Review

Photomicroelectrochemical detoxification of hazardous materials

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Abstract

The generation of hazardous wastes (chemical by-products) is endemic to most chemical manufacturing processes and to the large-scale users of many chemical-based materials. Approximately 300 million metric tons of hazardous waste under U.S. Federal and State regulation were generated annually according to the most recent estimates in 1984, and this is a world wide problem. It is particularly acute in the United States. The petrochemical and refinery industries produce about 70 percent of this waste on a national basis. Geographically, the greatest production of hazardous wastes occur along the Gulf Coast. Presently, land disposal is used for as much as 80 percent of the nationally regulated hazardous wastes, some of which may remain hazardous for years or even centuries. Inappropriate disposal of these wastes on land creates the risk of contaminating, particularly the ground water, causing adverse health effects. An effort will be made in this review to give an overall coverage on the topic of photomicroelectrochemical detoxification of hazardous materials.

1. Introduction

The environment and everything connected with it has been a major concern of the public because most of our ecological systems such as air, water and soil are being continuously polluted by domestic and industrial pollutants. These pollutants have their origins from a number of sources such as domestic and agricultural, pesticides and herbicides, industrial wastes, chemical fertilizer

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washes from lawns, gardens and agricultural fields, human and animal wastes, oils and grease from motor vehicles, air pollutants including effluent gases like SO_2 and other nitrogenous gases that lead to acid rains, salts and other chemicals used in deicing streets and highways, etc. Most of these pollutants are highly toxic to humans, animals and vegetation.

Toxic is a relative term which implies threats, dangers, hazards and the like to living objects while, a toxic substance poses a potential danger to human and animal life upon exposure to it thereby affecting the health and ecology. In this review, the terms destruction and detoxification have been used interchangeably for degradation of toxic substances into harmless products. The clean up of chemical wastes produced in industrial arenas has been a complex problem and this cannot be resolved by simple disposal, incineration or by any special treatment, but by a combination of complementary technologies. Before the disposal of the toxic wastes it is imperative to convert it to be non-toxic by proper chemical reactions. A number of methods are now available for the destruction of hazardous wastes before their safe disposals [1]. These include: (i) the process of molten salt combustion wherein, the polychlorinated biphenyls, chloroform, chloroethylene, trichloroethane, pesticides and herbicides are destroyed; (ii) the fluidized bed incineration wherein, chlorinated hydrocarbon wastes with 90% chlorine are destroyed; (iii) UV/ozonation technology is a more effective process for destroying polychlorinated biphenyls, nitrobenzene, dioxins and hydrazine than the use of ozonation alone.

Several thermal and non-thermal processes have been used to treat the organic wastes and these have their own limitations [2]. Oxidation is by far the most important destructive method [3]. Incineration is the ultimate in practical oxidative destruction. If incomplete or improper combustion takes place in an incinerator, it may cause more hazard. For instance, improper incineration of carbon tetrachloride and freons can yield phosgene, a highly toxic substance. In pursuit of better methods for the detoxification of hazardous materials, microheterogeneous photocatalysis has recently emerged as one of the potential techniques. The advantages of this method are: (i) complete degradation of the organic pollutant requiring relatively short periods lasting only a few hours, (ii) the formation of photocatalyzed products is avoided, instead complete mineralization into e.g. CO_2 and HCl can be achieved, and (iii) the process requires inexpensive reusable catalysts with high turnover which can be supported in proper reactors.

Over the past few years, the field of photo-induced electron-transfer reactions in heterogeneous systems has witnessed a number of new discoveries. The development of artificial photosynthetic systems to harvest sunlight and convert it into electricity or chemical fuels is rapidly advancing [4–6]. Particularly, the use of semiconductor particles as photocatalysts to degrade the organic hazardous pollutants in aqueous environment has been actively studied. In the present review, we shall restrict our discussion to the study of photomicroelectrochemical degradation of toxic waste materials. Every effort

will be made to include the relevant contributions of the period covering 1979 to present date. Wherever necessary, some of the earlier references are also cited. For more details, the readers are advised to consult the original papers and books.

2. Photomicroelectrocatalytic systems

Degradation of chemical wastes has been achieved chiefly, if not completely, by a number of technologies available today. Of these, the most prominent techniques are those from photochemistry and electrochemistry of toxic waste materials. In this section, a brief discussion on the chemistry and physics of the process of photodegradation of toxic chemicals will be attempted only qualitatively. The most common terminologies used in this area are defined. A photomicrocatalytic system is a medium consisting of colloidal size aggregates of a large number of molecules having particle sizes smaller than the wavelength of visible light. Thus, a majority of the microheterogeneous systems form optically transparent (non-turbid) solutions which can be studied by photochemical and pulsed photolysis methods [7]. The term "microheterogeneous" suggests that they are heterogeneous at the microscopic level in the presence of charged interfaces in hydrophobic or hydrophilic domains [8–18].

The particulate semiconductor photocatalysts have several interesting features: (i) each photocatalyst functions as a microphotoelectrode or a photochemical diode for a metal-loaded semiconductor particle, (ii) they possess a large surface area of about 10^4–10^6 cm^2 g^{-1} which is advantageous for surface reactions, (iii) they possess novel photophysical properties which depend on the quantum size effect, and (iv) their low cost and ease of fabrication makes them attractive in several practical applications. The energy band gap of TiO$_2$ is so large (>3 eV) that it becomes a good photoelectrocatalyst despite of its poor catalytic activity towards electron transfer reactions. Large band gap semiconductors prove to be better photocatalysts than the low band gap materials. Naked CdS is a poor photoelectrocatalyst; however, better catalytic properties may be imparted to it by attaching transition metal catalysts like Pt or Ru on its surface [19].

The principle objective of photoelectrocatalysis is to provide low-energy activation pathways for the passage of electric charge carriers through the electrode–electrolyte interface and in particular, for the photoelectrochemical generation of chemical products. As for an ordinary catalyst, a photoelectrocatalyst may not be consumed during its catalytic activity. The semiconductor photocatalysis functions as a pool of electrons or holes which is advantageous in multi-electron transfer reactions. The principle and application of semiconductor electrodes in photoelectrochemical cells as well as the principles of photodriven processes and application of semiconductors for carrying out heterogeneous photocatalysis, photoelectrosynthesis, etc., have been described by Bard [20, 21].

Absorption of light having energy greater than that of the band gap, by semiconductor dispersions leads to the generation of electron–hole pairs [22, 23] which, under the influence of the electric field, move (within the band gap) into the conduction and valence band, respectively. It is the resulting nonequilibrium distribution of conduction band electrons and valence band holes that leads to either reduction or oxidation processes. For instance, in heterogeneous photocatalysis, light excitation of TiO_2 (anatase, rutile or amorphous) aqueous dispersions with energies greater than band gap ($> 3\,eV$) leads to the charge separation of electrons and holes in a manner analogous to single crystal semiconductor electrodes. The dynamics of interfacial electron-transfer reactions have been studied with colloidal size semiconducting TiO_2 and CdS aqueous dispersions, by excitation using nano-second laser flash [24]. Biosynthesis of nanometer scale CdS semiconductor quantum crystallites (size approx. 20 Å) have been reported by Dameron et al. [25].

3. A critical appraisal of literature data

Our goal here is to give a qualitative coverage of the literature data on photomicroelectrochemical degradation of toxic waste materials by using colloidal size particles such as TiO_2. Innumerable review articles have been published in the past on heterogeneous photocatalysis covering several aspects [26–40] such as organic syntheses, preparation of photocatalysts, photosynthesis, water-splitting and hydrogen generation, photocatalytic systems etc. Pelizzetti et al. [41, 42] reviewed the photocatalytic processes in semiconductor suspensions such as water-cleavage, H_2S-cleavage, photocatalyzed decarboxylation of the organic carboxylic acids and photocatalyzed degradation of wastes. Fundamental aspects of the primary events in photocatalysis employing CdS and TiO_2 semiconductors have been described by Serpone and Pelizzetti [43].

The redox and photolytic mechanisms and the basic concepts of photocatalysis such as thermodynamic conditions for photoactivity have been reviewed by Schiavello [44]. Fox [45] described the photoreactions on heteropolyoxoanions on clays in native and modified forms, and on zeolites of varying sizes, selectivity and catalyst loading. Several oxidative and/or reductive cleavages of organic substrates which occur with different reaction pathways were also investigated. A photocatalytic process is the same as the catalytic process, wherein, the surface reaction follows the redox-type mechanism occurring through the separated holes and electrons, photogenerated by exciting a semiconductor with light. The criteria for a solid to become a semiconductor have been discussed by Finklea [46].

Several patents have appeared on the subject of this topic. Only the representative patents will be discussed here. Reduced TiO_2 serving as an effective photocatalyst and photoelectrode was prepared by Toshiba Corporation [47]. A highly specific catalyst composition comprising a zeolite and a photoactive

material was also prepared [48] which is capable of catalyzing reactions within the zeolite structures. A recent patent by Lichtin et al. [49] utilizes a solid transition metal oxide catalyst, namely TiO_2 and H_2O_2, which is capable of degrading organic pollutants in a polluted water to environmentally acceptable products such as CO_2, when irradiated with UV or visible light.

A membrane-separated photoelectrochemical cell which can be used to carry out a redox reaction has been patented by Onoda et al. [50]. The cell has a membrane having a semiconductor which divides the electrolyte. When the interface of the semiconductor and the electrolyte was irradiated with light, oxidation occurs in one side of the electrolyte and a reduction in the other. This cell finds applications in wastewater treatment, disinfection, hydrogen preparation, etc. Harada et al. [51] have prepared TiO_2 from aqueous $TiCl_4$ by three different methods: (i) neutralization with a 14% (w/v NH_4OH solution, (ii) hydrolysis in water at $>80\,°C$ and (iii) hydrolysis in $0.5\,N$HCl. Their photocatalytic activities were related to the degree of crystallinity. TiO_2–SiO_2 beads prepared by vapor-phase hydrolysis of titanium alkoxide adsorbed on SiO_2 beads were active in promoting perfect oxidation of acetone [52]. A different performance in photoinduced catalysis was observed among the platinum metal catalysts supported on these beads and on TiO_2 beads. We shall now further divide the discussion of literature data into nine separate classes as follows: (1) Aquatic pollutants, (2) halogenated aromatics and acetic acids, (3) PCBs, (4) phenols and chlorophenols, (5) surfactants, (6) cyanides, (7) toxic metals, (8) sulfur compounds, and (9) miscellaneous compounds.

3.1 Aquatic pollutants

Over the years, contamination of surface and well water by organic pollutants has increased considerably. These pollutants originated from several industries such as those including petroleum, chemical, textile processing, paper and pulp milling, etc. The contamination may be due to the direct industrial discharges, leakage from landfill, other land disposal sites and from underground storage tanks. In addition, use of fuels for transportation and heating, use of pesticides, herbicides and fertilizers in agriculture, use of aerosol sprays, detergents, etc., among others, lead to the release of pollutants which may directly pollute the aquatic media. Other possibilities of aquatic contamination include effluents from wastewater treatment plants, accidental spills, and uncontrolled or poorly chosen landfill hazardous waste sites [53]. As a consequence, more than 700 potentially hazardous compounds have been identified in drinking water [54]. The U.S. Environmental Protection Agency (EPA) has identified hundreds of compounds and elements from pollutants as 'priority pollutants' [55]. The photocatalytic process has also been applied to wastewater treatment containing contaminants even in the ppb range [56]. Thus, it is legitimate to apply the photocatalytic methods to solve the environmental problems caused by the discharge of toxic chemicals into aquatic and atmospheric ecosystems.

Two classes of hazardous materials which are known to pollute water are: organic and inorganic pollutants. Organic pollutants include pesticides, herbicides, halogenated aliphatics, monocyclic aromatics, phenols and polychlorophenols, cresols, polycyclic aromatics, nitrosoamines, nitrogen-containing compounds, ethers, phthalate esters and polychlorobiphenyls (PCBs). Metals, asbestos, hydrogen sulfide and cyanides are some of the examples of the inorganic pollutants. In a study by Sundstrom et al. [57], the destruction of the pollutants containing mixtures of benzene and trichloroethylene solvents was achieved by UV-catalysed oxidation with hydrogen peroxide.

A number of reviews exist on the topic of pollutants in aquatic environment. Zepp [58, 59] reviewed the photochemistry of organic pollutants in aquatic environment and discussed factors affecting the photochemical treatment of hazardous wastes. Fowler critically reviewed the existing concentration of heavy metals and chlorinated hydrocarbons in the marine environment [60]. In a study by Hemmerich et al. [61], photooxidation of organic pollutants in industrial wastewater was investigated wherein, an aqueous solution of aniline hydrochloride mixed with TiO_2 when irradiated for 48 h, the Chemical Oxygen Demand (COD) dropped from 23.9 to 18.8 g/L. Selective removal of heavy metals from wastewater using affinity dialysis method was studied by Hu et al. [62].

Ollis [63] reviewed the heterogeneous photocatalysis for the decomposition of halogenated organic compounds in water purification. Oliver and Carey [64] summarized the results on the photodegradation of organic pollutants in aquatic environment and wastewater treatment by photolysis. Pelizzetti and Serpone [65] have reviewed the photodegradation of organic pollutants in aquatic systems catalyzed by semiconductor systems. Practical aspects of photocatalysis employing CdS and TiO_2 semiconductor dispersions with reference to (i) photocleavage of H_2S, (ii) the treatment of wastes, and (iii) the photoreduction and recovery of metals on TiO_2 have been discussed by Borgarello et al. [66]. Pichat [67] presented the results of investigations of electron transfers between Pt and TiO_2 as well as between CdS and TiO_2 under various experimental conditions. Potential applications of heterogeneous photocatalysis like the recovery of toxic metals from dilute solutions and removal of water pollutants were also discussed.

3.2 Halogenated aromatics and halogenated acetic acids

While treating water by chlorination for urban supplies of drinking water, some low molecular weight chlorinated oxidation products resulting from the destruction of humic acids are known to be generated. Among the most common reaction products, the potentially hazardous compounds are chloroform and mono- or di-substituted acetic acids [68]. In recent years, extensive studies on the degradation of organic pollutants by heterogeneous photocatalysis have been made [69–71] by using TiO_2 as a powder catalyst. However, the complete mineralization into CO_2 and HCl is of great importance in water

purification because some partially oxidized compounds like chlorophenols are more toxic than their parent compounds.

The compounds such as CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, $CH_2ClCOOH$ and $CHCl_2COOH$ have been completely degraded to give HCl and CO_2 upon exposure to illuminated TiO_2 [72–75]. The presence of light, photocatalyst, oxygen and water showed a favorable effect on their degradations. The degradation of chloroform is known to follow the photocatalytic process [76] as shown below:

$$H_2O + CHCl_3 + \tfrac{1}{2}O_2 \xrightarrow[h\nu]{TiO_2} CO + 3\ HCl$$
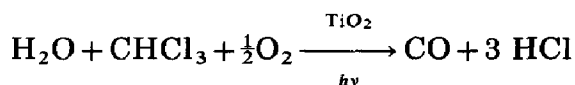
The photocatalytic decomposition of an aqueous solution of chloroform in the presence of TiO_2 under simulated solar irradiation was studied by Kawaguchi [77], wherein it was shown that its complete decomposition was affected by the pH and the amount of dissolved oxygen. However, halocarbons seem to degrade very slowly or not at all. For e.g., CCl_3COOH is essentially unreactive whereas, CCl_4 can be degraded only very slowly [75]. Masayuki et al. [78] used the rutile TiO_2 containing 0–10% of platinum photocatalysts for the degradation of chloroform. The photodegradation of dichloromethane into CO_2 and HCl has also been studied [79] by TiO_2 and Ti incorporated into aluminosilicate photocatalysts.

Wang and Tan [80] reported the reduction of trichloroethylene (TCE and CCl_4 in a platinum-catalyzed water photolysis system [Pt colloid/$Ru(bipy)_3^{2+}/MV^{2+}/EDTA$] with the natural sunlight irradiation. It is found that electron transfer reactions resulted in the cleavage of water to H_2 and OH^-. When chlorinated hydrocarbons, TCE and CCl_4 are added to the system, they were dechlorinated and subsequently reduced to low molecular weight hydrocarbons like methane and/or ethane during solar illumination.

Degradation of trace amounts of organohalogen solvents in water have been photocatalyzed by using the TiO_2 catalyst to reduce their toxicity levels to below those of the discharge standards [81]. Twelve organochlorine solvents such as di-, tri-, and tetrachloro derivatives of methane, ethane and ethylene were photocatalytically degraded on TiO_2, Pt-loaded TiO_2 and TiO_2 with added H_2O_2. For derivatives of these compounds, the degradation rates were in the order of $Cl_2 > Cl_3 > Cl_4$ and for those containing the same number of Cl substituents the order was ethylene > ethane. During the degradation of each organochlorine solvent, Cl^- was liberated simultaneously. On the Pt-loaded TiO_2, Cl^- was transformed photocatalytically into [82] ClO_3^-. The photocatalytic degradation of chloroform was investigated [83] in aqueous suspensions of TiO_2 over the wavelength region of 310–380 nm. A reaction mechanism was proposed in which the rate determining step is the reaction of surface-bound OH with adsorbed chloroform. The quantum efficiency ($\phi = 0.56$ at $\lambda = 330$ nm) of the degraded chloroform was inversely proportional to the square root of the incident light intensity.

Tanaka et al. [84] have shown that addition of H_2O_2 considerably enhanced the photodegradation rate of $CHClCCl_2$ and CCl_2CCl_2 in a suspension of TiO_2. The augmentation of the rate was attributed to the increase in the number of OH radicals formed on illuminated TiO_2. In fact, trichloroethylene ($CHClCCl_2$) and perchloroethylene (CCl_2CCl_2) were the most pervasive aliphatic halocarbons present in the environment due to their widespread applications in industrial solvents. The bromomethanes like CH_2Br_2 and $CHBr_3$ have been completely mineralized by photocatalysis with TiO_2. Their relative reactivities over TiO_2 followed the sequence: $CHBr_3 > CHCl_3 > CH_2Br_2 > CH_2Cl_2 > CCl_4$. Both 1,2-dibromoethane and its 1:1 isomer were completely degraded, as demonstrated by 100% recovery of initial bromine as bromide ion. Various TiO_2 catalysts for the oxidative dechlorination of CH_2Cl_2 to CO_2 and HCl were examined by Tanguay et al. [85]. TiO_2 (rutile) was found to be more active than its other forms, while pre-irradiation of the catalyst and the presence of oxygen supply enhanced the conversion; but, the chloride ion could inhibit it.

The aquatic environment is contaminated with a wide range of haloaromatic compounds and related derivatives. Such compounds have been used as preservatives for wood, leather, textiles, etc., and also they are used as herbicides, pesticides, insecticides, disinfectants and antimicrobials. These, in the course of time, reach surface water or associate sediments and contaminate the water. Such contamination by organochlorine compounds present a serious environmental problem due to their toxicities [86]. Chlorinated benzenes, biphenyls, phenols, pesticides (such as DDT) in addition to another extremely toxic compound, viz. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and its related derivatives including the chlorodibenzofurans, are among the most toxic compounds which contaminate our aquatic environment.

Removal of herbicides from irrigation wastewater by the natural volatilization, hydrolysis, photolysis and microbial degradation was known to proceed so slowly that adequate dissipation does not occur before wildlife and human drinking water supplies are threatened. In this pursuit, the photoassisted degradation of the herbicide 2,4,5-trichlorophenoxy acetic acid on TiO_2 has been studied [87]. Another popular class of herbicides, namely, atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), which is commonly used for grassy weed control in crops like corn, sorghum, sugarcane, pineapple, etc., can be detoxified by a photocatalytic method. Atrazine disappeared rapidly in an aqueous suspension of TiO_2 and in the presence of artificial or actual sunlight [56]. It is also reported that [88] the rice herbicides molinite (s-ethyl hexahydro-1H-azepine-1-carbothioate] and thiobencarb [s-(4-chlorophenyl) methyl-N,N-diethyl carbomothioate] were degraded rapidly in sunlight-irradiated suspensions of TiO_2 and ZnO. Here, ZnO served both as a semiconductor photooxidant and as the Zn(II) fertilizer which is generally used as plant nutrition.

The photocatalytic oxidation of aliphatic hydrocarbons in aqueous suspensions of TiO_2 was reported to give H_2 and CO_2 as final products [89].

Photooxidation of aromatic hydrocarbons such as benzene has been investigated [90, 91] in the presence of platinized TiO_2. Haloaromatics, like 3,3′-dichlorobiphenyl, DDT and 2,7-dichlorodibenzo-p-dioxin present in the 0.2 to 1.0 ppm ranges were shown to be degraded efficiently after prolonged exposure to light in the presence of TiO_2 [92]. Hustert et al. [93] reported the degradation of chloronitrobenzenes by irradiation in the presence of TiO_2 to give CO_2, HCl, water and nitric acid as the final products.

The degradation of some of the above mentioned undesired contaminants is possible through chemical, photochemical and microbiological processes. However, both chemical and thermal degradations are impracticable in water treatment. On the other hand, microbial degradation and naturally occurring hydrolysis require long periods. For instance, 4-chlorophenol in estuarine water at 21 °C showed a half life of 20 days. Though direct photodegradation may cause dechlorination, it requires high energy photons. Degradation of the contaminants may be incomplete while, it can also lead to the formation of dangerous products; partial dechlorination or ring closure can generate products which are more toxic than the starting materials. To overcome these problems, heterogeneous photocatalytic method has been suggested as an alternative practical approach for the detoxification of this class of compounds.

Complete mineralization of chlorobenzenes (monochlorobenzene and 1,2,4-trichlorobenzene) has been observed through exposure to light ($\lambda > 300$ nm) in an aerated aqueous 0.1% (w/v) suspension of TiO_2 [75, 94]. The primary photoproducts were *ortho-* and *para*-chlorophenols which were subsequently dechlorinated to give the corresponding hydroquinone and/or catechols which in turn were readily converted to benzoquinone [75]. TiO_2 particles do not seem to be good materials for decontamination of monochloro- and dichlorobenzenes containing water. This is because dechlorination is relatively slow and multiple photoproducts including PCBs are formed.

3.3 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are derivatives of the compound biphenyl wherein the available hydrogen atoms of the aromatic moieties have been replaced with chlorine atoms. The United States EPA has classified PCBs as extremely toxic and carcinogenic and has imposed several controls on their uses. They are known to cause tumors in laboratory animals, carcinogenic effects to human beings, and extremely toxic effects to several species of aquatic invertebrates and fish. Some of the toxic effects of PCBs include chloracne, discoloration of gums and nail beds, swelling of the joints, waxy secretion of the glands in the eyelids etc. There are about more than 200 possible PCB isomers, ranging from three monochloro isomers to one decachloro isomer. The commercial mixtures are very complex, each containing many isomers with traces of impurities, some of which are potentially toxic. However, most of the commercial PCB mixtures use mono- and hexachlorobiphenyls.

PCBs are used widely in electric transformers, circuit breakers, voltage regulators and capacitors because of their resistance to flammability, excellent cooling effects and extremely low electrical conductivities. They have applications as hydraulic fluids, heat transfer liquids, dye carriers in carbonless copy paper, additives in printing inks, in paints and adhesives. In spite of their restricted new uses, large quantities of PCBs still exist in electrical transformers, capacitors and numerous dumpsites. PCBs are less soluble in water but highly soluble in fats. The main problem with PCBs is that they are among the most stable chemical compounds and are stable to oxidation, hydrolysis and other chemical reactions occurring in the environment. Because they decompose very slowly over a very long period of time, they remain in the environment for decades after being released into the atmosphere. The efficient decontamination of materials is a major environmental problem. They require extremely severe reaction conditions or extremely reactive reagents for detoxification [95].

Apart from emerging technologies (molten salt combustion, incineration and UV/ozonation technology), non-thermal methods like catalytic dehydrochlorination, microwave plasma destruction, catalyzed wet air oxidation, high energy electron treatment, etc., have also been used for detoxification of PCBs and other trace organic compounds in aqueous solution. Nishiwaki [96] reviewed the photodecomposition and dechlorination of PCBs. Several other researchers [97–107] investigated the non-thermal methods including photolysis, radiolysis, catalytic dechlorination, etc., to destroy PCBs. By direct photolysis under sunlight in the presence of cyclohexane, hexane and iso-octane solvents, PCBs were significantly photodegraded to less chlorinated biphenyls [108–110]. Since typical pollutant concentrations were low, very little light is absorbed by the pollutant thus making it difficult to measure directly the environmental concentrations.

A review by Cesareo et al. [111] discusses the effectiveness of photochemical processes as detoxification mechanism in aqueous systems with reference to chlorinated aromatics. Phototransformation of PCBs in direct, sensitized and photocatalyzed degradations were compared and analyzed with the available literature data. Besides, the origin of PCBs in aquatic environment, their toxic effects have also been covered. Martinez [112] reviewed the destruction and detoxification of polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins, including thermal and chemical techniques, photolytic, radiolytic and catalytic processes, etc.

Shukla and Rusling [113] studied the photoelectrocatalytic reduction of 4-chlorobiphenyl using anion radicals and visible light. It was found that excitation of electrochemically generated anion radicals of anthracene and 9,10-diphenyl anthracene with visible light ($\lambda > 470$ nm) showed more than ten-fold increase in the rates of reductive dechlorination of 4-chlorobiphenyl. In another report by Rusling et al. [114], the reduction of 4-bromobiphenyl in cationic and non-ionic micelles has been studied. This study indicated new

possibilities to decompose halogenated pollutants in aqueous systems as well as to other difficult organic reductions.

Menassa et al. [115] studied the photodecomposition of different PCBs by surface modified TiO_2 in a medium containing hexane and water mixture. The dechlorination was monitored by GC/MS techniques. Sodium laurylbenzene sulfonate and PCBs have been photodecomposed by irradiation with a xenon lamp in aqueous solution containing platinized TiO_2 powders with oxygen bubbling [116]. The decomposition was initiated by the photogeneration of OH radicals at Pt and TiO_2 surfaces and the radicals reacted with organic compounds to give CO_2 as a final product. Tunesi and Anderson [117] have shown that the rate of destruction of 3,4-dichlorobiphenyl on a TiO_2 surface increases with temperature and light intensity. The suspension/semiconductor interface was then analyzed by cylindrical internal-Fourier transform infrared techniques (CIR-FTIR).

In a study by Carey et al. [118], several PCBs such as 4,4'-dichlorobiphenyl, 2,2'-dichlorobiphenyl, 2-chlorobiphenyl, 3-chlorobiphenyl and 4-chlorobiphenyl in 25 ppb aqueous suspensions of TiO_2 were irradiated separately at 365 nm for 30 min. The disappearance of chlorinated biphenyls and production of chloride ion showed that illuminated semiconductor catalysts could also provide a viable means of degradation of PCBs. Further, there was no trace of 3- or 4-chloro isomers after irradiation; however, 2-chlorobiphenyl did not degrade at all. Extraction of PCBs using microemulsions alone, is not good enough because extracted amounts were smaller than the amounts of surfactants needed. However, for the decontamination of PCBs in oil, the photocatalyst can be added to the microemulsion containing PCB plus oil; the system brought to the higher temperature, dechlorinated by exposure to light and then cooled to room temperature. A method for the determination of total chlorinated hydrocarbons in water has been reported by Kojima et al. [119] which involves mineralization by TiO_2-catalyzed photodecomposition followed by the measurement of liberated chloride anion.

3.4 Phenols and chlorophenols

Chlorinated phenols are the well known pollutants that have been introduced into the environment as herbicides and fungicides. These compounds are generally resistant to chemical, photochemical and biodegradation, making the disposal of contaminated water difficult. Chlorophenols are toxic and their toxicity depends on the number of chlorine substituents on the aromatic ring. The higher chlorinated phenols, like trichlorophenol (TCP), tetrachlorophenol (TTCP) and pentachlorophenol (PCP) contain biologically active impurities such as polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) [86, 120]. The TCP also comes from the partial decomposition of herbicides such as 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) giving 2,4,5-TCP, which is a precursor of the 2,3,7,8-TCDD dioxin. Further, municipal sewage treatment plants and the municipal incinerators are a continued source of these contaminants.

The photocatalytic degradation of 2-chlorophenol and 3-chlorophenol in TiO_2 aqueous suspensions at $\lambda > 340$ nm was faster than direct photolysis at 290 nm [121]. Mechanistic aspects of the photocatalytic oxidation of phenol in aqueous solutions by using TiO_2 and UV light have been studied [122]. The photocatalytic degradation of phenols and chlorophenols was investigated with different catalysts such as ZnO, TiO_2, Fe_2O_3 and CdS. Here, ZnO was the most active photocatalyst and phenols were completely oxidized to give di-hydroxybenzenes. The rate of photodegradation was found [123–125] to depend on pH, phenol and TiO_2 content, oxygen concentration and the anions present in dispersion. Photolysis of phenol, 2,4,6-trichlorophenol, and PCP containing wastewater in the presence of CdS indicated that the greater the Cl substitution on benzene moiety, the higher the degradation [126]. The rates of removal of halogen substitutions were higher than those of nitro- and methyl groups and the abstraction of Cl is not affected by its position in the benzene ring.

Degradation of 4-chlorophenol (4-CP) from a heterogeneous photoassisted process using TiO_2 suspension, gave CO_2 and HCl under sufficient aeration condition [71]. This degradation proceeds via an oxygen-containing radical attack and further Cl· reduction to Cl^- by conduction band electrons. Further oxidation to dihydroxybenzene derivatives and benzene ring breakdown lead to the final simple products. In a similar study, under the same experimental conditions, Barbeni et al. [127] have shown that PCP can be quantitatively mineralized at high rates. The photocatalytic degradation was studied in other semiconductor dispersions such as ZnO, CdS, WO_3 and SnO_2, but TiO_2 proved to be the most efficient. However, experiments with sunlight showed a promising route for water treatment processes.

The photocatalytic effect of TiO_2 (anatase) on the decomposition of chlorophenol was studied by Kawaguchi [128]. Photocatalytic decomposition of aqueous phenol solution with a high pressure mercury lamp in the presence of TiO_2 (anatase) as a photocatalyst at $40\,^\circ C$ has also been studied [129]. It was shown that the rate of phenol decomposition increased with TiO_2 concentration and decreased with initial concentration of phenol. Further, the addition of copper to TiO_2 increased the rate of decomposition of phenol. Hydroquinone and catechols were the main products as detected by HPLC.

A similar study, conducted recently by Augugliaro et al. [130] further corroborated the findings of Kawaguchi [128]. In this study, photocatalytic degradation of phenol using aqueous oxygenated TiO_2 (anatase) suspensions in a batch photoreactor and the influence of various parameters like pH, phenol and TiO_2 content, oxygen concentration, anions present in the dispersion, etc., on the degradation rate has been investigated. It was found that chlorophenols were dechlorinated completely during 3 hours of irradiation with a xenon lamp. With TiO_2 powder as a sensitizer, irradiation of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4,5-trichlorophenol (TCP-OH) by simulated sunlight resulted in the conversion of these materials to give HCl and CO_2 with half lives of 30–90 min. In contrast, Crosby and Wong [131] reported that in the absence of a sensitizer, irradiation of 2,4,5-T in a similar photoreactor as that of

Kawaguchi [128] resulted in only 8% conversion of the starting material into HCl and CO_2 after 200 hours. According to Pelizzetti and coworkers [94, 132] complete mineralization of halophenols (3,4-dichlorophenol and 2,4,5-trichlorophenol) by photocatalytic degradation methods in the presence of TiO_2 required prolonged exposure. Davis and Huang [133] have shown that phenols and chlorophenols can be oxidized by using the irradiated CdS photocatalyst particles. The oxidation rate was found to depend on pH, photointensity, oxygen and phenol concentration, and temperature.

3.5 Surfactants

Due to the increased usage of surfactants (both non-ionic and anionic) in everyday life, there is an increasing level of pollution by these surfactants in domestic and industrial wastewater. The metabolic behavior of the non-ionic surfactants of the alkylphenol polyethoxylate type is dependent on the conditions of wastewater or sludge treatment which often leads to the formation of more persistent and even more toxic metabolites.

Hidaka et al. [70, 134] investigated the TiO_2-photocatalyzed conversion of the anionic surfactant sodium dodecylbenzenesulfonate (DBS) as well as degradation of the component parts such as sodium dodecyl-1-sulfate (SDS) and sodium benzenesulfonate (BS). It was found that DBS and BS were rapidly photodegraded in aqueous aerated TiO_2 suspensions in the absence of noble metal catalysts. The degradation was found to be a better method for the wastewater treatment as compared to biodegradation which requires longer times. Further, it was shown that surfactants (anionic, cationic and non-ionic) had been completely photocatalyzed; on the other hand, the degradation of long chain hydrocarbons occurred at very low rates. Hidaka et al. [135] have shown that anionic dodecylbenzene sulfonate, cationic benzyl dodecyl-dimethylammonium chloride and nonionic *p*-nonylphenol poly(oxyethylene) surfactants can be photodegraded in aqueous suspensions of TiO_2 powder by solar exposure. The aromatic moiety in the surfactants was decomposed more easily than the alkyl/or ethoxylate groups. This photodegradation system was suggested to be a practical means for the treatment of wastewater containing surfactants.

Pelizzetti et al. [136] have investigated the photocatalytic degradation of *p*-alkylphenols and nonylphenol ethoxylate surfactants using TiO_2 particles. A complete conversion to CO_2 was demonstrated by the liquid chromatography from the measurements of CO_2 evolution, dissolved organic carbon, and particulate organic carbon. A stable 4-nonylphenol (an even more toxic compound) has been completely mineralized. Therefore, photocatalytic degradation process may be used to ensure final disposal of these undesirable products together with other treatment of wastes. Various kinds of anionic, cationic and nonionic surfactants were photodegraded in a heterogeneous dispersion of TiO_2 semiconductor particles under the UV-illumination to convert them into CO_2 [137].

3.6 Cyanides

Cyanide is ubiquitous in nature. The use of cyanides in industries is ever increasing. Cyanide is a problem in gold mine effluent because it is used to extract gold from the ore. The mine wastewater also contains cyanide complexes such as ferricyanide which are difficult to breakdown with chemical treatment. Precious metals and cyanides reach waste effluents through other industrial processes like electroplating and jewellery. Conventional means to dispose of cyanide involve oxidation by chlorine–alkaline solutions, chlorination, ozonation and electrolysis.

Serpone et al. [138] have reviewed the photoreduction and photodegradation of inorganic pollutants with special reference to cyanides. Frank and Bard [139, 140] have used the TiO_2 containing semiconductors to destroy cyanide photochemically to give OCN^- and H_2O. They also used CdS dispersions in alkaline media in the presence of oxygen. The gold–cyanide complex is not decomposed in excess cyanide; on the other hand, photodegradation of gold–cyanide complex was found to be most efficient under acidic conditions. In a study by Borgarello et al. [141], complete transformation of cyanide to the less toxic thiocyanate was achieved. These workers used the Rh-loaded CdS dispersions in the presence of a waste byproduct by using H_2S as an oxidizing agent under visible light to achieve a 25% conversion in the presence of air and at very high concentrations of cyanide. In another study, Borgarello et al. [142] have demonstrated that gold can be recovered efficiently from cyanide aqueous media via a light-induced process mediated by TiO_2 dispersions. Detoxification of actual industrial wastes was carried out by treating wastes with H_2O_2 or $S_2O_8^-$ in the presence of UV light to achieve 75% degradation.

The disposal of cyanide ions by peroxide and subsequent photochemical reduction of gold(III) on TiO_2 particles represents a good example of the application of photochemistry and photocatalysis in resolving the environmental and industrial pollution problems. UV/H_2O_2 decomposition of cyanide offers an alternative to the methods used presently [143, 144]. Serpone et al. [145] have investigated the reduction and recovery of gold from samples containing CN^- using TiO_2 semiconductor dispersions irradiated with UV light ($\lambda > 210$ nm) or AM1 simulated sunlight ($\lambda > 310$ nm). The degradation of CN^- was also investigated with peroxides such as H_2O_2 and $S_2O_8^-$ in the presence or absence of light. The treatment of cyanide solutions with H_2O_2 by UV-irradiation lead to the total degradation of cyanides into ammonia and CO_2 as the main products. However, the photocatalytic oxidation of cyanide in aqueous solutions with a heterogeneous system containing tungsten trioxide, α-ferric oxide and tungsten was carried out [146] for 4 hours to achieve about 99% removal of cyanide.

3.7 Toxic metals

An attractive and practical implementation of photocatalysis concerns the recovery and refining of noble metals such as gold, platinum, palladium,

rhodium and silver from industrial (waste) water effluents [142]. Several such toxic metals (in their various oxidation states) can neither be biodegraded nor chemically decontaminated. Environmental pollution by toxic metals depends on the form of the metals in addition to their bulk concentrations. Most of these pollutants enter the marine environment from disposals by the metallurgical industrial sites.

The reduction of metals on TiO_2 particles irradiated with UV light seems to be an active area of investigation due to: (i) the noble metals as well as others can be photoreduced on the surface of TiO_2 particles and thus can be removed from solution [147, 148] and (ii) photoreduction of metals on TiO_2 may show the possibility of preparing metal redox catalysts supported on TiO_2 [149]. Serpone et al. [150] reviewed the photoreduction and photodegradation of inorganic pollutants with special reference to metals such as Au, Pt, Pd, Rh, Hg and Pb. They have shown that the photocatalysis by semiconductor materials under UV light or by AM1 simulated sunlight is a better way to eliminate the unwanted toxic metals from waste pollutants. Using simulated and air equilibrated TiO_2 suspensions in 0.1 M chloride media, the complete removal of 100 ppm Hg (originally as $HgCl_2$) and 80 ppm $(CH_3)_2Hg(II)$ have been achieved. Photoreduction of dimethyl mercury did not occur under the conditions of natural pH value of TiO_2 aqueous suspensions but, it occurred only in the presence of methanolic aqueous media. The illuminated semiconductors such as TiO_2, ZnO, CdS and WO_3 have been used to achieve the photochemical reduction of dissolved metals including noble metals [142]. Photocatalytic deposition of metals on semiconductors has been reviewed by Otani [151].

Inorganic pollutants in wastewater have been oxidatively destroyed with H_2O_2 using supported metal catalyst systems [152]. These heterogeneous catalysts were more effective than the conventionally used homogeneous ones in oxidizing sulfides, thiosulfates, mercaptans and cyanides in wastewater. Metals and supports studied were transition metals on silica, alumina and various natural and synthetic zeolites; the choice of these metals varied with the nature of the pollutants. The advantage of these catalysts is that they are suitable under acidic and alkaline conditions. Complete reduction of rhodium (III) was achieved in oxygen-free solution within 45 minutes of irradiation whereas the photochemical reduction of palladium(II) on TiO_2, under sunlight illumination occurred in the same time interval [153]. Further, selective photoreduction and separation of Au, Pt and Rh from a mixture of their halides found in industrial wastes and on TiO_2 was also studied. Tanaka et al. [154] studied the photocatalytic deposition of Pb(II), Mn(II), Ti(I) and Co(II) onto Pt-loaded TiO_2 suspensions. The rate of deposition in Pt–TiO_2 suspensions increased when air was continuously bubbled, while a decrease in rate was observed when argon or nitrogen were bubbled before illumination. When Pt–TiO_2 was replaced by metal free-TiO_2, the efficiency of the metal ion deposition also decreased significantly.

Removal of toxic metals such as lead from wastewater under a variety of conditions using the irradiated platinized TiO_2 particles was studied [155]. The

photoassisted reduction of Cr(VI) to Cr(III) in aqueous suspensions of TiO$_2$ under UV-illumination was studied by determining the amount of Cr(VI) photoreduced at different irradiation times, the mass of catalyst in the suspension, the Cr(VI) initial concentration and the pH of the solution [156]. The photocatalytic reduction of dichromate to Cr(III) in wastewater in the presence of platinized synthetic rutile, anatase and WO$_3$ was studied [157]. Rutile was found to be a more active photocatalyst than anatase or WO$_3$.

Mercury is another toxic metal which occurs in the environment as mercury salts. Batti et al. [158] reported the presence of methyl mercury in river sediments. Tanaka et al. [154] showed the reduction of mercury from mercuric chloride, using illuminated TiO$_2$ semiconducting particulates. Elimination of mercury(II) in aqueous solutions by ZnO powder under UV-illumination has also been studied by Domenech and Andres [159]; however, higher percentages (95%) of elimination was reported for illumination with natural sunlight.

3.8 Sulfur compounds

Sulfides in the form of hydrogen sulfide occur widely in coal, natural gas fields, volcanic gases, sulfur springs and lakes. Hydrogen sulfide also comes from anerobic decomposition of sulfur-containing organics. It is also an undesired byproduct or waste material from a number of coal and petroleum related industries [160] such as: (i) in the production of carbon disulfide wherein sulfur is made to react with natural gas at high temperatures and half of the sulfur introduced is consumed in the production of H$_2$S, and (ii) substantial quantities of H$_2$S can be released in the production of coke or manufactured gases from coal. At high concentrations, H$_2$S is a deadly poison, nearly as toxic as hydrogen cyanide. H$_2$S is a potentially useful source in the quest for alternative to fossil fuels. Cleavage of H$_2$S into hydrogen and sulfur driven by visible light in the presence of semiconductor particles is known to take place very efficiently. As the enthalpy of the above reaction is +9.4 kcal/mol, it provides a method for energy conversion and storage as well as for recycling of hydrogen employed in hydrodesulfurization processes.

Conventional and photochemical methods of disposal of H$_2$S have been reviewed by Borgarello et al. [161-163]. The methods discussed were absorption-desorption, the direct oxidation of H$_2$S into sulfur (Claus process), direct/indirect thermal decomposition, electrolytic splitting, and chemical methods involving catalysts. The photoelectrochemical and photocatalytic methods appear to be promising and efficient as they seem to work well in 1 M NaOH solutions at 25-80 °C. Borgarello et al. [162] have also shown the cleavage of H$_2$S in aqueous CdS dispersions under illumination by visible light. The effect of ionic surfactants on the efficiency of photocatalytic cleavage of H$_2$S in the presence of RuO$_2$ was also investigated. Addition of ionic surfactants such as sodium lauryl sulfate below their critical micellar concentrations (CMC) increased the quantum yield by four-fold. In a photoelectrochemical

method investigated by Kainthala and Bockris [164], a thin chemically deposited cadmium selenide film was known to act as the photoanode and Pt as the photocathode for the photoelectrocatalysis of H_2S.

Production of hydrogen through microheterogeneous photocatalysis of H_2S is an active area of research. Extensive research by many research groups [165–167] has established that (i) hydrogen generation depends on both solution pH and RuO_2 loading [166, 167]. For example, at pH 13 and 0.5% w/w RuO_2 loading of the CdS particles, the rate of hydrogen generation is 10 mL/h with a quantum yield of 0.35, (ii) Addition of TiO_2 to naked CdS decreased the rate of hydrogen production, whereas deposition of Pt on TiO_2 virtually suppressed the hydrogen evolution from H_2S, and (iii) by contrast, RuO_2-loaded TiO_2 mixed with CdS exhibits a remarkable increase in the rate of hydrogen production than that of CdS/RuO_2 alone. The effect of RuO_2 is attributed to catalysis of the hole transfer from the valence band of CdS to H_2S or sulfide in solution: the band gap excitation of the CdS particles produce electrons in the conduction band and holes in the valence band. The former migrate to the interface where reduction of protons to hydrogen occurs, while the valence band holes oxidize S^{2-} to sulfur. Thus, the overall reaction corresponds to the splitting of H_2S into hydrogen and sulfur by four quanta of visible light. This study proved that (i) RuO_2 unambiguously accelerates the transfer of holes from the valence band of CdS to redox species in solution, (ii) reduction of water to hydrogen can occur on CdS particles efficiently even in the absence of noble metal catalysts such as platinum (this shows that the CdS particle itself operates as an efficient microelectrode for hydrogen generation), and (iii) sulfur formed as an oxidation product simultaneously with hydrogen, does not seem to interfere with the reduction of water (i.e., reduction of sulfur by conduction-band electrons of CdS, though thermodynamically favored, is strongly inhibited for kinetic reasons). Therefore, photocleavage of H_2S into H_2 and S can take place quantitatively. When sulfides such as CdS are used as semiconductors, the hole reaction with sulfides is very fast and the overall process occurs with a very high quantum yield approaching nearly 50% [165]. These investigations have found immense applications, not only in solar energy research, but also in the treatment and conversion of H_2S or sulfides into hydrogen.

The splitting of H_2S in colloidal dispersions of CdS [168] is known to occur in alkaline solutions with quantum efficiency of 0.45 for a rhodium-loaded CdS catalyst in the presence of SO_2 as a sulfur scavenger. The mechanism suggested is similar to the one with RuO_2-loaded CdS catalyst. When RuO_2-loaded CdS particles were dispersed in aqueous H_2S solutions and illuminated with visible light ($\lambda > 400$ nm), H_2 was generated at a very high rate [165, 169]. When 25 mL solution containing 25 mg of CdS loaded with 0.025 mg of RuO_2 in the presence of 0.1 M Na_2S at pH 13 was irradiated, hydrogen gas was generated at a rate of 3.2 mL/h until the complete decomposition of H_2S. Thewissen et al. [170] studied the effect of various anions on the cleavage of hydrogen sulfide to give hydrogen and sulfur in aqueous suspensions of CdS-loaded with RuO_2

under illumination of visible light; the addition of sulfite enhanced the production of hydrogen to about four times. A kinetic model for reactions containing CdS suspensions to produce hydrogen photocatalytically from sulfide and sulfite waste streams was proposed [171].

Serpone et al. [172, 173] studied the effect of CdS on the photocatalytic decomposition of H_2S in alkaline aqueous media. Irradiation with the visible light helps production of hydrogen from hydrogen sulfide in mixed semiconductor dispersions such as those containing CdS suspensions in the presence of RuO_2 or Pt-loaded anatase in alkaline solution containing bisulfide ions; this helped to improve the efficiency of hydrogen generation due to electron transfer from the conduction band of CdS to that of TiO_2 particles. Serpone et al. [174] have also shown that etching of well-defined spherical n-type CdS particles had an effect on its surface properties and thereby increasing the efficiency of photocatalytic cleavage of H_2S in aqueous alkaline medium. Also, coupling of CdS with TiO_2 semiconductor particles due to the inter-particle electron transfer affects the rate of hydrogen production. Barbeni et al. [175] investigated the improved efficiencies via modification of semiconductor particulate systems on the H_2S cleavage.

Mechanism of hydrogen evolution on platinum-loaded CdS photocatalyst from aqueous solutions of $Na_2S_2O_3$ was proposed by Matsumura et al. [176]. The effect of temperature, pH, and the enhanced evolution of hydrogen by the addition of small amounts of EDTA to the solution were discussed using the energy band model of the Pt/CdS photocatalyst. Pelizzetti et al. [177] in an effort to dispose H_2S and SO_2 proposed a cyclic system to convert solar energy into useful fuel (hydrogen) and chemicals ($S_2O_3^{2-}$). The photocatalytic cleavage of H_2S in alkaline aqueous suspensions of CdS containing sulfite lead to the formation of hydrogen and thiosulfate.

The oxidation of thio-salts is an interesting area wherein the photocatalytic methods have been applied. Photoreduction of thiosulfate in semiconductor dispersions (alkaline TiO_2 suspensions) irradiated with UV light lead to the formation of sulfide and sulfite [178]. This reaction was not successful both in dark or upon exposure in the absence of TiO_2. This observation is significant in milling of sulfide ores wherein, part of the sulfide content is oxidized by oxygen to thio-salts which when present even in minute concentrations can cause serious environmental contamination through oxidation to sulfuric acid in the water streams.

Chun et al. [179] have shown that illumination of suspensions of silicon powder when chemically modified with polypyrrole/RuO_2 system in aqueous sulfide solutions resulted in the generation of hydrogen and sulfur. It is suggested that this method is compatible with the large scale disposal of wastes from process streams. Borgarello et al. [180] were successful in achieving an efficient photochemical conversion of aqueous sulfides and sulfites in alkaline medium to hydrogen by using a Rh(III)-loaded CdS photocatalyst. A high quantum efficiency for the generation of hydrogen was observed at 436 nm. In a recent study [181] rhodium sulfide-coated CdS were used as photocatalysts for

the photochemical decomposition of aqueous sulfide. Among CdS, Rh/CdS, Rh_2S_3/CdS, and Rh_2S_3/Rh/CdS, the ternary system, namely Rh_2S_3/Rh/CdS, was the most active photocatalyst for the decomposition of aqueous sulfide.

Buhler et al. [182] and Aruga et al. [183] have reported the production of hydrogen, sulfate and dithionate from aqueous solutions of sulfite by the Pt-loaded CdS photocatalyst. By this method sulfate, dithionate and hydrogen were produced from sulfur dioxide. On the other hand, Matsumura et al. [184] investigated the reactivity of sulfur ion on cadmium sulfide, the stability of the photocatalyst, temperature dependence of the photocatalytic reaction, etc. Catalysts for the photodecomposition of H_2S and polysulfide ions including the photodecomposition of water, photoreduction of CO_2 and photodecarboxylation of carboxylic acids have been patented [185]. In this study, the colloidal particles of TiO_2 containing redox catalysts were used. Kalyanasundaram et al. [186] have produced hydrogen and elemental sulphur by the photoreduction of H_2S in a solution containing RuO_2-coated chlorine-doped n-type CdS catalyst. If the energy bands of a semiconducting solid are separated by a band gap i.e., a semiconducting material is characterized by band structure — a filled valence band (VB) separated by an energy gap from a vacant conduction band (CB). In case of CdS particles the band gap excitation produce electrons in the conduction band (e_{CB}^-) and holes (h_{VB}^+) in the valence band:

$$CdS \xrightarrow{h\nu} e_{CB}^- + h_{VB}^+.$$
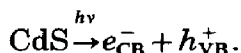
These electron–hole pairs diffuse to the surface of the particle where two redox reactions occur simultaneously as follows.

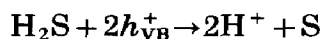(i) The migration of conduction band electron to interface results in the reduction of water to hydrogen
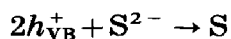
$$2e_{CB}^- + H_2O \rightarrow H_2 + 2OH^-$$

or simply

$$2e_{CB}^- + 2H^+ \rightarrow H_2$$
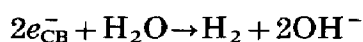
(ii) The valence band holes oxidize sulfide to sulfur

$$H_2S + 2h_{VB}^+ \rightarrow 2H^+ + S$$

or simply

$$2h_{VB}^+ + S^{2-} \rightarrow S$$

The overall reaction corresponds to splitting of H_2S into hydrogen and sulfur by four quanta of visible light. Pelizzetti et al. [187] reviewed the photoassisted cleavage of H_2S with semiconductor particles in those processes that are potentially interesting in solar energy conversion systems. Photoelectrolysis with suspensions of catalyst-coated semiconductor particle is displayed schematically in Fig. 1.
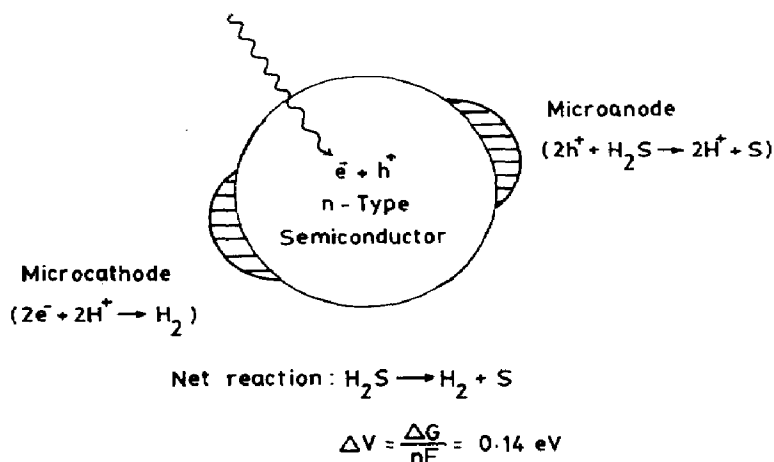
Fig. 1. Photoelectrolysis of H_2S with suspensions of catalyst-coated semiconductor particles. (Potential difference ΔV was calculated from Nernst's Law).

3.9 Miscellaneous pollutants

In this section, a number of miscellaneous pollutants will be covered. The photodehydrodimerization of cyclic ethers and cyclohexane by n-type ZnS and platinized CdS were studied by Kisch [188] on a preparative scale. Peyton and DeBerry [189] investigated the feasibility of photocatalytic oxidation for wastewater cleanup for reuse. Removal of chloroform, dimethylamine, methanol, phenol and ammonia were attempted by using Fe_2O_3, TiO_2 and ZnO semiconductors using Xe-lamp to simulate the solar radiation; Fe_2O_3 was ineffective for this purpose whereas, both ZnO and TiO_2 catalyzed systems were found to be effective for the removal of all the compounds.

The accelerated decomposition of organophosphorus compounds on semiconductor oxide surfaces (ZnO and TiO_2 powder) was investigated [190] as a method to destroy pesticide pollutants. Decomposition of organo-phosphorous compounds on photoactivated TiO_2 surfaces was studied and a mechanism was proposed for the degradative oxidation [191]. Photocatalytic degradations of organophosphorus insecticides in aqueous semiconductor suspensions were studied by Harada et al. [192]. A 5% decomposition of poly(vinyl alcohol) in wastewater was achieved by irradiating TiO_2 loaded with Pt placed in wastewater with visible and/or UV-light for 10 h [193]. Matthews [194] described the destruction of organic solutes in a thin film–TiO_2 reactor. An assessment of the role of suspended sediments and clays on the rate and mechanism of photolysis of organic pollutants like methanol, p-dichlorobenzene in water was carried out by Oliver et al. [195]. Even though semiconductor powders such as TiO_2 could photocatalyze such organic contaminants in water, no such reaction occurred with naturally occurring sediments or clays. In other studies [196], photoenhanced catalytic decomposition of isopropanol on V_2O_5 by UV-visible

photoirradiation, quantitative photoreduction of aliphatic ketones to alcohols using defect-free ZnS quantum crystallites [197] in the presence of $\lambda > 313$ nm light irradiation, and photocatalytic decomposition of kraft lignin into CO_2 and H_2O by TiO_2 [198] have been reported.

Different electrode systems with polycrystalline ZnO and tungsten trioxide have been attempted and their performance studied [199]. Photoinduced catalytic reactions of organic compounds like alcohols, amines, amides, etc., on the semiconducting oxide powders in suspension were compared with similar photoelectrocatalytic reactions. Differences in photocatalytic activities between TiO_2 and ZnO and the effect of Pt-loading of the semiconducting materials have been investigated by Anno and Tomonari [200]. It was shown that TiO_2 is 50 times less active than ZnO but Pt-loading accelerated the reaction by several orders of magnitude with respect to methylacetylene-H_2O reaction. TiO_2 and ZnO produced C_2H_6, CH_4, CO_2, ketones and aldehydes, whereas, Pt/TiO_2 and Pt/ZnO produced C_3H_6 and CO_2. However, with isobutene and oxygen, the major products were acetone and CO_2; TiO_2 was three to four times as active as ZnO, and Pt-loading accelerated the reaction by several orders of magnitude.

Cai et al. [201] have described a method of loading platinum on TiO_2 for the preparation of photocatalyst by combining the photoinfusion and reduction with hydrogen. The catalytic activity for the decomposition of organic carboxylic acids of the catalyst prepared by the combined method was higher than that by photoelectrochemical method. The photocatalytic destruction of phosphate-esters used as warfare agents and insecticides has been studied [202]. It was found that diethyl nitrophenyl phosphate can be destroyed within minutes on the surface of TiO_2 (anatase) particles under illumination with a solar simulator; this proves the high activity of the TiO_2 photocatalyst.

Photocatalytic activities of microcrystalline TiO_2 incorporated in the interstitial layers of the montmorillonite (a sheet silicate clay material) were investigated [203]. It was shown that the photocatalytic activities of the pillared TiO_2 was greater than those of the TiO_2 powder particles for the decomposition of 2-propanol to give acetone and hydrogen; similarly, carboxylic acids to give the corresponding alkanes and CO_2. Van Damme et al. [204] have reviewed the photocatalysis over clay support. Examples were provided to support the use of clay minerals in photocatalysis in (i) supporting homogeneous and heterogeneous redox catalysts including metals, oxides and sulfides and (ii) to intercalate photocatalytic transition metal complexes. Photocatalytic reactions can be performed either at solid–gas interface on clay powders or clay films. Photocatalytic layer of TiO_2 supported on glass-beads or thin films of TiO_2 deposited on glass surface were proved to be effective in destroying the organic pollutants [205, 206]. CdS was incorporated in porous Vycor glass, nafion, cellulose and on polycarbonate plates, whereas mixed ZnS–CdS were supported onto SiO_2, Al_2O_3, nafion®, nylon and clays.

4. Conclusions

The generation of hazardous wastes (chemical byproducts) is endemic to most chemical manufacturing processes and to the large-scale users of many chemical-based materials. Approximately 300 million metric tons of hazardous waste under U.S. Federal and State regulation were generated annually according to the most recent estimates in 1984. This is a world wide problem and is particularly acute in the United States. The petrochemical and refinery industries produce about 70 percent of this waste on a national basis. Geographically, the greatest production of hazardous wastes occur along the Gulf Coast. Presently, land disposal is used for as much as 80 percent of the nationally regulated hazardous wastes, some of which may remain hazardous for years or even centuries. Inappropriate disposal of these wastes on land creates the risk of contaminating, particularly the ground water, causing adverse health effects.

An effort has been made in this review to give an overall coverage on the topic of photomicroelectrochemical detoxification of hazardous materials. The most important findings of the research efforts of the noted researchers on the topic of photomicroelectrochemical detoxification of hazardous wastes have been discussed. While it is difficult to give all the details of the relevant methods, the important references are given from which the readers may get further details. In any case, disposal of hazardous waste is not an easy task. To alleviate or at least reduce this problem, it is recommended that our society should follow some important steps aimed at: (i) reducing the magnitude and hazardous nature of potential releases of waste components, (ii) improving the monitoring programs to quickly detect such releases and improving corrective actions to mitigate release effects, (iii) developing waste treatment procedures to reduce the hazard level — and possibly the amount of waste requiring disposal — and developing the ultimate disposal and dispersal of residues from previous steps in a manner that holds release into the environment to acceptable levels, and (iv) improve and expand the data and information on hazardous wastes and facilities which are necessary for more reliable risk assessments.

It is hoped that by following such procedures in the near future, it might be possible to alleviate the environmental pollution problems which are quite serious and pandemic that plague researchers working in this area.

5. References

1   D.C. Ackerman, L.S. Scinto, B.S. Bakshi, R.G. Delumyea, R.J. Johnson, G. Richard, A.M. Takata and E.M. Sworzyn, Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods, Noyes Data Corp., Park Ridge, NJ, 1983.

2   H.M. Freeman and R.A. Olexsey, A review of treatment alternatives for dioxin wastes, J. Air Pollut. Control. Assoc., 36 (1986) 67.

3   E.E. Heckman III, Toxic Organic Chemicals, Destruction and Waste Treatment, Noyes Data Corp., Park Ridge, NJ, 1978, pp. 29–79.

4   D. Duonghong, E. Borgarello and M. Gratzel, Dynamics of light-induced water cleavage in colloidal systems, J. Am. Chem. Soc., 103 (1981) 4685.

5   M. Gratzel, Artificial photosynthesis: Water cleavage into hydrogen and oxygen by visible light, Acc. Chem. Res., 14 (1981) 376.

6   K. Kalyanasundaram, M. Gratzel and E. Pelizzetti, Interfacial electron transfer in colloidal metal and semiconductor dispersions and photodecomposition of water, Coord. Chem. Rev., 69 (1986) 57.

7   J.H. Fendler, Membrane Mimetic Chemistry, Wiley, New York, 1982.

8   D.W. Breck, Zeolite Molecular Sieves, 2nd edn., Wiley, New York, 1984.

9   J.A. Rabo (Ed.), Zeolite Chemistry and Catalysis, ACS Monogr. No. 171, Am. Chem. Soc., Washington, DC, 1976.

10 G.D. Stucky and F.G. Dwyer (Eds.), Intrazeolite Chemistry, ACS Symp. Ser. No. 218, Am. Chem. Soc., Washington, DC, 1983.

11 H. Van Olphen, An Introduction to Clay Colloid Chemistry, 2nd edn., Wiley, New York, 1977.

12 B.K.G. Theng, The Chemistry of Clay Organic Reactions, Wiley, New York, 1974.

13 R.K. Iler, The Chemistry of Silica, 2nd edn., Wiley, New York, 1979.

14 M.L. Bender and M. Komiyama, Cyclodextrin Chemistry, React. Struct. Concepts Org. Chem. Ser. Vol. 6, Springer-Verlag, Berlin, 1978.

15 J. Szejtli, Cyclodextrins and their Inclusion Compounds, Akademiai Kiado, Budapest, 1982.

16 L.J. Mathies and C.W. Carrehar (Eds.), Crown Ether and Phase Transfer in Polymer Science, Plenum, New York, 1984.

17 M. Hiraoka, Crown Compounds: Their Characteristics and Applications, Elsevier, New York, 1982.

18 J.L. Atwood, J.E.D. Davis and D.D. McNicol (Eds.), Inclusion Compounds, Vols. 1–3, Academic Press, New York, 1984.

19 A.J. Frank, In: M. Gratzel, (Ed.), Energy Resources Through Photochemistry and Catalysis, Academic Press, New York, 1983, p. 467.

20 A.J. Bard, Photoelectrochemistry and heterogeneous photocatalysis at semiconductors, J. Photochem., 10 (1979) 59.

21 A.J. Bard, Photoelectrochemistry, Science, 207 (4427) (1980) 139.

22 H. Gerischer, Semiconductor electrochemistry, Discuss. Faraday Soc., 58 (1974) 219.

23 A. Henglein, Catalysis of photochemical reactions by colloidal semiconductors, Pure Appl. Chem., 56 (1984) 1215.

24 D. Duonghong, J. Ramsden and M. Gratzel, Dynamics of interfacial electron-transfer process in colloidal semiconductor systems, J. Am. Chem. Soc., 104 (1982) 2977.

25 C.T. Dameron, R.N. Reese, R.K. Mehra, A.R. Kortan, P.J. Carroll, M.L. Steigerwald, L.E. Brus and D.R. Winge, Biosynthesis of cadmium sulfide quantum semiconductor crystallites, Nature, 388 (1989) 596.

26 M. Formenti and S.J. Teichner, Heterogeneous photocatalysis, Catalysis (London), 2 (1978) 87.

27 T. Kawai and S. Kawai, Photocatalysis, Kagaku Gijutsushi MOL, 22 (1984) 21.

28   J.R. Ufford and N. Serpone, Titanium (transition metal chemistry, Coord. Chem. Rev.), 57 (1984) 301.
29   K. Kalyanasundaram and M. Gratzel, Heterogeneous Photocatalysis with Semiconductor Particulate Systems (Chem. Phys. Solid Surf. 5), Springer Ser. Chem. Phys., 35 (1984) 111.
30   P. Pichat, Room temperature oxidation, isotopic exchanges and dehydrogenations over illuminated heat or metal supporting conductor catalysts (Org. Phototransform. Nonhomogeneous Media) ACS Symp. Ser. 278, 1985, p.21.
31   J.C. Kuriacose, In: T.S.R.P. Rao, (Ed.), Catalytic Reactions on Illuminated Semiconductor Solids, Adv. Catal. (Proc.-Natl. Symp. Catal.) 7th, PL/17-PL/37, Wiley, New York, 1985.
32   S.J. Teichner and M. Formenti, Heterogeneous photocatalysis, NATO ASI Ser., Ser. C 146 (Photoelectrochem. Photocatal. Photoreact.), 1985, p.457.
33   S. Lunak, P. Lederer and S. Veprek-Siska, Catalytic influencing of photochemical reactions — Photocatalysis, Chim. Listy, 81 (1987) 1130.
34   H. Hennig, R. Billing and D. Rehorek, Photocatalysis induced by light-sensitive coordination compounds, J. Inf. Rec. Mater., 15 (1987) 423.
35   M.A. Fox, Photocatalytic Oxidation of Organic Substrates, NATO ASI Ser., Ser. C 237 (Photocatal. Environ.), 1988, p. 445.
36   T. Sakata, Photoexcitation of semiconductor and the basis of photocatalysis. Photoinduced electron transfer at semiconductor interface, Nippon Sashin Gakkaishi, 50 (1987) 207.
37   R.I. Bickley, Heterogeneous photocatalysis, Catalysis (London), 5 (1982) 308.
38   E. Pelizzetti, E. Pramauro, C. Minero and N. Serpone, Sunlight photocatalytic degradation of organic pollutants in aquatic systems, Waste Manag., 10 (1990) 65.
39   V.V. Gonchark, Photocatalytic purification of wastewater, Zh. Vses. Khim. O-va. im. D.I. Mendeleeva, 35 (1990) 112.
40   K. Tanaka, K. Harada and T. Hisanaga, Photocatalytic degradation of aqueous waste on semiconductor powder, Kagaku Gijutsu Kenkyusho Hokoku, 84 (1989) 637.
41   E. Pelizzetti, Homogeneous and heterogeneous photocatalysis, Chim. Ind. (Milan), 68 (1986) 51.
42   E. Pelizzetti, M. Barbeni, E. Pramauro, W. Erbs, E. Borgarello, M.A. Jamieson and N. Serpone, Photocatalytic and photosynthetic processes with semiconductor particulates, Quim. Nova, 8 (1985) 288.
43   N. Serpone and E. Pelizzetti, Fundamental Studies into Primary Events in Photocatalysis Employing Cadmium Sulfide and Titanium Dioxide Semiconductors: Photoluminescence, Laser Flash Photolysis and Pulse Radiolysis, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, p. 51.
44   M. Schiavello, Basic Concepts in Photocatalysis, NATO ASI Ser., Ser. C 237 (Photocatal. Environ.), 1988, p. 351.
45   M.A. Fox, Surface Mediated Photocatalysis, Report 1987, Available from NTIS. From Gov. Rep. Announce Index (U.S.) 1988, 88 (11), Abstr. No. 827,069.
46   H.O. Finklea, Photochemistry: Introductory concepts, J. Chem. Educ., 60 (1983) 325.
47   Toshiba Corporation, Reductive treatment of titanium dioxide, Japan Patent 59,121,120 (84,121,120), 1984. Chem. Abstr., 101: 140970v.
48   T.P. Goldstein, Photochemical process using shape-selective photo assisted heterogeneous catalyst compositions, Mobil Oil Corp., U.S., U.S. Patent 4,495,041 (1985). Chem. Abstr., 102: 140671u.
49   N.N. Lichtin, T.M. Dimauro and R.C. Svrluga, Catalytic process for degradation of organic materials in aqueous and organic fluids to produce environmentally compatible products, PCT Int. Appl. WO 89 08, 079 (1989). Chem. Abstr., 112: 41924d.
50   K. Onoda, Y. Ogose and S. Izumi, A redox method and membrane-separated photoelectrochemical cell, (Shiken Ltd.) Japan Patent 63 28,895 (88 28,895) (1985). Chem. Abstr., 109: 63262b.

51   H. Harada, H. Kanno and K. Ueda, Photocatalytic activity arising from crystallization of titanium dioxide, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 53 (1985) 736.

52   K. Matsuo and K. Nakano, Performances of Platinum Metal Catalysts Supported on Titanium Coated Silica Prepared from Metal Organics, Appl. Surf. Sci., 33–34 (1–4) (1987) (Publ. 1988) 269–276.

53   Water Quality Criteria Documents, U.S. Environmental Protection Agency, Washington, DC, 1979.

54   J.H. Stacha and F.W. Pontius, An overview of water quality and treatment activities in the United States, J. Am. Water Works Assoc., 76 (1984) 73.

55   U.S. Environmental Protection Agency, Fed. Regist., 44 (1979) 233.

56   E. Pelizzetti, C. Minero, E. Pramauro, M. Barbeni, V. Maurino and M. Tosato, Photocatalytic degradation of atrazine at ppb levels under solar light and in the presence of titania particles, Chim. Ind. (Milan), 69 (1987) 88.

57   D.W. Sundstrom, B.A. Weir and K.A. Redig, Destruction of mixtures of pollutants by UV-catalyzed oxidation with H_2O_2, ACS Symp. Ser. No. 422, 1989 (Pub. 1990) (Emerging Technol. Hazard. Waste Manag.), pp. 67–76.

58   R.G. Zepp, Assessing the photochemistry of organic pollutants in aquatic environments, In: R. Haque (Ed.), Dyn. Exposure Hazard Assess. Toxic Chem., (Pap. Symp.), Ann Arbor Sci. Publ., Ann Arbor, MI, 1980, p. 69.

59   R.G. Zepp, Factors affecting the photochemical treatment of hazardous waste, Environ. Sci. Technol., 22 (1988) 256.

60   S.W. Fowler, Critical review of selected heavy metal and chlorinated hydrocarbon concentrations in the marine environment, Marine Environ. Res., 29 (1990) 1.

61   H.P. Hemmerich, H. Ritter, H.J. Rosenkranz and E. Bandtel, Photo-oxidation of waste water loaded with organic material, German Patent, 2,729,760 (1979). Chem. Abstr., 90: 174281r.

62   S. Hu, R. Govind and J.C. Davis, Selective removal of metals from wastewater using affinity dialysis, ACS Symp. Ser. No. 422, 1989 (Pub. 1990) (Emerging Technol. Hazard. Waste Manag.), pp. 187–213.

63   D.F. Ollis, Heterogeneous Photocatalysis for Water Purification: Prospects and Problems, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, pp. 651–656.

64   B.G. Oliver and H. Carey, Photodegradation of Wastes and Pollutants in Aquatic Environment, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, pp. 629–650.

65   E. Pelizzetti and N. Serpone, Photodegradation of Organic Pollutants in Aquatic Systems Catalyzed by Semiconductor Systems, NATO ASI Ser., Ser. C 237 (Photocatal. Environ.), 1988, p. 469.

66   E. Borgarello, N. Serpone, M. Barbeni, C. Minero, E. Pelizzetti and E. Pramauro, Putting Photocatalysis to Work, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, p. 673.

67   P. Pichat, Powder Photocatalysts: Characterization by Isotopic Exchanges and Photoconductivity; Potentialities for Metal Recovery, Catalyst Preparation and Water Pollutant Removal, NATO ASI Ser., Ser. C 237 (Phocatal. Environ.), 1988, p. 399.

68   B.G. Oliver and J. Lawrence, Haloforms in drinking water: a study of precursors and precursor removal, J. Am. Water Works Assoc., 71 (1979) 161.

69   D.F. Ollis, Contaminant degradation in water, Environ. Sci. Technol., 19 (1985) 480.

70   H. Hidaka, H. Kubota, M. Gratzel, E. Pelizzetti and N. Serpone, Photodegradation of surfactants. II. Degradation of sodium dodecylbenzenesulfonate catalyzed by titanium dioxide particles, J. Photochem., 35 (1986) 219.

71   M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello, M. Gratzel and N. Serpone, Photodegradation of 4-chlorophenol catalyzed by titanium dioxide particles, Nouv. J. Chim., 8 (1984) 547.

72   A.L. Pruden and D.F. Ollis, Degradation of chloroform by photoassisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide, Environ. Sci. Technol., 17 (1983) 628.

73   C.Y. Hsiao, C.L. Lee and D.F. Ollis, Heterogeneous photocatalysis: degradation of dilute solutions of dichloromethane, chloroform and carbon tetrachloride with illuminated titania photocatalyst, J. Catal., 82 (1983) 418.

74   A.L. Pruden and D.F. Ollis, Photoassisted heterogeneous catalysis: the degradation of trichloroethylene in water, J. Catal., 82 (1983) 404.

75   D.F. Ollis, C.Y. Hsiao, L. Budiman and C.L. Lee, Heterogeneous photoassisted catalysis: conversions of perchloroethylene, dichloroethane, chloroacetic acids and chlorobenzenes, J. Catal., 88 (1984) 89.

76   L.P. Childs and D.F. Ollis, Is photocatalysis catalytic? J. Catal., 66 (1980) 383.

77   H. Kawaguchi, Photocatalytic decomposition of chloroform in the presence of titanium dioxide, Suishitsu Odaku Kenkyu, 9 (1986) 668.

78   M. Masuyuki, I. Kiminori, O. Yasumasa and K. Kazuyoshi, Photocatalytic degradation of chloroform on platinized titanium dioxide powder, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 57 (1989) 1221.

79   J.F. Tanguay, R.F. Coughlin and S.L. Squib, Photodegradation of dichloromethane with titanium catalysts, ACS Symp. Ser. No. 437 (Novel Mater. Heterog. Catal.), 1990, pp. 114–118.

80   T.C. Wang and C.K. Tan, Reduction of chlorinated hydrocarbons with natural sunlight in a platinum-catalyzed water photolysis system, Environ. Sci. Technol., 22 (1988) 916.

81   T. Hisanaga, K. Harada and K. Tanaka, Degradation of Trace Amount of Organohalogen Solvent in Water, Kogyo Yosui, 379 (1990) 11.

82   T. Hisanaga, K. Harada and K. Tanaka, Photocatalytic degradation of organochlorine compounds in suspended TiO_2, J. Photochem., Photobiol., A54 (1990) 113.

83   C. Kormann, D.W. Bahnemann and M.R. Hoffmann, Photolysis of chloroform and other organic molecules in aqueous titanium dioxide suspensions, Environ. Sci. Technol., 25 (1991) 494.

84   K. Tanaka, T. Hisanaga and K. Harada, Photocatalytic degradation of organohalide compounds in semiconductor suspension with added hydrogen peroxide, New J. Chem., 13 (1989) 5.

85   J.F. Tanguay, R.W. Coughlin and S.L. Squib, Photodegradation of dichloromethane with titanium catalyst, Prepr. Am. Chem. Soc., Div. Pet. Chem., 34(3) (1989) 497.

86   D.Y. Lai, Halogenated benzenes, naphthalenes, biphenyls and terphenyls in the environment: their carcinogenic, mutagenic and teratogenic potential and toxic effects, J. Environ. Sci. Health, Part C: Environ. Carcinog. Rev., C2, (1984) 135.

87   M. Barbeni, M. Morello, E. Pramauro, E. Pelizzetti, M. Vincenti, E. Borgarello and N. Serpone, Sunlight photodegradation of 2,4,5-trichlorophenoxy acetic acid and 2,4,5-trichlorophenol on titanium dioxide. Identification of intermediates and degradation pathway, Chemosphere, 16 (1987) 11.

88   R.B. Draper and D.G. Crossby, Catalyzed photodegradation of the herbicides molinite and thiobencarb, In: R.G. Zika and W.J. Cooper (Eds.), Photochemistry of Environmental Aquatic Systems, Am. Chem. Soc., Washington, DC, 1987, p. 240.

89   K. Hashimoto, T. Kawai and T. Sakata, Photocatalytic reactions of hydrocarbons and fossil fuels with water. Hydrogen production and oxidation, J. Phys. Chem., 88 (1984) 4083.

90   I. Izumi, W.W. Dunn, K.O. Wilbourn, F.F. Fan and A.J. Bard, Heterogeneous photocatalytic oxidation of hydrocarbons on platinized titanium dioxide powders, J. Phys. Chem., 84 (1980) 3207.

91   M. Fujihara, Y. Satoh and T. Osa, Heterogeneous photocatalytic oxidation of aromatic compounds on TiO_2, Nature, 293 (5829) (1981) 206.

92   D.F. Ollis, E. Pelizzetti and N. Serpone, Heterogeneous photocatalysis in the environment: Application to water purification, In: Photocatalysis, Fundamentals and Applications, Wiley, New York, 1989, Ch. 18, p. 603.

93   K. Hustert, D. Kotzias and F. Korte, Photocatalytic decomposition of chloronitrobenzoles with titanium dioxide in aqueous phases, Chemosphere, 16 (1987) 809.

94   M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello, N. Serpone and M.A. Jamieson, Photochemical degradation of chlorinated dioxins, biphenyls, phenols and benzene on semiconductor dispersions, Chemosphere, 15 (1986) 1913.

95   T.O. Tiernam, M.L. Taylor, J.G. Solch, G.F. Vannes, J.H. Garrett and M.D. Porter, In: J. Exner (Ed.), Detoxification in Hazardous Waste, Ann Arbor Sci. Publ., Ann Arbor, MI, 1982, pp. 143–184.

96   T. Nishiwaki, Photodecomposition of PCB's, Yuki Gosel Kagaku Kyokaishi, 39 (1981) 228.

97   T. Sawai and Y. Shinozaki, Radiolytic Dechlorination of polychlorinated biphenyls (PCB) in organic solutions, Chem. Lett., 10 (1972) 865.

98   M. Koshioka, J. Kanazawa, H. Iizuka and T. Murai, Photodegradation of decachlorobiphenyl, Bull. Environ. Contam. Toxicol., 38 (1987) 409.

99   S. Mochizuki, Photochemical dechlorination of PCB's, Chem. Eng. Sci., 32 (1977) 1205.

100   T. Nishiwaki, M. Usui, K. Anda and M. Hida, Dechlorination of polychlorinated biphenyls by UV irradiation. 6. Positional selectivity of polychlorobenzenes towards photodechlorination in both neutral and alkaline 2-propanol, Bull. Chem. Soc. Jpn., 52 (1979) 821.

101   S. Arai, M. Matsui, J. Moriguchi and M. Imamura, Radiation chemical and photochemical dechlorination of polychlorobiphenyl, Rika Gaku Kenkyusho Hokoku, 48 (1972) 185.

102   N.J. Bunce, Photodechlorination of PCB's: current status, Chemosphere, 11 (1982) 701.

103   W.J. Janis, J.S. Ferrie and J.M. Braun, Dechlorination and Reclamation of PCB-contaminated Insulating Fluids, IEEE Transactions on Power Apparatus and Systems, Vol. PAS-102, No. 12, 1983.

104   T. Nishiwaki, T. Shinoda, K. Anda and M. Hida, Dechlorination of polychlorinated biphenyls by UV irradiation. IX. Reactions of monochlorobiphenyls in a 2-propanol solution, Bull. Chem. Soc., Jpn., 55 (1982) 3569.

105   G.A. Epling, E.M. Florio, A.J. Bourque, X.H. Qian and J.D. Stuart, Borohydride, micellar, and exciplex-enhanced dechlorination of chlorobiphenyls, Environ. Sci. Technol., 22 (1988) 952.

106   S.K. Chaudhary, R.H. Mitchell and P.R. West, Photodechlorination of polychlorinated biphenyls in the presence of hydroquinone in aqueous alcoholic media, Chemosphere, 13 (1984) 1113.

107   W.H. Dennis Jr., Y.H. Chang and W.J. Cooper, Catalytic dechlorination of organochlorine compounds. V. Polychlorinated biphenyls — Aroclor, Bull. Environ. Contam. Toxicol., 22 (1979) 750.

108   N.J. Bunce, Y. Kumar, L. Ravanal and S.H. Safe, Photochemistry of chlorinated biphenyls in iso-octane solution, J. Chem. Soc., Perkin II, (1978) 880.

109   O. Hutzinger, S.H. Safe and V. Zitco, The Chemistry of PCB's, CRC Press, Cleveland, OH, 1974.

110   L.O. Ruzo, M.J. Zabik, R.D. Scheutz, Photochemistry of bioactive compounds. Photochemical processes of polychlorinated biphenyls, J. Am. Chem. Soc., 96 (1974) 3809.

111   D. Cesareo, A. DiDomenico, S. Marchini, L. Passerini and M.L. Tosato, Environmental Photochemistry of Chlorinated Aromatics in Aqueous Media: A Review of Data, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, p. 573.

112   D. Martinetz, Detoxification of polychlorinated biphenyls and dibenzodioxins — A review, Chem. Technol. (Leipzig), 39 (1987) 466.

113   S.S. Shukla and J.F. Rusling, Photocatalytic reduction of 4-chlorobiphenyl using anion radicals and visible light, J. Phys. Chem., 89 (1985) 3353.

114   J.F. Rusling, Chun-Nian Shi, D.K. Gosser and S.S. Shukla, Electrocatalytic reactions of organized assemblies. Part I. Reduction of 4-bromophenyl in cationic and nonionic micelles, J. Electroanal. Chem., 240 (1988) 201.

115   P.E. Menassa, M.K.S. Mak and C.H. Langford, A study of the photodecomposition of different chlorinated biphenyls by surface modified titanium(IV) oxide particles, Environ. Technol. Lett., 9 (1988) 825.

116   I. Izumi, Photoassisted decomposition of LBS and PCB on platinized titanium dioxide powders, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 53 (1985) 178.

117   S. Tunesi and M.A. Anderson, Photocatalysis of 3,4-DCB in titanium dioxide aqueous suspensions; effects of temperature and light intensity; CIR-FTIR interfacial analysis, Chemosphere, 16 (1987) 1447.

118   J.H. Carey, J. Lawrence and H.M. Tosine, Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions, Bull. Environ. Contam. Toxicol., 16 (1976) 697.

119   T. Kojima, Y. Asada, W.P. Li and F. Morishita, Photodecomposition of chlorinated hydrocarbons by titanium dioxide for the determination of total organochlorine content in water, Anal. Sci., 5 (1989) 229.

120   C. Rappe, In: O. Hutzinger (Ed.), The Handbook of Environmental Chemistry, Vol. 3A, Springer Verlag, Berlin, 1980, p. 157.

121   J.C. O'Oliveira, G. Al Sayed and P. Pichat, Photodegradation of 2- and 3-chlorophenol in TiO$_2$ aqueous suspensions, Environ. Sci. Technol., 24 (1990) 990.

122   J. Tseng and C.P. Huang, Mechanistic aspects of the photocatalytic oxidation of phenol in aqueous solutions, ACS Symp. Ser. No. 422 (Emerging Technol. Hazard. Waste Manag.), 1989 (Pub. 1990) pp. 12–39.

123   K. Okamato, Y. Yamamoto, H. Tanaka, M. Tanaka and A. Itaya, Heterogeneous photocatalytic decomposition of phenol over anatase powder, Bull. Chem. Soc. Jpn., 58 (1985) 2015.

124   K. Okamato, Y. Yamamoto, H. Tanaka and A. Itaya, Kinetics of heterogeneous photocatalytic decomposition of phenol over anatase titanium dioxide powder, Bull. Chem. Soc. Jpn., 58 (1985) 2023.

125   H. Kawaguchi and T. Uejima, Photochemical decomposition of phenol in the presence of photocatalyst, Kagaku Kogaku Ronbunshu, 9 (1983) 107.

126   A.P. Davis and C.P. Huang, The photocatalytic oxidation of toxic organic compounds, In: Y.C. Wu (Ed.), Int. Conf. Physicochem. Biol. Detoxification of Hazard. Wastes, 1988, Vol. 1, Technomic, Lancaster, PA, 1989, p. 337.

127   M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello and N. Serpone, Photodegradation of pentachlorophenol catalyzed by semiconductor particles, Chemosphere, 14 (1985) 195.

128   H. Kawaguchi, Photocatalytic decomposition of chlorophenols in the presence of TiO$_2$, Suishitsu Odaku Kenkyu, 8 (1985) 443.

129   H. Kawaguchi, Photocatalytic decomposition of phenol in the presence of titanium dioxide, Environ. Technol. Lett., 5 (1984) 471.

130   V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero and E. Pelizzetti, Photocatalytic degradation of phenol in aqueous titanium dioxide dispersions, Toxicol. Environ. Chem., 16 (1988) 89.

131   D.G. Crossby and A.S. Wong, Photodecomposition of *p*-chlorophenoxyacetic acid, J. Agric. Fd. Chem. 21 (1973) 1049.

132   E. Pelizzetti, M. Barbeni, E. Pramauro, N. Serpone, E. Borgarello, M.A. Jamieson and H. Hidaka, Sunlight photodegradation of haloaromatic pollutants catalyzed by semiconductivity particulate materials, Chim. Ind. (Milan), 67 (1985) 623.

133   A.P. Davis and C.P. Huang, Removal of phenols from water by a photocatalytic oxidation process, Water Sci. Technol., 21 (1989) 455.

134   H. Hidaka, H. Kubota, M. Gratzel, N. Serpone and E. Pelizzetti, Photodegradation of surfactants. I. Degradation of sodium dodecylbenzenesulfonate in aqueous semiconductor dispersions, Nouv. J. Chim., 9 (1985) 67.

135   H. Hidaka, S. Yamada, S. Suenaga, H. Kubota, N. Serpone, E. Pelizzetti and M. Gratzel, Photodegradation of surfactants. V. Photocatalytic degradation of surfactants in the presence of semiconductor particles by solar exposure, J. Photochem. Photobiol., A47 (1989) 103.

136   E. Pelizzetti, C. Minero, V. Maurino, A. Sclafani, H. Hidaka and N. Serpone, Photocatalytic degradation of nonylphenol ethoxylated surfactants, Environ. Sci. Technol., 23 (1989) 1380.

137   H. Hidaka, Y. Yamada, S. Suenega, J. Zhao, N. Serpone and E. Pelizzetti, Photodegradation of surfactants. Part VI. Complete photocatalytic degradation of anionic, cationic and nonionic surfactants in aqueous semiconductor dispersions, J. Mol. Catal., 59 (1990) 279.

138   N. Serpone, E. Borgarello and E. Pelizzetti, Photoreduction and Photodegradation of Inorganic Pollutants. I. Cyanides, NATO ASI Ser., Ser. C 237 (Photocatal. Environ.), 1988, p. 499.

139   S.N. Frank and A.J. Bard, Semiconductor electrodes. 12. Photoassisted oxidations and photoelectrosynthesis at polycrystalline TiO_2 electrodes, J. Am. Chem. Soc., 99 (1977) 4667.

140   S.N. Frank and A.J. Bard, Heterogeneous photocatalytic oxidation of cyanide ions in aqueous solutions of titanium dioxide powder, J. Am. Chem. Soc., 99 (1977) 303.

141   E. Borgarello, R. Terzian, N. Serpone, E. Pelizzetti and M. Barbeni, Photocatalyzed transformations of cyanide to thiocyanate by rhodium-loaded cadmium sulfide in alkaline aqueous sulfide media, Inorg. Chem., 25 (1986) 2135.

142   E. Borgarello, R. Harris and N. Serpone, Photochemical deposition and photorecovery of gold using semiconductor dispersions. A practical application of photocatalysis, Nouv. J. Chim., 9 (1985) 743.

143   M.I. Brittan, Gold recovery in South Africa, Am. Sci., 62 (1974) 402.

144   E.M. Wise, Gold Recovery, Properties and Applications, Van Nostrand, Princeton, NJ, 1964.

145   N. Serpone, E. Borgarello, M. Barbeni, E. Pelizzetti, P. Pichat, J.M. Herrmann and M.A. Fox, Photochemical reduction of Gold(III) on semiconductor dispersions of titanium dioxide in the presence of cyanide ions: disposal of cyanide by treatment with hydrogen peroxide, J. Photochem., 36 (1987) 373.

146   S. Li and X. Wen, Photocatalytic oxidation of cyanide in aqueous solution with heterogeneous tungsten trioxide/α-ferric oxide/tungsten, Huaxue Shijie, 26 (1985) 204.

147   H. Reichie, W.W. Dunn and A.J. Bard, Heterogeneous photocatalytic and photosynthetic deposition of copper on TiO_2 and WO_3 powder, J. Phys. Chem., 83 (1979) 2248.

148   J.S. Curran, J. Domenich, N. Jaffrezic-Renault and R. Phillippe, Kinetics and mechanism of platinum deposition by photoelectrolysis in illuminated suspensions of semiconducting titanium dioxide, J. Phys. Chem., 89 (1985) 957.

149   B. Kraeutler and A.J. Bard, Heterogeneous photocatalytic preparation of supported catalysts. Photodeposition of platinum on TiO_2 powder and other susbstrates, J. Am. Chem. Soc., 100 (1978) 4317.

150   N. Serpone, E. Borgarello and E. Pelizzetti, Photoreduction and Photodegradation of Inorganic Pollutants. II. Selective Reduction and Recovery of Au, Pt, Pd, Rh, Hg and Pb, NATO ASI Ser., Ser. C 237 (Photocatal. Environ.), 1988, p. 527.

151   B. Otani, Photocatalytic deposition of metals on semiconductor, Kagaku Kogyo, 39 (1988) 219.

152   R.A. Bull and J.T. McManamon, Supported catalysts in hazardous waste treatment. Destruction of inorganic pollutants in wastewater with H_2O_2, ACS Symp. Ser. No. 422 (Emerging Technol. Hazard. Waste Manag.) 1989 (publ. 1990), pp. 52–66.

153 E. Borgarello, N. Serpone, G. Emo, R. Harris, E. Pelizzetti and C. Minero, Light-induced reduction of rhodium(III) and palladium(II) on titanium dioxide dispersions and the selective photochemical separation and recovery of gold(III), platinum(IV) and rhodium(III) in chloride media, Inorg. Chem., 25 (1986) 4499.

154 K. Tanaka, K. Harada and S. Murata, Photocatalytic deposition of metal ions onto titanium dioxide powder, Sol. Energy, 36 (1986) 159.

155 D. Lawless, A. Res, R. Harris, N. Serpone, C. Minero, E. Pelizzetti and H. Hidaka, Removal of toxic metals from solutions by photocatalysis using irradiated platinized titanium dioxide; removal of heat, Chim. Ind. (Milan), 72 (1990) 139.

156 J. Munoz and X. Domenech, Titania catalyzed reduction of chromium(VI) in aqueous solutions under ultraviolet illumination, J. Appl. Electrochem., 20 (1990) 518.

157 Y. Xu and X. Chen, Photocatalytic reduction of dichromate over semiconductor catalysts, Chem. Ind. (London), 15 (1990) 497.

158 R. Batti, R. Magnaval and E. Lanzola, Methyl mercury in river sediments, Chemosphere, 4 (1975) 13.

159 J. Domenech and M. Andres, Elimination of mercury(II) ions from aqueous solutions by photocatalytic reduction over zinc oxide powder, New J. Chem., 11 (1987) 443.

160 J.B. Hyne, In: M.E.D. Raymont (Ed.), Sulfur: New Sources and Uses, ACS Symp. Ser. No. 183, Am. Chem. Soc., Washington, DC, 1982, Chem. Technol., p. 628.

161 E. Borgarello, R. Pappa, N. Serpone and E. Pelizzetti, Disposal of Hydrogen Sulfide: Conventional and Photochemical Methods, NATO ASI Ser., Ser. C 237 (Photocatal. Environ.), 1988, p. 567.

162 E. Borgarello, W. Erbs, M. Gratzel and E. Pelizzetti, Visible light induced cleavage of hydrogen sulfide and photosynthesis of thiosulfate in cadmium sulfide dispersions, Nouv. J. Chim., 7 (1983) 195.

163 E. Borgarello, N. Serpone, M. Gratzel and E. Pelizzetti, Production of hydrogen through microheterogenous catalysis of hydrogen sulfide cleavage, Presented at Adv. Hydrogen Energy, 4, Hydrogen Energy Prog., 3(5) (1984) 1039.

164 R.C. Kainthala and J.O.M. Bockris, Photoelectrolysis of H_2S using an n-CdSe photoanode, Int. J. Hydrogen Energy, 12 (1987) 23.

165 E. Borgarello, K. Kalyanasundaram, M. Gratzel and E. Pelizzetti, Visible light induced generation of hydrogen from hydrogen sulfide in cadmium sulfide dispersions with hole transfer catalysis by ruthenium(IV) oxide, Helv. Chim. Acta, 65(21) (1982) 243.

166 K. Kalyanasundaram, E. Borgarello and M. Gratzel, Visible light induced water cleavage in cadmium sulfide dispersions loaded with platinum and ruthenium oxide (RuO_2), hole scavenging by RuO_2, Helv. Chim. Acta, 64 (1981) 362.

167 K. Kalyanasundaram, E. Borgarello, D. Duonghong and M. Gratzel, Water cleavage by irradiation of colloidal cadmium sulfide solutions with visible light; suppression of photocorrosion by ruthenium dioxide, Angew. Chemie, Int. Ed., 20 (1981) 987.

168 E. Borgarello, N. Serpone, M. Barbeni, C. Minero, E. Pelizzetti and E. Pramauro, Putting photocatalysis to work, Chim. Ind. (Milan), 68 (1986) 53.

169 M. Gratzel, Molecular engineering in photoconversion systems, In: M. Gratzel, (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, Ch. 3, p. 71.

170 D.H.M.W. Thewissen, A.H.A. Tinnemans, M. Eeuwhorst-Reinten, K. Timmer and A. Mackor, Visible light-induced formation of hydrogen and thiosulfate from aqueous sulfide/sulfite solutions in cadmium sulfide suspensions, Nouv. J. Chim., 7 (1983) 191.

171 J. Sabate, S. Cervera-March, R. Simarro and J. Gimenz, Photocatalytic production of hydrogen from sulfide and sulfite waste streams: A kinetic model for reactions occurring in illuminated suspensions of cadmium sulfide, Chem. Eng. Sci., 45 (1990) 3089.

172 N. Serpone, E. Borgarello, M. Barbeni and E. Pelizzetti, Effect of cadmium sulfide preparation on the photo-catalyzed decomposition of hydrogen sulfide in alkaline aqueous media, Inorg. Chim. Acta., 90 (1984) 191.

173 N. Serpone, E. Borgarello and M. Gratzel, Visible light induced generation of hydrogen from hydrogen sulfide in mixed semiconductor dispersions; improved efficiency through inter-particle electron transfer, J. Chem. Sec., Chem. Commun., 6 (1984) 342.

174 N. Serpone, E. Borgarello and E. Pelizzetti, The semiconductor particle as a photoelectrochemical cell and its application to photocatalysis, In: Proc. Electrochem. Soc. 88–14 (Photoelectrochem. Electrosynthesis Semicond. Mater.), 1988, p. 1.

175 M. Barbeni, E. Pelizzetti, E. Borgarello, N. Serpone, M. Gratzel, L. Balducci and M. Visca, Hydrogen from hydrogen sulfide cleavage. Improved efficiencies via modification of semiconductor particulates, Int. J. Hydrogen Energy, 10 (1985) 249.

176 M. Matsumura, T. Uchihara, K. Hanafusz and H. Tsubomura, Mechanism of hydrogen production at platinum-loaded cadmium sulfide photocatalyst, In: Proc. -Electrochem. Soc. 88–14 (Photoelectrochem. Semicond. Mater.), 1988, pp. 59–66.

177 E. Pelizzetti, E. Borgarello, N. Serpone and M. Gratzel, Photocatalytic cleavage of hydrogen sulfide and organo sulfur compounds, Stud. Surf. Sci. Catal., 19 (Catal. Energy Scene), (1984) 327.

178 E. Borgarello, J. DeSilvestro, M. Gratzel and E. Pelizzetti, Photoreduction of thiosulfate in semiconductor dispersions, Helv. Chim. Acta., 66 (1983) 1827.

179 Yu. B.C. Chun, S. Kapusta and N. Hackerman, Photogeneration of hydrogen and sulfur on polypyrrole/ruthenium dioxide modified silicon powder, J. Electrochem. Soc., 133 (1986) 934.

180 E. Borgarello, N. Serpone, E. Pelizzetti and M. Barbeni, Efficient photochemical conversion of aqueous sulfides as a photocatalyst for photochemical decomposition of aqueous sulfide, J. Photochem., 33 (1986) 35.

181 I.B. Rufus, V. Ramakrishna, B. Vishwanathan and J.C. Kuriacose, Rhodium and rhodium sulfide coated cadmium sulfide as a photocatalyst for photochemical decomposition of aqueous sulfide, Langmuir, 6 (1990) 565.

182 N. Buhler, K. Meier and J.F. Reber, Photochemical hydrogen production with cadmium sulfide suspensions, J. Phys. Chem., 88 (1984) 326.

183 T. Aruga, K. Domen, S. Naito, T. Onishi and K. Tamaru, The role of sulfite anion as a scavenger in the photocatalytic hydrogen formation from water on cadmium sulfide semiconductor under illumination of visible light, Chem. Lett., 7 (1983) 1037.

184 M. Matsumura, Y. Saho and H. Tsubomura, Cadmium Sulfide Photocatalyzed Hydrogen Production from Aqueous Solutions of Sulfite, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, p. 581.

185 M. Visca and C. Scotti, Catalysts for photoassisted oxidation-reduction reactions, Chem. Abstr., 98: 207487h.

186 K. Kalyanasundaram, E. Borgarello and E. Pelizzetti, Hydrogen and elemental sulfur by photochemical redox reaction of hydrogen sulfide and sulfides. Chem. Abstr., 98: 152745h.

187 E. Pelizzetti, E. Borgarello and N. Serpone, Photoassisted cleavage of hydrogen sulfide with semiconductor particles. The thiosulfate cycle, NATO ASI Ser., Ser. C 146 (Photoelectrochem. Photocatal. Photoreact.), 1985, 293.

188 H. Kisch, Heterogeneous photocatalysis by metal sulfide semiconductor powders, J. Inf. Rec. Mater., 17 (1989) 363.

189 G.R. Peyton and D.W. DeBerry, Feasibility of Photocatalytic Oxidation for Wastewater Clean-up and Reuse, Report 1981. Available from NTIS. From Gov. Rep. Announce Index (U.S.), 82(2) (1982) 276.

190 T.J. Lewis, B. Aurian-Blajeni and T.L. Rose, Decomposition Reactions of Dimethylmethylphosphanate on Heated and Irradiated Semiconductor Surfaces, Report 1988. Available from NTIS. From Gov. Rep. Announce Index (U.S.) 1988, 88(19), Abstr. No. 850,129.

191 C.K. Gratzel, M. Jirousek and M. Gratzel, Decompositon of organophosphorus compounds on photoactivated TiO_2 surfaces, J. Mol. Catal., 60 (1990) 375.

192   K. Harada, T. Hisanaga and K. Tanaka, Photocatalytic degradation of organophosphorus insecticides in aqueous semiconductor suspensions, Water Res., 24 (1990) 1415.

193   Toshiba Corporation, Decomposition of poly(vinylalcohol) in wastewater (Jpn. Kokai Tokyo Koho), Japan Patent 58 11,095 (1983). Chem. Abstr., 98: 221335p.

194   R.W. Matthews, Photooxidation of organic impurities in water using thin films of titanium dioxide, J. Phys. Chem., 91 (1987) 3328.

195   B.G. Oliver, E.G. Cosgrove and J.H. Carey, Effect of suspended sediments on the photolysis of organics in water, Environ. Sci. Technol., 13 (1979) 1075.

196   A.Z. Moshfegh and A. Ignatiev, Photoenhanced catalytic decomposition of isopropanol on vanadium pentoxide, Catal. Lett., 4 (1990) 113.

197   S. Yanagida, M. Yoshia, T. Shiragami, C. Pac, H. Mori and H. Fujita, Semiconductor photocatalysis. I. Quantitative photoreduction of aliphatic ketones to alcohols using defect-free zinc sulfide quantum crystallites, J. Phys. Chem., 94 (1990) 3104.

198   K. Kobayakawa, Y. Saito, S. Nakamura and A. Fujishima, Photodecomposition of kraft lignin catalyzed by titanium dioxide, Bull. Chem. Soc. Jpn., 62 (1989) 3433.

199   K.R. Thampi, T.V. Reddy, V. Ramakrishnan and J.C. Kuriacose, J. Indian Chem. Soc., 60 (1983) 1156.

200   M. Anno and M. Tomonari, Photocatalytic reactions on Pt-loaded and unloaded semiconductor materials. Differences in photoreactivities between TiO_2 and ZnO, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 57 (1989) 1219.

201   N. Cai, C. Jian and Q. Dong, Study of the method of loading platinum on titania photocatalyst, Cuihua Xuebao, 10 (1989) 137.

202   C. K. Gratzel, M. Jirousk and M. Gratzel, Accelerated decomposition of active phosphates on titanium dioxide surfaces, J. Mol. Catal., 39 (1987) 347.

203   H. Yoneyama, S. Haga and S. Yamanaka, Photocatalytic activities of microcrystalline TiO_2 incorporated in sheet silicates of clay, J. Phys. Chem., 93 (1989) 4833.

204   H. Van Damme, F. Bergaya and D. Challal, Photocatalysis Over Clay Supports, NATO ASI Ser., Ser. C 174 (Homogeneous Heterog. Catal.), 1986, p. 479.

205   N. Serpone, E. Borgarello, R. Harris, P. Cahill and E. Pelizzetti, Photocatalysis over titanium dioxide supported on a glass substrate, Sol. Energy Mater., 14 (1986) 121.

206   J. Kuczynski and J.K. Thomas, Photophysical properties of cadmium sulfide deposited on porous Vycor glass, J. Phys. Chem., 89 (1985) 2720.