Chapter 6
Photodegradation of Pesticides and Photocatalysis in the Treatment of Water and Waste

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Abstract A brief overview on the main photoprocesses applied to the treatment of water and wastewater is presented. The photodegradation methods that have been applied to the oxidation of organic pollutants are described. A review on advanced oxidation processes (AOP's) and photooxidation mechanisms in homogeneous and heterogeneous solution is presented and some practical applications discussed. Combinations of biological and chemical treatments are considered to be a good approach to improve the removal efficiencies and reduce costs.

6.1 Introduction

Water is critical and vital for life. As a consequence, environmental laws and regulations concerning its quality have become more stringent, in particular with reference to the presence of pesticides and other pollutants, such as chlorophenols, with admissible threshold values less than 0.5 micrograms per litre in water [1]. It is imperative to enforce the protection and correction of environmental problems

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and thus adequate treatment of contaminated waters is of primary concern in order to preserve the natural ecosystem.

The increasing worldwide pollution of freshwater is mainly due to contamination of surface water and groundwater with chemical compounds arising from industrial discharges, excess use of pesticides or fertilizers applied in agriculture and leaching from landfilling of domestic wastes.

In order to cope with water scarcity and pollution of the hydrosphere, two main strategies of water treatment are applied: (1) chemical treatment of polluted drinking water, surface water, groundwater and (2) chemical treatment of wastewaters containing biocidal or non-biodegradable components.

Persistent organic chemicals present as pollutants in wastewater effluents can be found in ground water, as well as in surface waters. They have to be removed to protect water resources or to achieve drinking water quality. Unfortunately, the majority of organic pollutants, and in particular pesticides, are not biodegradable and are noted as biorecalcitrant organic compounds. Therefore, it is very important to develop eco-friendly methods capable of reducing a significant part of this pollution by destroying the toxic and hazardous organic pollutants.

Physicochemical methods, such as flocculation, membrane filtration or adsorption on activated carbon just transfer the pollutants from one phase to another without destroying them. Currently, the main progress in the decontamination of water is focussed on the use of advanced oxidation processes (AOP's) for the degradation of synthetic organic species resistant to conventional treatments, particularly those applying photochemical and photocatalytic reactions, which have the main advantage that they can be used for the treatment of relatively low levels of pollution in aqueous media [2, 3].

All AOP's are based largely on hydroxyl radical chemistry, generated *in situ* normally by using UV lamps or solar energy. The hydroxyl radical ($HO^\bullet$) has a high reduction potential (2.8 V) and is able to react rapidly and non-selectively with a wide range of organic compounds [4].

The most attractive feature of AOP's is that hydroxyl radical species are strongly oxidising and react with most organic substances, normally either by hydrogen abstraction or electrophilic addition to double bonds. Organic free radicals from the pollutant may react further with molecular oxygen to give a peroxy radical, initiating a sequence of oxidative degradation reactions, which may lead to complete mineralisation of the contaminant [5]. In addition, hydroxyl radicals may attack aromatic rings at positions occupied by a halogen, generating a phenol homologue. However, although hydroxyl radicals are among the most reactive species known, they only react slowly with chlorinated alkane compounds, which are frequent pollutants [6].

In this chapter, we describe the photodegradation methods applied to the oxidation of organic pollutants, namely pesticides. We have made the approach of the direct, sensitised and photocatalytic degradation of pollutants with a scheme of treating these in terms of the possible mechanisms. Further, we give an overview of AOP's in homogeneous and heterogeneous solutions and the corresponding mechanisms.

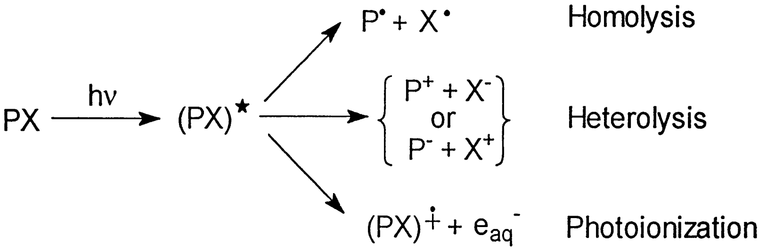
At the end, we will give examples of the treatment of some important pollutants in water.

6.2 Direct Photodegradation

Most pesticides show UV absorption bands at relatively short UV wavelengths (UV-A and UV-B). Since sunlight reaching the Earth's surface (mainly UV-A, with varying amounts of UV-B) contains only a very small amount of this short wavelength radiation [7], the direct photodegradation of pesticides by sunlight is expected to be, in general, of only limited importance.

Direct irradiation will lead to the promotion of the pesticides to their excited singlet states, which may then intersystem cross to produce triplet states. Such excited states can undergo, among other processes: (i) homolysis, (ii) heterolysis or (iii) photoionisation, as depicted in Scheme 6.1 [3].

The reader can find a variety of the literature for several chemical classes of pesticides in the review by Burrows *et al.* [3]. As a consequence of only limited direct photodegradation, in order to use solar energy to obtain significant degradation or mineralisation most research is directed towards photosensitised and photocatalytic reactions.



Scheme 6.1 Possible chemical events taking place upon direct photolysis [3]

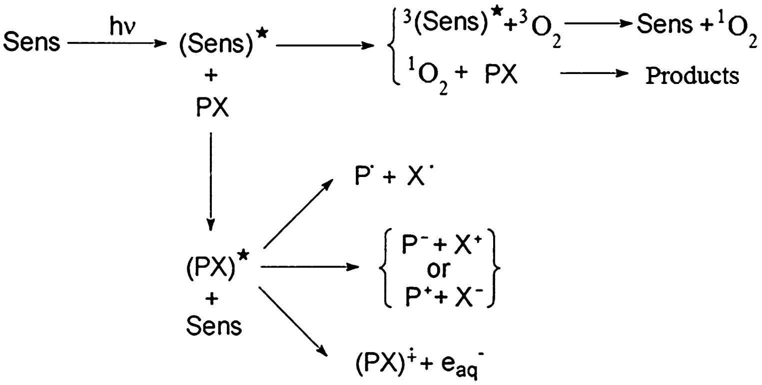
6.3 Photosensitised Degradation

An important advantage of photosensitised photodegradation is the possibility of using light of wavelengths longer than those corresponding to the adsorption characteristics of the pollutant. Photosensitised degradation is based on the absorption of light by a strongly absorbing molecule that is not the pollutant (e.g. methylene blue, Rose Bengal, riboflavin, acetone, tris-2,2′-bipyridyl ruthenium (II), peroxy disulphate, porphyrins, phthalocyanines, etc.). Following light absorption, the photosensitiser (Sens) can transfer energy from its excited state to the pollutant, which can then undergo different intermolecular reactions or intermolecular photophysical processes [3]. A second photophysical pathway which is of great importance in many systems, including photocatalysis, involves the intermolecular transfer of electronic energy from the excited sensitiser, as donor molecule (D*) to an energy acceptor (A):

$$D^* + A \rightarrow D + A^* \qquad (6.1)$$

Probably, the most important cases of energy transfer for photocatalysis involve sensitisation by the triplet state of an appropriate donor and its interaction with the ground state (triplet) of molecular oxygen to form the highly reactive singlet oxygen (Scheme 6.2).

Photosensitisation may also involve redox processes such as those observed in the photo-Fenton process to produce hydroxyl free radicals (see Sect. 6.5).



Scheme 6.2 Chemical events taking place upon photosensitised photolysis involving energy transfer [3]

6.4 Photocatalytic Reactions/Heterogeneous Catalysis

Although different definitions have been suggested for photocatalysis, we will use photocatalytic reaction to mean cyclic photoprocesses in which the substrate photodegrades and spontaneous regeneration of the catalyst occurs to allow the sequence to continue indefinitely until all the substrate is destroyed [8, 9].

In conventional heterogeneous catalysis, the overall process consists of a sequence of events, which can be broken down into five elementary steps:

1. Diffusion of the reactants through the bulk to the surface.
2. Adsorption of at least one reactant.
3. Reaction in the adsorbed phase.
4. Desorption of the products.
5. Removal of products away from the interface.

In heterogeneous photocatalysis, the only difference with conventional catalysis lies in step 3, where the usual thermal activation is now replaced by photonic activation. The activation mode is not concerned with steps 1, 2, 4 and 5, although photoadsorption and photodesorption processes of some reactants, particularly oxygen, do exist. The photoinduced molecular transformations and reactions, involving electron transfer or energy transfer, will take place at the surface of the catalyst solely in step 3 as will be described later (Sect. 6.6). Therefore, a heterogeneous photocatalytic system for oxidative degradation of organic or inorganic compounds includes the following components: (1) a reactant; (2) a photon of the appropriate wavelength; (3) a catalyst surface (normally a semiconductor, such as TiO_2 or immobilised sensitisers, such as porphyrins or phthalocyanines, polyoxomethalates etc.); (4) a strong oxidising agent [10, 11].

6.5 Advanced Oxidation Processes (AOP's)

An improvement in oxidative degradation procedures for organic compounds is based on a group of catalytic and photochemical methods, which are referred to as *advanced oxidation processes* (AOP's), and which can be used in homogeneous or heterogeneous media. However, heterogeneous catalysts have the advantage that they can be recovered and reused.

Some of the most frequently used AOP's involve molecules that generate the hydroxyl radical ($HO^\bullet$) *in situ* in homogeneous or heterogeneous media. This can be achieved by various ways, such as:

1. Addition of **hydrogen peroxide**, which undergoes homolysis upon photolysis:

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{6.2}$$

2. Photolysis of **ozone**, either with the generation of atoms of singlet oxygen, which then react with water to generate $HO^\bullet$:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad \lambda < 310\,\mathrm{nm} \tag{6.3}$$

$$O(^1D) + H_2O \rightarrow 2HO^\bullet \tag{6.4}$$

or through direct reaction with water to produce hydrogen peroxide:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{6.5}$$

followed by its homolysis to generate hydroxyl radicals.

3. Aqueous photolysis of Fe^{3+}, generated through oxidation of Fe^{2+} by H_2O_2—the **photo-Fenton** process:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{6.6}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^\bullet + H^+ \tag{6.7}$$

4. **Radiolysis** (or vacuum UV photolysis) of water:

$$H_2O \rightarrow H^+ + HO^\bullet + e^-_{aq} \qquad \lambda = 193 \text{ nm} \tag{6.8}$$

The $HO^\bullet$ radical can then react by:

$$\textbf{electron transfer}: \quad HO^\bullet + P \rightarrow OH^- + P^{+\bullet} \tag{6.9}$$

$$\mathbf{H^\bullet}\text{ abstraction}: \quad HO^\bullet + PH \rightarrow H_2O + P^\bullet \tag{6.10}$$

$$\textbf{or addition to aromatic rings}: \quad HO^\bullet + P \rightarrow P - OH^\bullet \tag{6.11}$$

5. **Polyoxometalates**. Because of their excellent spectroscopic and electronic features, polyoxometalates (POMs) form an important family of compounds that can be used for several interesting applications such as redox and photoredox reactivity, conductivity and ionic charge effects [12]. In particular, these oxygen-bridged metal anion clusters are efficient photocatalysts and because of their wide range of redox potentials they may be used efficiently in various homogeneous oxidation and reduction reactions. These oxides, among them $W_{10}O_{32}{}^{4-}$, show good solubility, and have been intensively studied from the photochemistry point of view [13–15]. They have been shown to be promising candidates for treating contaminated and complex aqueous systems. The decatungstate polyoxometalate, which shows low toxicity, absorbs in the UV with a maximum at 320 nm. Its UV absorption spectrum clearly overlaps the solar emission spectrum indicating the possible use of this inexhaustible source of energy for the degradation of organic as well as inorganic substrates. Supported decatungstate can also be considered as a good candidate for the recovery of the photocatalyst for example on silica [16] and carbon fibres [17].

The application of tungstate-based photocatalysts was proposed by Satari and Hill [18]. These authors clearly showed that the light excitation of $W_{10}O_{32}{}^{4-}$ permits the oxidation of organic compounds with an effective cleavage of carbon–halogen bonds. This interesting application in the field of water decontamination has been seriously explored by Papaconstantinou and collaborators for the photochemical degradation and also efficient mineralisation of substrates such as chlorophenols and various chloroacetic acids [19, 20]. Within this work, a comparative study was carried out on the photocatalytic efficiency of TiO_2 and $Na_4W_{10}O_{32}$ at $\lambda > 300$ nm. The organic pollutants used were phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, atrazine, imidachloprid and oxamyl in aqueous solution. TiO_2 was found to be the most effective photocatalyst in terms of the degradation rate and of the mineralisation of the compounds. However, the decatungstate anion appeared to be particularly efficient in the case of pesticides formulations, such as those prepared in the presence of surfactants [21]. Since mineralisation with decatungstate anions occurs over a longer time range, its use should be restricted only to pollutants that produce non-toxic intermediates.

Intensive studies have been devoted to obtain mechanistic information on photocatalysis by POMs that give a precise overview on the cascade of events, lifetime and quantum yield of formation of the primary intermediate species, which proceed after light absorption before leading to final reaction products [21–24]. These were performed using laser flash photolysis and pulse radiolysis, in combination with continuous photolysis studies. Within such studies, the light excitation of decatungstate leads to the formation of a very short lived charge transfer excited state (about 30 ps lifetime) which forms a longer lived species designated as WO with a formation quantum yield of 0.6. This latter species is most likely to be the reactive species in photocatalytic systems [23]. Furthermore, in aqueous solution, the photooxidation performance can be enhanced by the production of highly reactive hydroxyl radicals formed through the direct reactionof water with the excited decatungstates. In the presence of, for example, an organic substrate XH, WO reacts to form the one electron reduced species through either a hydrogen abstraction process or electron transfer. In aerated conditions, $W_{10}O_{32}{}^{5-}$ is then reoxidised by O_2 leading to the formation of the starting $W_{10}O_{32}{}^{4-}$, according to Scheme 6.3.

This type of photocatalytic cycle can efficiently be used for the degradation of organic substrates with the total recovery of the photocatalyst. They have also been used for the reduction of metal ions [25] and in simultaneous conversion of dye and hexavalent chromium using visible light illumination [26]. Some specific examples are described below.

$$W_{10}O_{32}^{4-} \xrightarrow{h\nu} WO$$

$$WO + XH \longrightarrow W_{10}O_{32}^{5-} + XH^{+\bullet}$$

$$WO + H_2O \longrightarrow W_{10}O_{32}^{5-} + HO^{\bullet}$$

$$W_{10}O_{32}^{5-} + XH \longrightarrow HW_{10}O_{32}^{4-} + X^{\bullet}$$

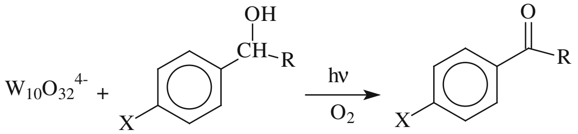
$$W_{10}O_{32}^{5-} + O_2 \longrightarrow W_{10}O_{32}^{4-} + O_2^{-\bullet}$$

$$O_2^{-\bullet} + H^+ \rightleftarrows HO_2^{\bullet}$$

Scheme 6.3 Photochemical primary processes upon excitation of $W_{10}O_{32}{}^{4-}$

i) Oxidation of Aryl Alkanols

A series of 1-aryl alkanols were investigated using polyoxometalates such as $W_{10}O_{32}{}^{4-}$ as a photocatalyst (Scheme 6.4). A clean oxidation reaction of the side chain of the aryl alkanol led to the formation of the aryl ketone. This process supports a hydrogen transfer mechanism as the rate determining step. The efficiency of the reaction was mainly determined in the presence of oxygen [27].

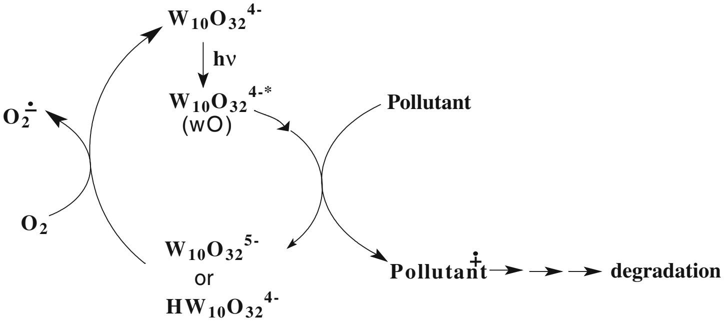


Scheme 6.4 Oxidation process induced by excitation of $W_{10}O_{32}^{4-}$

ii) Decolorisation of Dye Solutions and Pesticide Degradation

The photocatalytic degradation of textile and industry dyes (Brilliant Red X3B and Acid Orange 7) and pesticides was efficiently observed using POMs as inducers at $\lambda > 320$ nm. The photooxidative decomposition of Acid Orange (4[2-hydroxy-1-naphthyl)azo]benzene sulfonic acid) leads to the formation of several by-products that disappear in turn by excitation of POMs. Among them are 1-(4-hydroxyphenyl)azo-2-naphthol, 1-(phenylazo)-2-naphthol, 2-naphthol, 4-methyl-1-naphthol. Such reactivity demonstrates the involvement of an electron transfer process. In most cases, particularly in the presence of oxygen, the process leads to mineralisation of the solution showing the great reactivity of the POMs used towards the majority of the compounds (initial and intermediates) [28–30]. The following photocatalytic cycle has been proposed as shown in Scheme 6.5.

6. **Semiconductors** excited by appropriate energy photons. Two well-defined AOP's systems which have special interest, because natural solar light can be used, are heterogeneous photocatalysis with TiO_2 and homogeneous photocatalysis by the photo-Fenton process. These processes are covered in detail in the following sections.



Scheme 6.5 Photocatalytic cycle of $W_{10}O_{32}^{4-}$ in the presence of organic pollutant

6.6 Heterogeneous Photocatalysis by Semiconductors

Heterogeneous photocatalysis by semiconductor materials has gained increasing interest because, as a green technology, it can be widely applied both to environmental purification (non-selective process) and selective organic transformations of fine chemicals in both gas and liquid phases [31, 32].

Inorganic semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS and ZnS) can act as sensitisers for light-induced redox processes due their electronic structure, which is characterised by a filled valence band (VB) separated by a relatively small energy from an empty conduction band (CB) (see Chap. 4). The separation between the two bands is particular to each semiconductor, and is referred to as the *bandgap* (E_g). When the semiconductor is illuminated with light (hν) of energy greater than that of the bandgap, an electron is promoted from the VB to the CB, thus leaving a positive hole in the valence band; that is, absorption of light with sufficient energy ($\geq$the bandgap energy, E_g) leads to the formation of an electron/hole pair. In the absence of suitable scavengers, the stored energy is dissipated within a few nanoseconds by charge recombination. However, if a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence band holes are powerful oxidants (+1.0 to +3.5 V *vs.* NHE (Normal Hydrogen Electrode)), depending on the semiconductor and pH, while the conduction band electrons are good reductants (+0.5 to −1.5 V *vs.* NHE). Most organic photodegradation reactions use the oxidising power of the holes either directly or indirectly. However, to prevent a build-up of charge one must also provide a reducible species to react with the electrons.

Within the large number of inorganic semiconductors that are known, TiO_2 and ZnO are the most commonly used in photocatalysis, due to both low cost and acceptable bandgap energy.

Titanium dioxide-based materials have proved to be the most suitable for the majority of environmental applications. TiO_2 is abundant, chemically inert, stable to photo- and chemical corrosion, inexpensive, relatively non-toxic, with good electronic and optical properties. However, it should be noted that the toxicity of TiO_2 in the form of nanoparticles is currently under study [33, 34]. TiO_2 is of special interest since it can use natural solar-UV radiation for excitation, which makes it a promising candidate in photocatalysis using solar light as energy source.

Considering the appropriate energetic separation between the valence and conduction bands in TiO_2, which has to be overcome by the energy of a UV solar photon, the (VB) and (CB) energies are +3.1 and −0.1 V, respectively, such that the bandgap energy is 3.2 eV, which corresponds to absorption of near UV light ($\lambda < 387$ nm).

Under these conditions, valence band electrons are excited and move to the conduction band leaving behind holes; thus generating an electron/hole pair (e^- to h^+). The electron and holes must then migrate to the surface of the semiconductor to promote reduction and oxidation reactions of adsorbed species or of species that are in close proximity to the surface of the semiconductor (Fig. 6.1). However, electron–hole recombination, at the surface or in the bulk of the catalyst competes with the above process and limits the overall quantum yield of photocatalytic reactions [35, 36]. Activation of this process proceeds through the excitation of the solid but not the reactants: there is no photochemical process in the adsorbed phase, but only a true heterogeneous photocatalytic reaction. The photocatalytic activity can be reduced by the electron–hole recombination, as described in Fig. 6.2, which corresponds to the degradation of the photoelectronic energy into heat.

The following chain reactions can be postulated:

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{TiO_2(e^- + h^+)} \tag{6.12}$$

$$\mathrm{TiO_2(e^-) + RX_{ads} \rightarrow TiO_2 + RX_{ads}^{-\bullet}} \tag{6.13}$$

$$\mathrm{TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + HO^{\bullet}_{ads} + H^+} \tag{6.14}$$

$$\mathrm{TiO_2(h^+) + OH^-_{ads} \rightarrow TiO_2 + HO^{\bullet}_{ads}} \tag{6.15}$$

The reaction mechanism described by Eqs. 6.14 and 6.15 appears to be of greater importance in oxidative degradation processes compared with the reductive route (Eq. 6.13), probably due to the high concentration of H_2O and HO^- molecules adsorbed at the particle surface with the generation of $HO^\bullet$ a powerful oxidising species. Molecular oxygen, which must be present in all oxidative degradation processes, is the accepting species in the electron-transfer reaction from the conduction band of the photocatalyst (Eq. 6.16). The superoxide anion, and its

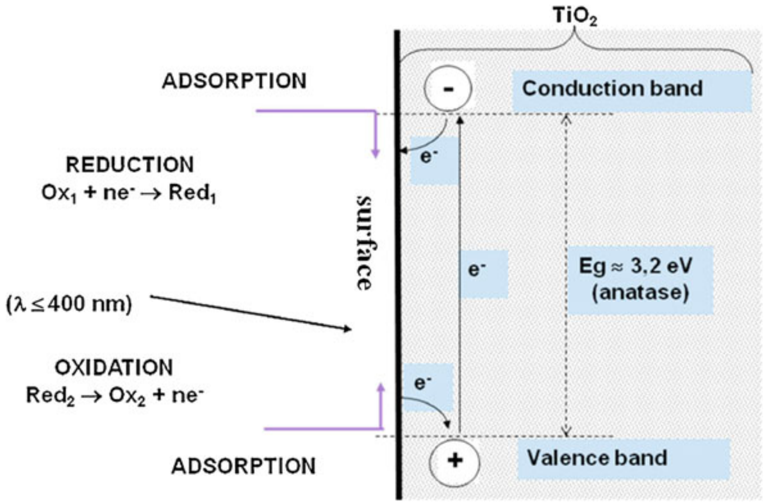


Fig. 6.1 Energy band diagram and activation of titanium dioxide (reproduced from Ref. [35] with personal permission of Jean-Marie Herrmann)

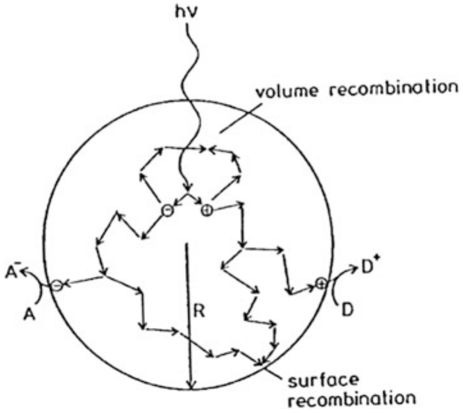


Fig. 6.2 Fate of electrons and holes within a spherical particle of TiO_2 in the presence of an acceptor (A) and (D) molecule (adapted with permission from Ref. [36], Copyright 1993, Elsevier)

protonated form, subsequently yield hydrogen peroxide (or peroxide anion) and molecular oxygen (Eq. 6.18).

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{-\bullet} \tag{6.16}$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \tag{6.17}$$

$$H^+ + O_2^{-\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{6.18}$$

Anatase and rutile are the most common forms of TiO_2, and anatase is the most effective in photocatalytic wastewater treatment, mainly because it has a higher surface area and higher surface density of active sites for adsorption and catalysis. Brookite is not likely to be involved in photodegradation.

It has been pointed out that the photodegradation reaction rate is much more rapid with anatase than with rutile, and that the reaction rate is mainly affected by the crystalline state surface area and particle size of TiO_2 powder. However, these factors often vary in opposite ways, since a high degree of crystallinity is achieved through a high-temperature thermal treatment leading to a reduction in the surface area, while optimal conditions are required for photocatalysis. The photocatalytic activity of TiO_2 depends not only on the bandgap energy, but also, to a large extent, on its surface properties, which are affected both by the synthetic process [37] and the calcination atmosphere [38].

Although TiO_2 is cheap, the efficiency of the photocatalysis process with solar energy is low because only 10 % of the overall solar intensity is in the UV-A region where TiO_2 is excited. The effective goal now is to achieve TiO_2-type photocatalysis with commercial viability using solar energy and high activity of photodegradation of pollutants. Within recent years, research has responded to this challenge. New TiO_2 photocatalysts have been synthesised by sol–gel or hydrothermal methods.

Doping the semiconductor with a variety of metal ions, such as Sn^{4+}, Au^{3+}, Bi^{3+}, Mg^{2+}, Ba^{2+}, etc. [39–42] has induced a bathochromic (red) shift, extending its absorption towards the visible light region. However, we should note that cationic doping may be detrimental for photocatalysis, since the doping cations may act as charge recombination centres [35]. Enhanced photocatalytic activity may be obtained by the introduction of non-metallic anions (N, C, S and F) [43–45], or by coupling two semiconductor systems TiO_2/CdS, TiO_2/SnO_2, TiO_2/ZnO, TiO_2/WO_3 [46, 47], in which there is coupling between a large gap semiconductor (3.2 eV TiO_2) and a smaller bandgap one. For example, in TiO_2/CdS the photogenerated electrons (2.4–2.6 eV in CdS) are transferred onto TiO_2 particles while the holes remain on the CdS particles, which makes long-term charge separation possible, by decreasing the recombination, and at the same time allowing the extension of the response of the photocatalyst into the visible region. Serpone et al. [46] provided the first report of the photocatalysed oxidation of phenols by coupled semiconductors in which the beneficial effect of charge transfer was demonstrated.

Immobilisation techniques on different supports have been also investigated. Among these materials, titanium dioxide with activated carbon, carbon nanotubes, activated carbon fibres, silica and alumina have all shown higher activity in photodegradations because of their surface properties, compared with TiO_2 alone [48, 49].

6.7 Photocatalysis in the Treatment of Water and Waste

Water purification treatment is currently a very hot subject within scientific research, and several books and reviews have been devoted to this problem [2, 3, 11, 36, 50–56]. One of the challenges facing water purification treatment is the elimination of low concentrations of toxic biorecalcitrants, particularly when present as components of complex mixtures, including chlorinated aromatics, pesticides, pharmaceuticals, hormones, surfactants, etc. [57, 58].

René *et al.* [63] indicate three scientific challenges in water quality problems caused by such micropollutants: (i) to develop and refine the tools to assess the impact of these pollutants on aquatic life and human health; (ii) the cost-effective and appropriate remediation and water treatment technologies must be explored and implemented, and (iii) usage and disposal strategies must be applied, coupled with intensive research and development of environmentally more benign products and processes.

TiO_2 has shown, so far, the best photocatalytic performance of all the inorganic semiconductors studied in the catalysed photodegradation of pesticides, and titania nanomaterials have been successfully used for the degradation of several classes of pollutants (pesticides, chlorinated aromatics, etc.), leading in some cases to complete mineralisation. However, these contrast, with the high cost of separation of the catalysts.

Photocatalysed degradation of s-triazine type herbicides with TiO_2 has been studied and it was observed that cyanuric acid is the final photoproduct [59–62].

This is photostable and complete mineralisation was not observed. In some countries restrictions on the use of s-triazines, such as atrazine, have been implemented, while in others, these have even been banned. Atrazine has, however, been detected above the recommended levels (0.1 ppb or μg dm^{-3}) throughout Europe and the United States and is considered as a priority toxic substance by the EC. Considerable efforts are being made to eliminate it from water.

Immobilised TiO_2 films have been tested in photocatalytic water treatment with atrazine but total mineralisation has not yet been achieved [63]. Microwave assisted degradation of atrazine with TiO_2 nanotubes, however, appears to be a good potential route way to mineralise atrazine [64].

Porphyrins and metalloporphyrins supported on TiO_2 also can degrade atrazine and 4-nitrophenol under visible light irradiation. However, lower efficiency is observed for atrazine than for the phenol. It is also possible to mineralise 4-nitrophenol with porphyrin/TiO_2 based composites, and the addition of H_2O_2 improves this process when atrazine is used as substrate [65–67].

Indeed, porphyrins are good sensitisers for visible light sensitisation, with high extinction coefficients for their absorptions around 400 nm corresponding to the Soret band (see Chap. 4). They have been used as photosensitisers with polycrystalline TiO_2 in order to enhance the visible light-sensitivity of the TiO_2 matrix, and therefore increase its photocatalytic activity [67, 68]. For heterogeneous photocatalysis, immobilisation of porphyrins provides another route towards photodegradation of pesticides [69, 70].

Titanium dioxide in films has been proved to be a good photocatalyst towards degradation of chloroaromatics, such as chlorophenols [71], although overall mineralisation with chlorophenols has not been reported. Herrmann *et al.* [72] have studied the photocatalytic degradation with TiO_2 under solar irradiation of 2,4-dichlorophenoxyacetic acid leading to the complete mineralisation of the substrate.

Chlorophenols appear commonly in industrial effluents, but research into photocatalytic degradation of these compounds [73, 74] by TiO_2 indicates that mineralisation is not effective.

In order to have a practical application of these systems, both the use of visible light source and an enhanced degradation rate are essential. Doped TiO_2 semiconductors show photocatalytic activity for the photodegradation of phenol and chlorophenol using visible light [41, 43, 44, 75].

Coupled systems, such as TiO_2/WO_3, have been tested with 4-chlorophenol, and have shown efficient degradation under visible light irradiation. A much higher hydroxyl radical concentration is found for the TiO_2/WO_3 system than using TiO_2 alone [47].

Immobilisation of TiO_2 on solid supports appears to be an attractive alternative avoiding the separation step in photocatalysis. Immobilisation of titanium dioxide has been adapted to a pilot scale solar photoreactor in a compound parabolic collector (CPC), and shown to be effective on the degradation and mineralisation of phenol and some emergent contaminants in a municipal effluent [57, 76].

Sequential biological—advanced oxidative—biological processes are proving to be promising in photodegradation of chlorophenols as model substrates, and promote total degradation [77].

We have focused on triazines and chlorophenols, but the same methodology can be applied to other systems.

6.8 Photo-Fenton Reaction in the Treatment of Water and Waste Water

Among the various advanced oxidation processes, Fenton reactions and their combination with light, namely photo-Fenton reaction, have been efficiently used for the destruction of toxic and persistent organic pollutants [78–80]. Fenton treatment consists of the *in situ* formation of a highly reactive species, *i.e.* the hydroxyl radical. This is as an efficient oxidant ($E = 2.8$ V *vs*. NHE) lower than fluorine (3.0 V) and higher than ozone (2.07 V) and hydrogen peroxide (1.78 V), which is able to react with almost all the organic compounds with rate constants close to those for diffusion controlled processes. Its reactions towards organic compounds can proceed *via* H-abstraction, electron transfer and/or addition to carbon–carbon unsaturated bonds.

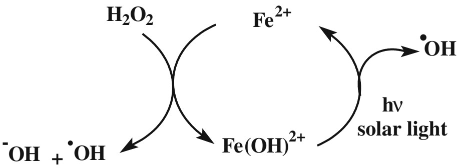
Even though the process is very complex, the production of the hydroxyl radical through the Fenton reaction is considered to be due to the interaction of hydrogen peroxide with ferrous ion, which occurs with a rate constant of 63 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ [80–82].

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet} \tag{6.19}$$

The destruction rate of several organic pollutants was shown to increase when light illumination of the solution is used simultaneously with the above Fenton reaction. In this process, the iron salts ($\mathrm{Fe^{2+}}$, $\mathrm{Fe^{3+}}$) are used as photosensitisers and the hydrogen peroxide as an oxidising agent leading to a better production of hydroxyl radicals. The increase of the hydroxyl production rate is due to the involvement in the iron (III) photo reduction reaction of the iron aquacomplex, $\mathrm{[Fe(H_2O)(OH)]^{2+}}$ (represented by $\mathrm{Fe(OH)^{2+}}$) through light excitation into the ligand to metal charge transfer transition (Eq. 6.20) [83–85].

$$\mathrm{Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + OH^\bullet} \tag{6.20}$$

Such a reaction regenerates ferrous ion showing that only low concentration of $\mathrm{Fe^{2+}}$ is needed in the system [86]. Moreover, the photo-Fenton process may proceed using photons of wavelength close to 500 nm in the case of mixtures of ferric ion and hydrogen peroxide. It can also be performed by solar irradiation making it a low cost process [79, 80, 87, 88]. The photocatalytic cycle may be presented as shown in Scheme 6.6.



Scheme 6.6 Photocatalytic cycle of iron in the photo-Fenton process

As shown in the photocatalytic cycle, the continuous production of hydroxyl radicals as well as the presence of hydrogen peroxide leads to the oxidation of the organic pollutants and also of the generated by-products. This phenomenon permits, in many cases, the total mineralisation of the solution [89].

6.9 Conclusions

In conclusion, current research on the degradation of organic pollutants has been focused on the combination of chemical (AOP's) processes and biological treatment and these have been tested on biorecalcitrant compounds such pesticides and chlorophenols [76, 90–92]. The results have shown that such AOP's have the ability to degrade the pollutants and produce by-products with high bio-degradation efficiency. Furthermore, by using the combination of biological and chemical treatments, in addition to improving the removal efficiencies, there is also a marked reduction of the overall costs, thus overcoming one of the main economic hindrance to practical exploitation.

Powdered TiO_2 is widely used in suspension (slurry) with excellent performance, but it requires filtration. Immobilisation of TiO_2 on solid supports such as glass, polymers and ceramics removes the need for filtration to separate the catalyst from treated water, making the process less expensive.

Solar photocatalytic degradation of water contaminants with titania and photo-Fenton catalysts has been carried out on a pilot-plant scale at the solar photochemical facilities of the *Plataforma Solar de Almeria* (PSA) in Spain, and show how solar photocatalysis is likely to become important within the next few decades in wastewater treatment and development of new AOP technologies [93, 94].

The testing and development of reactors to maximise the optical efficiencies are also being carried out at PSA. Unfortunately, at present there are no general rules for the photocatalysed degradation of several pollutants, and preliminary research is always required to optimise the best conditions.

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