺ : 1 mM, Temperature: 28°C, pH: 2.8, 15 W fluorescent black light blue tubes, light intensity: 2.15 mW/cm ² , 300-400 nm, centered at 360 nm	Sun and Pignatello, 1993 [93]
Pentachlorophenol, Trifluralin, Hexadecane, and Dieldrin spiked on soils	200 mg/kg	3 h for PCP 5 h for rest	Stoichiometric recovery of chloride, 99% loss of PCP and trifluralin ~65% loss of Hexadecane and dieldrin	Chloride formation and TOC reduction for PCP	2.5 g of soil in 40-mL borosilicate glass vial, H ₂ O ₂ : 120,000 mg/L, iron addition: 200 and 400 mg/L, soil organic carbon: 2,000 to 16,000 mg/kg soil adjusted to pH: 3	Tyre et al., 1991 [90]
Thiosulfate/Sulfide laden wastewater	Not reported	~10 min	90% removal	Sulfates	Beaker tests, H ₂ O ₂ at equimolar concentrations with thiosulfate/sulfide, transition metal added at a few ppm	Walton et al., 1985 [73]
Pretreatment of: o-Cresol, and 2,4-Dinitrophenol prior to biodegradation by mixed aerobic cultures	200 or 600 ppm 100	Not reported	100% removal 100% removal	Formic and oxalic acids	Batch reactor volume: 500 mL, molar ratio of H ₂ O ₂ to o-cresol: 4:1 and 5:1 and for 2,4-dinitrophenol: 5:1, ratio of ferrous chloride to contaminant concentration: 1:100, pH: 3-4, molar ratio of H ₂ O ₂ to 2,4-dinitrophenol used were 2.5-4.5 which reduced methanogenic toxicity by 50%	Wang, 1992 [83,84]
Pentachlorophenol (PCP) spiked on soils	250 mg/kg of soil, obtained by spiking	24 h	100% disappearance of PCP and 100% reduction in total organic carbon of filtrate from soil slurry	Chloride	2.5 g of soil in 40-mL vial, silica sand and two fine loamy soils, molar ratio of peroxide to PCP 10200:1, wt ratio of peroxide to soil: 0.327:1, FeSO ₄ : 480 mg/L as Fe ²⁺ and Fe ³⁺ in the aqueous phase.	Waus et al., 1990 [58]

TABLE 3
Summary of Fenton's Reagent Treatment

Octachlorodibenzo- <i>p</i> -dioxin (OCDD) spiked on surface soils	200 µg OCDD/kg of soil	3 h	75 to 96% removal depending on type of soil	None Found	1 g of four types of spiked soils in 40-mL glass vial, H ₂ O ₂ : 12%, ferrous sulfate: 0.10 mmole, temperatures: 20, 40, 60, and 80°C, pH: 2.5-3.5, H ₂ O ₂ @ 35% more effective in silica sand, higher removals at higher temperatures	Watts et al., 1991 [89]
Oil and fuel hydrocarbon-contaminated soil	> 2000 mg/kg	7 days	< 100 mg/kg	Bound polymer residues are likely end products	2.5 g of soil in 40-mL borosilicate glass vial, H ₂ O ₂ : 2 and 7%, no iron addition, temperature: 20°C, soils adjusted to pH 2 and 3, Pilot system: 1.25 cubic yards of soil in 55-gallon drum	Watts, 1992 [91]

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

Contaminant	Initial Concentration	Degradation or Mineralization Rate/ Reaction time	Degradation/ Mineralization Efficiency or Final Concentration	Products	Conditions/Comments	Reference
TCE Trichloromethane	50 ppm 50	3 h	99% mineralization	HCl, CO ₂	Temperature: 25 to 40°C, TiO ₂ : 0.3 wt %, sunlight: 0.276 m ² , reactor volume: 414 mL, recirculation flow rate: 44 mL/sec	Ahmed and Ollis, 1984 [104]
4-Chlorophenol	64 ppm	3 h for complete mineralization using lamp; 180 min for complete disappearance using solar exposure	>98% mineralization	HCl and CO ₂	Temperature: 35-45°C, pH: 4.5, TiO ₂ : 2 g/L, Suntest lamp, 340-830 nm, intensity: 100 mW/cm ² , or solar exposure, reactor volume: 20 mL	Barbeni et al., 1984 [126]
Pentachlorophenol (PCP)	4.5 x 10 ⁻⁵ M	1.5 h for complete disappearance, time for 50% degradation using sunlight: 8 min	100% mineralization	CO ₂ and HCl	Temperature: 45-50°C, pH: 3, TiO ₂ : 2 g/L, Solarbox lamp, 310-830 nm, photon absorption rate: 3.3 x 10 ⁻² Einstein/min, reactor volume: 20 mL, 4-chlorophenol is degraded slightly faster (in about 45 min) than PCP	Barbeni et al., 1985 [160]
4-Chlorophenol 3,4-Dichlorophenol 2,4,5-Trichlorophenol PCP Sodium Pentachlorophenate Chlorobenzene 1,2,4-Trichlorobenzene 2,4,5-T 4,4'-DDT 3,3'-Dichlorobiphenyl 2,7-Dichlorodibenzo- <i>p</i> -dioxin	6 ppm 18 20 12 12 45 10 32 1 1 0.2	Half-lives (min): 14 45 55 20 15 90 24 40 46 10 46	Not reported	CO ₂ and HCl after long irradiation times	Temperature: 45-50°C, pH: 3, TiO ₂ : 2 g/L, Solarbox lamp, 310-830 nm	Barbeni et al., 1986 [161]
2,4,5-Trichlorophenoxyacetic acid 2,4,5-Trichlorophenol	1 x 10 ⁻⁴ M 1 x 10 ⁻⁴	Half-lives 30-90 min	100% mineralization	Intermediates: several hydroxylated aromatic compounds, endproducts: CO ₂ , HCl	Temperature: 35-45°C, pH: 3, TiO ₂ : 2 g/L, Solarbox lamp, > 340 nm, photon absorption rate: 3 x 10 ⁻⁵ Einstein/min, reactor volume: 20 mL	Barbeni et al., 1987 [130]

DDT
Aroclor 1254 4,4'-Dichlorobiphenyl 2,2'-Dichlorobiphenyl 2-Chlorobiphenyl 3-Chlorobiphenyl 4-Chlorobiphenyl Biphenyl
TCE (gas-phase)
TCE (gas-phase)
2-Chlorophenol (2-CP) 3-Chlorophenol (3-CP)
Removal and concentration of copper ions
TCE PCE
Trimethyl phosphate Trimethylphosphite <i>o,o</i> -Dimethyl ammonium phosphodithioate Organophosphorus insecticides: Dimethyl-2,2-dichlorovin phosphate (DDVP) Dimethyl-2,2,3-trichloro-hydroxyethyl phosphonate (DEP)

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

DDT	1 ppm	Half-life of disappearance: 40 min, 80% mineralization after more than 25 h of irradiation	> 90% disappearance	Inorganic chloride	pH: 3, TiO ₂ : 2 g/L, Solarbox lamp with 1500 W Xenon lamp, > 340 nm, photon flux: 3×10^{-5} Einstein/min	Borello et al., 1989 [139]
Aroclor 1254 4,4'-Dichlorobiphenyl 2,2'-Dichlorobiphenyl 2-Chlorobiphenyl 3-Chlorobiphenyl 4-Chlorobiphenyl Biphenyl	50 ppb 50 25 25 25 25	30 min	100% disappearance of Aroclor 1254, 3- and 4-chlorobiphenyl and 4,4'-dichlorobiphenyl; 2,2'-dichlorobiphenyl; no reaction with 2-chlorobiphenyl	Not identified	TiO ₂ : 0.5%, BLAK-RAY B-100A UV light at 365 nm	Carey et al., 1976 [162]
TCE (gas-phase)	mole fraction: 1.89×10^{-4}	Reaction rate: 0.4 $\mu\text{mol/g}$ of TiO ₂ -min	Not reported	Not reported	TiO ₂ : 56 mg, 4 W fluorescent blacklight bulb, photon flux: 4.1×10^{-9} Einstein/cm ² -s, reactor volume: 3.14 mL, inlet gas flow rate: 20-100 mL/min	Dibble and Raupp, 1990 [143]
TCE (gas-phase)	5.5-67 ppm	Reaction rate: 2 $\mu\text{mol/g}$ of TiO ₂ -min	23.5-100% conversion	Not reported	Silica-supported TiO ₂ : 0.5-0.6 g, 4 W fluorescent bulb, 300-500 nm, photon flux: 6×10^{-8} Einstein/s, flat-plate fluidized-bed reactor, reactor volume: 3.14 mL, inlet gas flow rate: 261-360 mL/min	Dibble and Raupp, 1992 [144]
2-Chlorophenol (2-CP) 3-Chlorophenol (3-CP)	20 ppm 20	Degradation time: 120 min for 2-CP and 110 min for 3-CP in smaller reactor 7 h for 3-CP degradation and 24 h for 3-CP mineralization in larger reactor	100% mineralization	Intermediates: chlorohydroquinone, hydroxyhydroquinone, and catechol, CO ₂ and inorganic chloride final products	pH: 4.5 for 2-CP and 4.7 for 3-CP, TiO ₂ : 2.5 or 1.25 g/L, high pressure mercury lamp, intensity: 50 or 60 mW/cm ² , >340 nm, photoreactor: 90 or 180 mL, suspension volume: 20 or 135 mL	D'Oliveira et al., 1990 [129]
Removal and concentration of copper ions	51 $\mu\text{g/mL}$ Cu ²⁺	5 min for deposition of Cu ²⁺ on the TiO ₂ surface (during photoreduction) and 20 min for dissolution (during air oxidation)	86% concentration of Cu ²⁺ in 7% of the initial volume	Cu ²⁺ ions are reduced to Cu ⁺ during photoreduction which are oxidized during air oxidation to Cu ²⁺	pH: 3.6, TiO ₂ : 2 g/L, 15 W black light lamp (mostly 365 nm), intensity: 2.9 mW/cm ² , annular photoreactor, suspension volume: 5 batches of 500-mL each, recirculation flow rate: 8 mL/sec, photoreduction was conducted in the absence of oxygen with nitrogen followed by air oxidation	Foster et al., 1993 [177]
TCE PCE	0.047-0.33 mM 0.0053-0.17 mM	87-262 min 88-180 min	100% disappearance of TCE in 100 min @ 0.047 mM, rate constants of 0.00095 and 0.0021 mmol/L-min	< 4% of TCE degraded was recovered as dichloroacetaldehyde and dichloroacetic acid and trace of trichloroacetaldehyde and trichloroacetic acid, < 15% of PCE degraded recovered as dichloroacetic acid and trichloroacetic acid	pH: 7 for TCE and 8 for PCE, TiO ₂ : 0.1-0.11 wt%, 150 W Xenon lamp, photoreactor volume: 5.5 L, detailed mechanistic studies performed	Glaze et al., 1993 [182]
Trimethyl phosphite Trimethylphosphite o,o-Dimethyl ammonium phosphodithioate	0.1 mM	4 h	100% degradation	Phosphate and sulfate	TiO ₂ : 5 g/L, 500 W super-high pressure mercury lamp or sunlight, reaction volumes: 3 or 250 mL	Harada et al., 1987 [155]
Organophosphorus insecticides: Dimethyl-2,2-dichlorovinyl phosphate (DDVP) Dimethyl-2,2,3-trichloro-1-hydroxyethyl phosphonate (DEP)	10 ⁻³ M 10 ⁻⁴	half-lives 90 and 35 min using TiO ₂ and 20 min and 5 min using Pt-loaded TiO ₂ for DDVP and DEP, respectively, rate constants 0.007 and 0.027 min ⁻¹ for DDVP using TiO ₂ and using Pt-loaded TiO ₂ , and 0.019 and 0.128 min ⁻¹ for DEP using TiO ₂ and using Pt-loaded TiO ₂ , respectively	100% mineralization 100% mineralization	Inorganic chloride, phosphate, H ⁺ , and CO ₂ were endproducts, formaldehyde was an intermediate	TiO ₂ : 4 or 5 g/L, TiO ₂ used with and without Pt loading, 500 W super-high pressure mercury lamp or sunlight from 10 am to 4 pm, reaction volumes: 3 or 250 mL, degradation under solar exposure as fast as or faster than lamp illumination, addition of 1.2×10^{-2} M H ₂ O ₂ shortened half-lives 10- and 2-fold for DDVP and DEP, respectively	Harada et al., 1990 [156]

of four types of spiked soils in 40-mL glass vial, I ₂ : 12%, ferrous sulfate: 0 mmole, temperatures: , 40, 60, and 80°C, pH: 2.5-3.5, I ₂ @ 35% more effective in silica sand, higher removals at higher temperatures	Watts et al., 1991 [89]
.5 g of soil in 40-mL borosilicate glass vial, I ₂ O ₂ : 2 and 7%, no iron ion, temperature: 20°C, soils adjusted to pH 2 and 3, lot system: 1.25 cubic yards of soil in 55-gallon drum	Watts, 1992 [91]

Conditions/Comments	Reference
Temperature: 25 to 40°C, TiO ₂ : 1%, sunlight: 0.276 m ² , reactor volume: 414 mL, circulation flow rate: 44 mL/sec	Ahmed and Ollis, 1984 [104]
Temperature: 35-45°C, pH: 4.5, TiO ₂ : 2 g/L, Suntest lamp, 340-nm, intensity: 100 mW/cm ² , reactor exposure, reactor volume: L	Barbeni et al., 1984 [126]
Temperature: 45-50°C, pH: 3, TiO ₂ : 2 g/L, Solarbox lamp, 310-nm, photon absorption rate: 10 ⁻⁵ Einstein/min, reactor volume: 20 mL, 4-chlorophenol is degraded slightly faster (in about 45 min) than PCP	Barbeni et al., 1985 [160]
Temperature: 45-50°C, pH: 3, TiO ₂ : 2 g/L, Solarbox lamp, 310-nm	Barbeni et al., 1986 [161]
Temperature: 35-45°C, pH: 3, TiO ₂ : 2 g/L, Solarbox lamp, > 340 nm, photon absorption rate: 3 x 10 ⁻⁵ Einstein/min, reactor volume: 20 mL	Barbeni et al., 1987 [130]

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

Sodium dodecylbenzene sulfonate	50 ppm	2 h	100% degradation	Not identified	Temperature: 35-40°C, TiO ₂ : 50 mg, 450 W Xenon lamp, >330 nm, solution volume: 25 mL	Hidaka et al., 1985 [166]
Sodium dodecylbenzene sulphonate	50 ppm	1 h for disappearance, 4 days for disappearance of the aromatic unit	100% degradation	Cleavage of the aromatic group and the alkyl chain, sulphate	Temperature: 37°C, TiO ₂ : 2 g/L, 450 W Xenon lamp (>330 nm; 80 mW/cm ²), suntest lamp (100 mW/cm ²), solution volume: 25 mL	Hidaka et al., 1986 [167]
Non-ionic surfactants: p-nonylphenyl ploy(oxyethylene) ethers	0.1 mM	Degradation half-life ranged from 17 to 136 min for various surfactants	100% degradation	Aromatic and ethoxy fragments, CO ₂	pH: 3.5, 7.0 or 9.3, TiO ₂ : 50 mg, 500 W Xenon lamp, >330 nm, solution volume: 25 mL	Hidaka et al., 1988 [169]
Permethrin	0.44 mM	20 h, 1st order rate constant: 1.73 x 10 ⁻³ min ⁻¹ , half-life: 400 min, 10 h	90% degradation, 80% degradation under solar exposure	Inorganic chloride, CO ₂	pH: 12, 7 or 2, TiO ₂ : 2 g/L, mercury lamp, >330 nm, solar exposure: 1-6 mW/cm ² , 330-480 nm, solution volume: 50 or 0.5 mL	Hidaka et al., 1992 [159]
KCN Cyanide-containing industrial wastewater	21 mM - 500 ppm 200 ppm	30 h treatment times were 3-4 times longer than for KCN reagent	100% degradation 100% degradation	Intermediate: OCN ⁻ , endproducts: CO ₂ and nitrogen	pH: 12, TiO ₂ : 2 g/L, 100 W mercury lamp, >330 nm, solution volume: 50 mL, 5 L reactor volume also tested	Hidaka et al., 1992 [138]
Dichloromethane Chloroform Carbon tetrachloride 1,1-Dichloroethane 1,2-Dichloroethane 1,1,1-Trichloroethane 1,1,2-Trichloroethane 1,1,1,2-Tetrachloroethane 1,1,2,2-Tetrachloroethane 1,2-Dichloroethylene Trichloroethylene Tetrachloroethylene	0.5 mM for all	Half-lives of degradation (min) with TiO ₂ , Pt/TiO ₂ , and TiO ₂ /H ₂ O ₂ : 80, 47, 40 65, 54, 65 480, 480, 480 97, 47, 31 53, 31, 20 125, 150, 140 68, 53, 37 69, 60, 45 55, 46, 44 51, 17, 2 63, 38, 7 48, 56, 16	100% degradation	Inorganic chloride, ClO ₃ ⁻ in the case of Pt-loaded TiO ₂	TiO ₂ : 2.8 g/L, 500 W super-high pressure mercury lamp, solution volume: 25 mL	Hisanaga et al., 1990 [125]
Dichloromethane Chloroform Carbon tetrachloride	10-200 ppm	Langmuir-Hinshelwood rate constant k: 1.6, 5.2, and 0.18 ppm/min-g of catalyst, respectively, adsorption constant K: 2 x 10 ⁻² , 3.7 x 10 ⁻³ , and 8.9 x 10 ⁻³ ppm ⁻¹ , respectively	100% mineralization, rate constants for dichloromethane, chloroform, and carbon tetrachloride are 1.6, 5.2, and 0.18 ppm/min-g of catalyst, respectively	HCl, CO ₂	Temperature: 27-29°C, TiO ₂ : 0.1 wt %, illumination: 6.6 x 10 ⁻⁴ Einstein/min, 320-400 nm, photoreactor as in Pruden and Ollis, 1983a and b, chloride ion inhibits rate of degradation	Hsiao et al., 1983 [122]
Benzene Hexane Cyclohexane Heptane Nonane Decane Kerosene	20% (v/v) 50% (v/v) for aliphatic hydrocarbons	72 h 24 24 48 46 291 72	1.85 mmol of CO ₂ generated, CO ₂ production rate (μmol/h): 65.2 86.4 60.4 65.6 34.1 17.2	Phenol is an intermediate, CO ₂ endproduct	Temperature: 36°C, platinized TiO ₂ : 10%, 6000 W Xenon lamp, output: 5000 W, intensity: 35 mW/cm ²	Izumi et al., 1980 [110]
Chloroform Urea	200 or 25 mg/L 100 mg/L	6 h 12 min	44% degradation of chloroform at 200 mg/L 83% degradation for urea	CO ₂ , inorganic chloride	pH: 7, Ag-loaded TiO ₂ : 0.1% (w/v), 125 W medium pressure mercury lamp, light intensity between 40 and 100 W/m ²	Kondo and Jardim, 1991 [123]
Phenylphosphonic acid Butylphosphonic acid Benzylphosphonic acid	0.05-10 mM	Rate constant (μM/min) and adsorption constants (mM): 32±0.3, 46.6±17.3 9.4±3.1, 8.6±1.6 13.5±2.6, 4.4±0.4	Not reported	Intermediates from benzylphosphonic acid: benzyl alcohol, benzaldehyde, bibenzyl, and phosphoric acid, endproducts: inorganic phosphate and CO ₂	Temperature: 50°C, TiO ₂ : 0.5 g/L, 350 nm bulbs in Rayonet photoreactor, reactor volume: 100 mL	Krosley et al., 1993 [158]
2,4-Dichlorophenol	3.067 x 10 ⁻⁴ M	5 h for removal, 11 h for mineralization	100% mineralization	CO ₂	Temperature: 28°C, pH: 6.5, TiO ₂ : 1.016 g/L, low pressure mercury vapor lamp of 5.8 W near 254 nm, intensity: 500 μm/cm ² , reactor volume: 100 mL	Ku and Hsieh, 1992 [95]

Nitroaromatics and amines: n-Pentylamine Piperidine Pyridine Phenylalanine Desipramine Thiothiazine Penicillamine Isosorbide dinitrate 4-Nitrocatechol 2,4-Dinitrophenol Cyclophosphamide 5-Fluorouracil Atrazine Ethylenediaminetetracetic acid Tetrabutylammonium phosphate Benzamide	5 g at conc for flux and d (c)
Methyl vinyl ketone PCP 2,4-Dichlorophenol	75 g
Metoxuron Carbamate	
Salicylic acid	
Phenol	
2-Chlorophenol 4-Chlorophenol Benzoic acid	
2-Naphthol	
Naphthalene	
Fluorescein	

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

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temperature: 35-40°C, TiO ₂ : 50 mg, 450 W Xenon lamp, >330 nm, solution volume: 25 mL	Hidaka et al., 1985 [166]
temperature: 37°C, TiO ₂ : 2 g/L, 40 W Xenon lamp (>330 nm; 80 W/cm ²), suntest lamp (100 W/cm ²), solution volume: 25 L	Hidaka et al., 1986 [167]
λ: 3.5, 7.0 or 9.3, TiO ₂ : 50 mg, 40 W Xenon lamp, >330 nm, solution volume: 25 mL	Hidaka et al., 1988 [169]
λ: 12, 7 or 2, TiO ₂ : 2 g/L, mercury lamp, >330 nm, solar exposure: 1-6 mW/cm ² , 330-480 nm, solution volume: 50 or 0.5 L	Hidaka et al., 1992 [159]
λ: 12, TiO ₂ : 2 g/L, 100 W mercury lamp, >330 nm, solution volume: 50 mL, 5 L reactor volume also tested	Hidaka et al., 1992 [138]
O ₂ : 2.8 g/L, 500 W super-high pressure mercury lamp, solution volume: 25 mL	Hisanaga et al., 1990 [125]
temperature: 27-29°C, TiO ₂ : 0.1%, illumination: 6.6 x 10 ⁻⁴ mW/cm ² , 320-400 nm, reactor as in Pruden and Ollis, 13a and b, chloride ion inhibits rate of degradation	Hsiao et al., 1983 [122]
temperature: 36°C, platinumized TiO ₂ : 10%, 6000 W Xenon lamp, input: 5000 W, intensity: 35 W/cm ²	Izumi et al., 1980 [110]
λ: 7, Ag-loaded TiO ₂ : 0.1% v/v, 125 W medium pressure mercury lamp, light intensity between 40 and 100 W/m ²	Kondo and Jardim, 1991 [123]
temperature: 50°C, TiO ₂ : 0.5 g/L, 100 nm bulbs in Rayonet reactor, reactor volume: 100 mL	Krosley et al., 1993 [158]
temperature: 28°C, pH: 6.5, TiO ₂ : 16 g/L, low pressure mercury lamp or lamp of 5.8 W near 254 nm, intensity: 500 μW/cm ² , reactor volume: 100 mL	Ku and Hsieh, 1992 [95]

Nitroaromatics and amines: n-Pentylamine Piperidine Pyridine Phenylalanine Desipramine Thiothiazine Penicillamine Isosorbide dinitrate 4-Nitrocatechol 2,4-Dinitrophenol Cyclophosphamide 5-Fluorouracil Atrazine Ethylenediaminetetraacetic acid Tetrabutylammonium phosphate Benzamide	5 ppm for soluble compounds, saturation concentration for atrazine, fluorouracil, and isosorbide dinitrate (< 5 ppm)	40 min	Not reported	Carbonate, nitrate, ammonium, and phosphate ions	Apparatus same as used by Matthews [1988a], borosilicate glass spiral tube wound around a 20 W blacklight blue fluorescent tube, reactor surface coated with a thin layer of TiO ₂ , solution volume: 40 mL	Low et al., 1991 [151]
	20 ppm	100 min 150 h	100% disappearance 100% mineralization to CO ₂ and NO ₃ ⁻	Hydroxy benzamide isomers, CO ₂	Temperature: ambient, pH: 7, TiO ₂ : 2.5 g/L, 125 W high-pressure mercury lamp, solution volume: 20 mL	Mailard et al., 1992 [153]
Methyl vinyl ketone PCP 2,4-Dichlorophenol	75 mg/L for all	6 h 9 6	100% detoxification in each case	Not reported	TiO ₂ : 1 g/L, sunlight between 9:00 am and 4:00 pm, solution volume: 600 mL, toxicity measured by effect on respiration of activated sludge microorganisms	Manifal et al., 1992 [131]
Metoxuron Carbetamide	20 ppm 20	Half-life for carbetamide: 84 min	Not reported	Hydroxylated and ring-cleavage products, initial product: hydroxycarbetamide	Temperature: 20-25°C, TiO ₂ : 150 ppm, 125 W high pressure mercury vapor lamp	Mansour et al., 1992 [26]
Salicylic acid	1 μM 2 4 10 20 30 40 50 100	6.81 min 6.77 7.01 7.11 8.08 8.09 8.54 9.97 13.35	100% mineralization of salicylic acid (in 12 min)	CO ₂	Temperature: 25°C, TiO ₂ : 75 mg, coated on the inside of tubing, 7 m long borosilicate glass tubing wrapped around 20 W blacklight fluorescent lamp, solution volume: 500 mL, recirculation flow rate: 120 mL/min	Matthews, 1987 [111]
Phenol	1 2 10 20 50 100	5.97 6.79 7.17 9.34 12.3 17.0				
2-Chlorophenol 4-Chlorophenol Benzoic acid	10 10 10 20 50	8.22 8.73 6.92 7.42 9.84				
2-Naphthol	1 2 5 10 20 50 100	7.45 8.17 7.80 8.53 10.3 11.2 17.1				
Naphthalene	1 2 5 10 20 50	3.98 3.94 4.20 4.33 4.50 5.50				
Fluorescein	1 2 5 10 20	5.29 5.54 5.82 6.41 7.61				

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

Benzoic acid Salicylic acid Phenol Biphenylate 2-Chlorophenol 3-Chlorophenol Chlorobenzene Nitrobenzene Methanol Ethanol n-Propanol 2-Propanol Acetone Ethyl acetate Acetic acid Formic acid Sucrose 2-Naphthol Umbelliferone Chloroform TCE Dichloroethane	100 mg/L for all	6.43 mg/L/min (Rate of degradation to CO ₂) 8.84 7.20 7.67 9.20 8.10 5.10 4.00 6.70 6.80 6.80 3.34 3.50 5.60 5.70 13.3 6.20 4.10 5.00 7.80 8.50 4.30	Not reported	Phenol and muconaldehyde intermediates, CO ₂ and water are endproducts	Temperature: 40°C, pH: 3.6, TiO ₂ : 75 mg, coated on the inside of tubing, 7 m long borosilicate glass tubing wrapped around 20 W blacklight fluorescent lamp, recirculated solution volume: 40 mL, degradation rates were also reported for 1, 10, and 50 mg/L of contaminant	Mathews, 1988 [97]
Salicylic acid Phenol	10 µM 10 µM	1st order rate constants of 0.188 min ⁻¹ and 0.141 min ⁻¹ ; 100% degradation of phenol in a single pass	100% degradation	Not reported	70 g Silica gel was used as an adsorbent for 1.26 g TiO ₂ , 40 W tubular low pressure mercury vapor fluorescent lamp, 300-460 nm, annular reactor volume: 646 mL, recirculation flow rate: 20 mL/min	Mathews, 1988 [112]
Benzoic acid Salicylic acid Phenol 2-Chlorophenol 3-Chlorophenol 4-Chlorophenol Nitrobenzene Methanol Ethanol Acetic acid Formic acid	50 mg/L for all	2-3 h	90% mineralization, twice the rate for formic acid	CO ₂	Temperature: 40°C, pH: 3.5, TiO ₂ : 0.1% (w/w), near UV light (4 W blacklight blue fluorescent tube) or 1 m ² of sunlight, reactor volume: 40 mL, flow rate: 270 mL/min	Mathews, 1990 [184]
Colored organics: Methylene blue Rhodamine Methyl orange Salicylic acid	10 µM	12-22 min for 50% removal and 21-46 min for 50% mineralization	Not reported	CO ₂	TiO ₂ supported on sand, 100 W medium pressure mercury lamp or sunlight, 13.8 L/min per m ² of sunlight, reactor volume: 250 mL system, flow rate: 230 mL/min	Mathews, 1991 [133]
TCE and other volatile organics in groundwater	200 ppb	6 min	5 ppb	Not reported	Field scale system, flow rate: 30 gpm, field test costs reduced from \$16/1000 gal to \$8/1000 gal using non-concentrating photoreactors instead of trough reactors and other process improvements	Mehos and Clyne, 1992-93 [203]
Fluorinated aromatics 2-, 3-, 4-Fluorophenol 2,4-, 3,4-difluorophenol	2 x 10 ⁻⁴ M	30 min for degradation; 150 min for mineralization	100%	CO ₂	Temperature: 60°C, pH: 3, TiO ₂ : 50-100 mg/L, simulated sunlight 60 mW/cm ² (> 310 nm) or 1500 W xenon lamp	Minero et al., 1991 [140]
1,1-Dibromoethane 1,2-Dibromoethane	35 ppm	500 min for 100% degradation of 1,2-dibromoethane Specific rate constants for bromoform, dibromoethane, 1,1-dibromoethane, 1,2-dibromoethane were 6.17, 4.07, 3.93, and 2.19 ppm/min-g of catalyst, respectively	100% mineralization	HBr and CO ₂ , vinyl bromide is an unstable intermediate in the case of 1,2- dibromoethane	Temperature: 30°C, TiO ₂ : 0.1 wt %, illumination: 6.6 x 10 ⁻⁴ Einstein/min, photoreactor described by Pruden and Ollis, 1983a	Nguyen and Ollis, 1984 [124]

PCE Dichloroethane Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid Monochlorobenzene Dichlorobenzene	
Trichloroethylene	
2-Chlorodibenzo-p-dioxin (CDD) 2,7-Dichlorodibenzo-p- dioxin (DCDD) 3,3'-Dichlorobiphenyl	
Herbicide: bentazon	
Dodecane	
Herbicides: Atrazine Simazine Trietazine Prometon Prometryn Carbon tetrachloride Chloroform Methylene Chloride Trichloroethane (TCA) PCE TCE	
Chloroform	
TCE	10
TCE PCE	3
Mercurochrome dye	0

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

<p>perature: 40°C, pH: 3.6, : 75 mg, coated on the inside ing, 7 m long borosilicate tubing wrapped around 20 W light fluorescent lamp, ulated solution volume: 40</p> <p>dition rates were also reported 10, and 50 mg/L of minant</p>	Mathews, 1988 [97]
<p>ilica gel was used as an bent for 1.26 g TiO₂, 40 W r low pressure mercury vapor scent lamp, 300-460 nm, ar reactor volume: 646 mL, ulation flow rate: 20 mL/min</p>	Mathews, 1988 [112]
<p>perature: 40°C, pH: 3.5, 0.1% (w/w), near UV light blacklight blue fluorescent or 1 m² of sunlight, reactor ie: 40 mL, flow rate: 270 in</p>	Mathews, 1990 [184]
<p>upported on sand, 100 W m pressure mercury lamp or ht, 13.8 L/min per m² of ht, reactor volume: 250 mL, i, flow rate: 230 ml/min</p>	Mathews, 1991 [133]
<p>scale system, flow rate: 30 field test costs reduced from 00 gal to 58/1000 gal using ncentrating photoreactors l of trough reactors and other s improvements</p>	Mehos and Clyne, 1992-93 [203]
<p>perature: 60°C, pH: 3, TiO₂:) mg/L, simulated sunlight /cm² (> 310 nm) or 1500 W lamp</p>	Minero et al., 1991 [140]
<p>perature: 30°C, TiO₂: 0.1 wt imination: 6.6 x 10⁻⁴ n/min, photoreactor described den and Ollis, 1983a</p>	Nguyen and Ollis, 1984 [124]

<p>PCE Dichloroethane Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid</p>	46.4 ppm	70 min	100% mineralization	HCl, CO ₂ for PCE, mono- and dichloroacetic acid, no chloride reported for trichloroacetic acid	Temperature: 28°C, TiO ₂ : 0.1 wt %, 7 black light fluorescent bulbs (320-400 nm), intensity: 6.6 x 10 ⁻⁴ , quartz annular reactor, liquid volume: 635 mL.	Ollis et al., 1984 [117]
<p>Monochlorobenzene Dichlorobenzene</p>	67 ppm 70-400 ppm	3 h 2 h	100% mineralization 5% dechlorination Both chlorobenzenes not mineralized.	<i>o</i> - and <i>p</i> -chlorophenol, corresponding benzoquinones and hydroquinones, and dichlorobiphenyl were products from chlorobenzene, dichlorophenols were additional products from dichlorobenzene, no ring fission observed		
Trichloroethylene	1.2 ppm	4.25 min	< 50 ppb	Not reported	TiO ₂ : 0.1 %, solar radiation: 300-400 nm, 1600 W, 38 W/L, flow rate: 100 L/min, parabolic trough system, collector area: 465 m ² , residence time: 2.5 min, H ₂ O ₂ : 100 ppm	Pacheco and Tyner, 1990 [202]
<p>2-Chlorodibenzo-<i>p</i>-dioxin (CDD) 2,7-Dichlorodibenzo-<i>p</i>-dioxin (DCDD) 3,3'-Dichlorobiphenyl</p>	100 ppm	2 h for CDD, 90 h for DCDD, 1.5 h for DCB	100% mineralization	Inorganic chloride quantitatively recovered for CDD and DCDD	pH: 3, TiO ₂ : 4 g/L (0.5 g/L is also effective), TiO ₂ showed highest activity in comparison with ZnO, CdS, TiO ₂ /Pt, and Fe ₂ O ₃ , 900 W Xenon lamp, > 340 nm, electron scavengers Ag ⁺ and Fe ³⁺ increase activity of TiO ₂	Pelizzetti et al., 1988 [163]
Herbicide: bentazon	20 ppb 50 ppm	10 min, half-life of degradation: 30 min @ pH 2 and 4 min @ pH 7	0.1 ppb	Sulfate, CO ₂	TiO ₂ : 0.5 or 2 g/L, 1500 W xenon lamp, reaction volume: 5 or 500 mL	Pelizzetti et al., 1989 [147]
Dodecane	2 x 10 ⁻⁴ M	6 h, 6-8 h for quantitative CO ₂ production	100% degradation	CO ₂	TiO ₂ : 2 g/L, 1500 W xenon lamp, > 340 nm, reaction volume: 5 mL	Pelizzetti et al., 1990 [107]
<p>Herbicides: Atrazine Simazine Trietazine Prometon Prometryn</p>	25 ppm 3 15 25 25	less than 20 min	100% disappearance	Cyanuric acid is a stable endproduct, other products include nitrate, chloride, and sulfate	TiO ₂ : 0.5 g/L, 1500 W xenon lamp, flux: 5.8 x 10 ⁻⁵ Einstein/min-cm ² , reaction volume: 5 or 25 mL	Pelizzetti et al., 1990 [148]
<p>Carbon tetrachloride Chloroform Methylene Chloride Trichloroethane (TCA) PCE TCE</p>	1 ppm	374 min 32 min 23 min 19 min 1.8 min 3.1 min	99% conversion	Not reported	TiO ₂ : 0.1 wt %, direct radiation: 1000 W/m ² (30 W/m ² below 400 nm), flow rate: 20 to 100 L/min, residence time: 12.5 to 2.5 min, parabolic trough reactor: 220 m long, collector area: 465 m ² , bicarbonate significantly hinders TCE degradation	Prairie et al., 1992 [96]
Chloroform	104 ppm	180 min	100% mineralization	Chloride	Temperature: 34-44°C, TiO ₂ : 0.1 wt %, quartz annular photoreactor using 7 15 W black light fluorescent lamps, 320-440 nm, intensity: 6.6 x 10 ⁻⁴ ; Einstein/min	Pruden and Ollis, 1983 [119]
TCE	10.3-45.9 ppm	1st order reaction rates of 0.365 to 0.198 min ⁻¹	100% mineralization	HCl, CO ₂ dichloroacetaldehyde is an intermediate	Temperature: 36-38°C, TiO ₂ : 0.1 wt %, quartz annular photoreactor using 7 black light fluorescent lamps, 320-440 nm, liquid volume: 625 mL, illuminated volume: 300 mL, recirculation flow rate: 40 mL/s, batch mode	Pruden and Ollis, 1983 [120]
TCE PCE	3.5 x 10 ⁻⁴ M	20 min	100%	Small amounts of acetic acid found as an intermediate, inorganic chloride endproduct	pH: 3.5, TiO ₂ : 1.2 g/L, 500 W superhigh pressure mercury lamp, 7-fold enhancement of degradation rate by H ₂ O ₂ addition (4 x 10 ⁻³ M) to approx. 1.75 x 10 ⁻⁵ M/min	Tanaka et al., 1989 [118]
Mercurochrome dye	0.375 ppm	40 min for complete disappearance, 150 min for complete mineralization	100% mineralization	CO ₂ , Hg deposition on TiO ₂	Temperature: 26°C, TiO ₂ : 0.5 mg/L, 400 W medium pressure mercury lamp, reaction volume: 400 mL	Tennakone et al., 1993

TABLE 4
Summary of TiO₂-Assisted Photocatalytic Treatment

Chlorophenols: 2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 2,3-Dichlorophenol 2,4-Dichlorophenol 3,5-Dichlorophenol 2,6-Dichlorophenol 3,4-Dichlorophenol 2,3,5-Trichlorophenol 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol	10 ⁻³ M for all	8 h	89% 96 102 43 113 98 98 97 52 89 0 CO ₂ produced as % of theoretical value	Various hydroxylated and dechlorinated products, CO ₂ , and inorganic chloride	Temperature: 25°C, pH: 7, TiO ₂ : 10 g/L, 1600 W medium pressure mercury vapor discharge lamp, 228- 420 nm, intensity: 17 W/m ² , reaction volume: 15 mL, oxygen atmosphere	Tseng and Huang, 1991 [128]
Phenol	100 mg/L	2 h	35%	Not reported	Temperature: 35°C, pH: 6.5, TiO ₂ : 1-3 mg/L, 400 W mercury lamp, light intensity: 2.3 x 10 ⁻⁴ Einstein/s, reactor volume: 1.065 L	Wei and Wan, 1991 [113]

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Temperature: 25°C, pH: 7, TiO ₂ : 1 g/L, 1600 W medium pressure mercury vapor discharge lamp, 228-0 nm, intensity: 17 W/m ² , reaction volume: 15 mL, oxygen atmosphere	Tseng and Huang, 1991 [128]
Temperature: 35°C, pH: 6.5, O ₂ : 1-3 mg/L, 400 W mercury lamp, light intensity: 2.3 x 10 ⁻⁴ einstein/s, reactor volume: 1.065	Wel and Wan, 1991 [113]

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