
Recent Overview on the Abatement of Pesticide Residues in Water by Photocatalytic Treatment Using TiO_2

Nuria Vela, Gabriel Pérez-Lucas, José Fenoll and Simón Navarro

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Abstract

The water bodies' pollution with phytosanitary products can pose a serious threat to aquatic ecosystems and drinking water resources. The usual appearance of pesticides in surface water, waste water and groundwater has driven the search for proper methods to remove persistent pesticides. Although typical biological treatments of water offer some advantages such as low cost and operability, many investigations referring to the removal of pesticides have suggested that in many cases they have low effectiveness due to the limited biodegradability of many agrochemicals. In recent years, research for new techniques for water detoxification to avoid these disadvantages has led to processes that involve light, which are called advanced oxidation processes (AOPs). Among the different semiconductor (SC) materials tested as potential photocatalysts, titanium dioxide (TiO_2) is the most popular because of its photochemical stability, commercial availability, non-toxic nature and low cost, high photoactivity, ease of preparation in the laboratory, possibility of doping with metals and non-metals and coating on solid support. Thus, in the present review, we provide an overview of the recent research being developed to photodegrade pesticide residues in water using TiO_2 as photocatalyst.

Keywords: titania, pesticides, water, photocatalytic degradation

1. Introduction

Pesticide may be defined as 'any substance or mixture of substances intended for preventing, destroying, or controlling any pest including vectors of human or animal diseases, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, or marketing of food, agricultural commodities, wood and wood

products, or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes chemicals used as growth regulators, defoliants, desiccants, fruit thinning agents, or agents for preventing the premature fall of fruits, and substances applied to crops either before or after harvest to prevent deterioration during storage or transport' [1]. There are many hundreds of them including herbicides, insecticides, fungicides, rodenticides, nematocides, plant growth regulators and others. Pesticide products contain both 'active' and 'inert' ingredients: active ingredients are the chemicals in pesticide products that kill, control or repel pests. All other ingredients are called 'inert ingredients,' which are important for product performance and usability.

Pesticides have been widely applied to protect agricultural crops since the 1940s, and their use increased steadily during the subsequent decades. The *Green Revolution* was the notable increase in cereal-grain production in many developing countries in the 1960s and 1970s. This tendency resulted from the introduction of hybrid strains of wheat, rice and corn and the adoption of modern agricultural technologies, including irrigation and large doses of agrochemicals, fertilisers and pesticides [2]. However, Rachel Carson (1907–1964) with the publishing of her sensational book *Silent Spring* in 1962 [3] warned of the dangers to all natural systems from the misuse of some pesticides such as DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl) ethane). As a result, a wider audience was warned of the environmental effects of the widespread use of pesticides, and DDT was banned for agricultural use 10 years later in the USA, and the regulation of chemical pesticide use was strengthened. Currently, all pesticides are subject to strict registration as meaning 'the process whereby the responsible national government authority approves the sale and use of a pesticide following the evaluation of comprehensive scientific data demonstrating that the product is effective for the purposes intended and not unduly hazardous to human or animal health or the environment' [4]. In evaluating a pesticide registration application, a wide variety of potential human health and environmental effects associated with their use must be tested. Registrants must generate the necessary scientific information to address concerns corresponding to the identity, composition, potential adverse effects and environmental fate of each pesticide. These data allow evaluating whether a pesticide could harm certain nontarget organisms and endangered species.

Protection of crop losses/yield reduction and increase in food quality are key benefits associated with the use of pesticides in agriculture. However, most organic pesticides characterised as persistent in the environment can bioaccumulate through the food web and can be transported in long distances [5], as evidenced by the accumulation in regions where persistent pesticides have never been used [6]. Persistent organic pollutants (POPs) are *chemical compounds that persist in the environment and adversely affect human health and the environment around the world* [7]. Because they can be transported by wind and water, most POPs can affect human health and wildlife far from where they are applied. They have high persistence in the environment and can accumulate passing from one species to the next through the food chain. To treat this environmental concern, the USA joined forces with 90 other countries and the European Community to sign the agreement United Nations treaty in Stockholm (Sweden, May 2001). The *Stockholm Convention on Persistent Organic Pollutants*, approved by Council Decision 2006/507/EC [8], entered into force on 17 May 2004. The aim of the Convention was to protect human health and the environment from POPs. Under the treaty, known as the *Stockholm Convention*,

countries agreed to reduce or eliminate the production, use and/or release of 12 key POPs ('the dirty dozen', mainly organochlorine (OC) insecticides) and specified under the Convention a scientific review process that has led to the addition of other POP chemicals of global concern. Currently, there are 30 substances catalogued as POPs including mainly pesticides, industrial chemicals and by-products.

In addition, many pesticides are endocrine-disrupting chemicals (EDCs), *compounds that alter the normal functioning of the endocrine system of both wildlife and humans increasing incidence of breast cancer, abnormal growth patterns and neurodevelopmental delays in children, as well as changes in immune function* [9–11]. Most of them are organochlorine (OC) pesticides that affect the reproductive function.

Worldwide consumption of pesticides for agricultural use is constantly increasing as increased human population and crop production, and it has undergone significant changes since the 1960s. Nowadays, the worldwide consumption of pesticides is about 2 million tonnes per year, which 45% is used by Europe alone, 25% is consumed in the USA and 30% in the rest of the world. The proportion of herbicides in pesticide consumption increased rapidly, from 20% in 1960 to 47.5% in 2015. However, the proportion of consumption of insecticides (29.5%) and fungicides/bactericides (17.5%) declined despite their sales increased with other accounts for 5.5% only [12]. The rapid increase of herbicide consumption enhanced agricultural intensification and productivity.

The application of chemical pesticides, in particular the organic-synthesised pesticides, has been a significant mark of human civilisation, which greatly protects and facilitates agricultural productivity. Worldwide, insect pests cause an estimated 14% loss, plant pathogens cause a 13% loss, and weeds causes a 13% loss [13]. Pesticides are so indispensable in agricultural production. About one-third of the agricultural products are produced by using pesticides [14]. Without pesticide application, the loss of fruits, vegetables and cereals from pest injury would reach 78, 54 and 32%, respectively [15]. Ideally, a pesticide must be lethal to the targeted pests, but not to nontarget species, including humans. Unfortunately, this is not the case, so the controversy of use and abuse of pesticides is obvious. Consequently, the risks of using pesticides are serious as well [13]. Most pesticides are not spontaneously generated, and they are toxic to humans and the environment in greater or lesser degree [16]. Pesticides and their degraded products can pass into the atmosphere, soils and water, resulting in the accumulation of toxic substances and thus threatening human health and the environment. In addition, accumulated application leads to loss of biodiversity. Because many pesticides are barely degradable, they persist in soil and pollute surface water and groundwater. Depending on their chemical properties, they can bioaccumulate in food chains and consequently affect human health.

For many pesticides, there is evidence of long-term ubiquity in the aquatic environment at the European Union (EU) level, and therefore they need special consideration as regards their impact on the presentation of chemical status under the European Water Framework Directive (EWFD) [17]. The EWFD establishing a framework for community action in the field of water policy lays down a strategy against the pollution of water. Directive 2008/105/EC [18], amended by Directive 2013/39/EU [19] on environmental quality standards in the field of water policy,

lays down environmental quality standards in accordance with the EWFD, for the 33 priority substances. The EWFD also sets out general provisions for the protection and conservation of groundwater. The establishment of detailed quality criteria for the assessment of groundwater chemical status in Europe was laid down in the European Groundwater Directive [20]. For this reason, the EU established the following groundwater quality standards: $0.1 \mu\text{g L}^{-1}$ for individual pesticide and $0.5 \mu\text{g L}^{-1}$ for the sum of all individual pesticides to safeguard people from harmful effects.

During the 1990s of the last century, atrazine (herbicide) and endosulfan (insecticide) were found most often in surface waters in the USA and Australia due to their widespread use. In addition, although in lower proportions, other pesticides such as pronofos, dimethoate, chlordane, diuron, prometryn and/or fluometuron were detected [21]. Studies that are more recent also reported the presence of several pesticides in environmental waters (surface water, groundwater and seawater) close to agricultural lands over the world [22–34]. In addition, different studies have corroborated the presence of some pesticides in drinking water [35–38].

Pesticides are being continuously released into the aquatic environment through anthropogenic activities. Their detection in storm and wastewater effluent has been reported to be a major obstacle as regards wide-ranging acceptance of water recycling [39]. In addition, their variety, toxicity and persistence present a threat to humans through pollution of drinking water resources (e.g. surface water and groundwater). The frequent occurrence of pesticides in surface water and groundwater has prompted the search for suitable methods to destroy them. Although conventional biological treatments of water offer some advantages such as their low cost and easy operation, most studies concerning the treatment of pesticides have concluded that they are not very effective due to their low biodegradability [40, 41]. Other technologies such as adsorption or coagulation merely concentrate pesticides by transferring them in other phases but still remain and not being completely eliminated. To solve this problem, apart from reducing emissions, two main water strategies are followed: (i) chemical treatment of drinking water, surface water and groundwater and (ii) chemical treatment of wastewaters containing biocides and bio-recalcitrant pollutants as pesticides. Chemical treatments of polluted surface water, waste water and groundwater are part of a long-term strategy to improve the quality of water by removing toxic compounds of anthropogenic origin before returning the water to its natural cycle. The Directive 2013/39/EU [19] promotes the preventive action and the polluter pays principle, the identification of pollution causes, dealing with emissions of pollutants at the source, and finally the development of innovative wastewater treatment technologies, avoiding expensive solutions. Therefore, effective, low-cost and robust methods to decontaminate waters are needed, as long as they do not further stress the environment or endanger human health, particularly prior to direct or indirect reuse of reclaimed water. In this context, the development of Solar Chemistry Applications is of special relevance, especially photochemical processes where solar photons are absorbed by reactants and/or a catalyst causing a chemical reaction. Consequently, in recent years there has been growing interest in the use of advanced oxidation processes (AOPs) to remove pesticide residues as alternative to methods that are more conventional because they allow the abatement of them by mineralisation.

2. Advanced oxidation processes to remove pesticides from water

AOPs have been commonly defined as *near-ambient temperature treatment processes based on highly reactive radicals*, especially the hydroxyl radical ($\cdot\text{OH}$). Other radicals and active oxygen species involved are superoxide radical anions ($\text{O}_2^{\cdot-}$), hydroperoxyl radicals (HO_2^{\cdot}), triplet oxygen ($^3\text{O}_2$) and organic peroxy radicals (ROO^{\cdot}). In all probability, the $\cdot\text{OH}$ ($E_0 = 2.8 \text{ V}$) is among the strongest oxidising species used in water treatment and confers the potential to greatly accelerate the rates of pesticide oxidation. Hydroxyl radicals can degrade indiscriminately micropollutants with reaction rate constants usually around $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [42], yielding CO_2 , H_2O and, eventually, inorganic ions as final products. After fluorine ($E_0 = 3.1 \text{ V}$), $\cdot\text{OH}$ is the strongest oxidant [43], and its production can be achieved by many pathways, which allows one to choose the appropriate AOP according to the specific characteristics of the target water/wastewater and treatment requirements. Regarding the methodology to generate hydroxyl radicals, AOPs can be divided into chemical, electrochemical, sono-chemical and photochemical processes. Typical AOPs can be also classified as homogeneous that occur in a single phase and heterogeneous processes because they make use of a heterogeneous catalyst like metal-supported catalysts, carbon materials or semiconductors such as TiO_2 , WO_3 , ZnO , CdS , SnO_2 , ZnS and others [44]. **Figure 1** shows some homogeneous and heterogeneous processes [41, 45].

When the chemical process (mineralisation) destroys the contaminants and their reaction intermediate products (metabolites), critical secondary wastes are not generated and, thus, post-treatment or final disposal is not required [46]. However, if complete mineralisation is not achieved or the reaction period is too long, a final post-treatment may be necessary. A higher biodegradability and lower toxicity of the reaction by-products, in comparison with the parent compounds, are desirable benefits of applying AOPs to treat wastewaters. However, in some cases, these by-products are less biodegradable and/or more toxic than the parent compounds. For this reason, AOPs can be applied as post- or pretreatment of biological processes. The integration of different AOPs in a sequence of treatment processes is a common

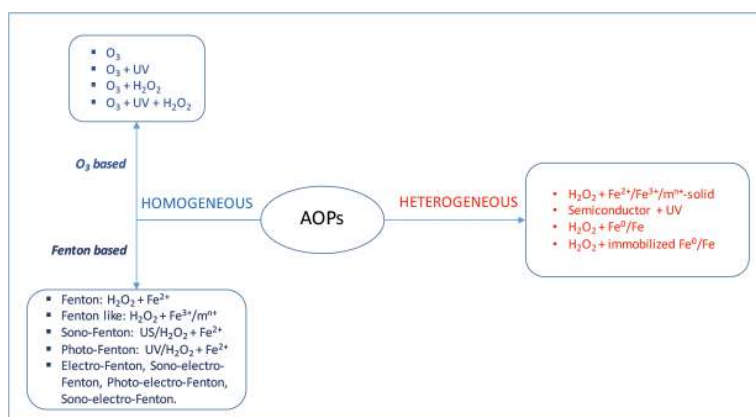


Figure 1. Scheme for conventional AOPs.

approach to achieve a biodegradable effluent, which can be further treated by a conventional biological process, reducing the residence time and reagent consumption in comparison with AOPs alone. **Figure 2** shows possible integration of AOPs in wastewater and drinking water treatment plants.

One drawback of these processes is the presence of scavengers in wastewaters because these species consume $\cdot\text{OH}$, competing with pesticides. They can be organic matters (e.g. humic and/or fulvic acids, amino acids, proteins and carbohydrates) or inorganic ions (CO_3^{2-} , HCO_3^- , S^{2-} , Br^- , NO_3^- and others). Because most natural waters contain these scavengers, optimisation of AOPs must be performed bearing them in mind. The knowledge of their effect on the process efficiency is difficult because they have different reactivities, as well as due to the constant variations in the aqueous phase when the parent pollutants are continuously transformed into many different intermediates. Among these techniques, photocatalytic methods in the presence of artificial or solar light, like heterogeneous photocatalysis (HP), have been proven very effective for the degradation of a wide range of pesticides [48].

2.1. Basis of heterogeneous photocatalysis

Photocatalysis may be defined as the *acceleration of a photoreaction by the presence of a catalyst*. HP, the use under irradiation of a stable solid semiconductor for stimulating a reaction at the solid/solution interface, is a technique of environmental interest for the treatment of pesticide-polluted water combining the low cost, the mild conditions and the possibility of using natural sunlight as the source of irradiation [39, 49]. Progress and challenges of HP can be reviewed in recent published papers [50, 51]. In brief, HP is based on the irradiation of semiconductor (SC) particles, usually suspended in aqueous solutions, with wavelength energy $h\nu \geq E_g$ (band-gap energy). Thus, an electron (e^-) is driven to the conduction band (cb), remaining a positive hole (h^+) in the valence band (vb). Both the e^- and h^+ migrate to the particle surface (**Figure 2**). The e^-_{cb} and the h^+_{vb} can recombine on the surface or in the bulk of the particle in

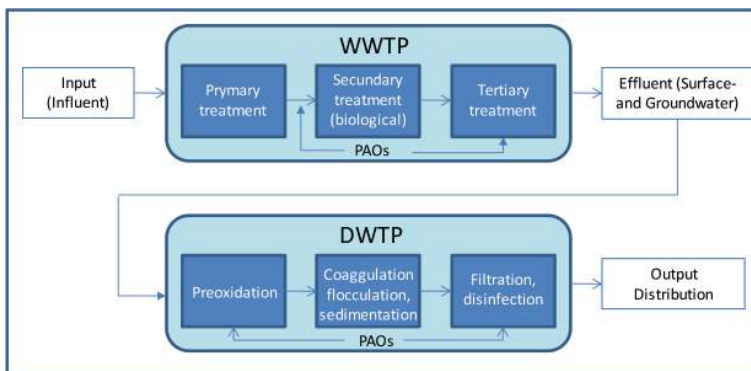


Figure 2. Possible implementation of AOPs in waste water and drinking water treatment plants (adapted from Petrovic et al. [47]).

short time, and the energy dissipated as heat. In addition, they can be trapped on the surface reacting with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle [52] as can be seen in **Figure 3**. The wavelength (λ) of radiation required to activate the catalyst must be equal or lower than the calculation by Planck's equation, $\lambda = hc/E_g$, where h is Planck's constant ($6.626176 \times 10^{-34} \text{ J s}^{-1}$), c is the speed of light and E_g is the semiconductor band-gap energy.

As a rule, TiO₂ is considered the best photocatalyst due to different qualities such as high photochemical stability, high efficiency, non-toxic nature and low cost, whose behaviour is very well documented in the recent literature [53, 54]. Excellent reviews have been published during the last years on the photoactivity of TiO₂ to purify pesticide-polluted waters [39, 48, 55–60].

2.2. Properties and characteristics of titanium dioxide photocatalysts

Titanium dioxide is by far, the most investigated photocatalyst to remove organic pollutants from water. The photocatalytic activity of TiO₂ slurries depends on physical properties of the catalyst (crystal and pore structure, surface area, porosity, band gap, particle size and surface hydroxyl density) [61, 62]. On the other hand, operating conditions such as light intensity and wavelength, initial concentration and type of pollutants, catalyst loading, oxygen content, interfering substances, presence of oxidants/electron acceptor, pH value and configuration of photoreactor have a key role [39, 58, 63–66]. Finally, the mode of TiO₂ application (suspended, immobilised or doped) is fundamental to rate the photocatalytic activity.

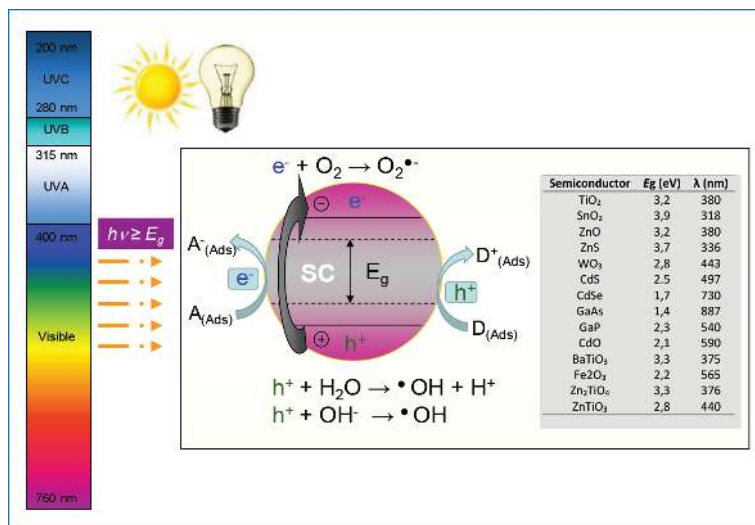


Figure 3. Scheme for the heterogeneous photocatalysis.

2.2.1. Composition of TiO_2 and its types

Titanium dioxide is known to occur in nature as anatase (At), brookite (Bk) and rutile (Rl) (**Figure 4**). Rl is usually considered to be the high-temperature and high-pressure phase relative to At, whereas Bk is often considered to be of secondary origin. Rl is the most common, most stable and chemically inert and can be excited by both visible and ultraviolet (UV) light (wavelengths smaller than 390 nm) [67]. At is only excited by UV light and can be transformed into Rl at high temperatures. Both Rl and At have a tetragonal ditetragonal dipyramidal crystal system but have different space group lattices. UV light does not excite Bk, but its orthorhombic crystal system can be transformed into Rl with the application of heat.

Generally, At exhibits higher photocatalytic activities than Rl. However, the reasons for the differences in photocatalytic activity between At and Rl are still being debated. Although At has lower absorbance ability to solar light than Rl because its band gap is larger (3.2 eV) than that of Rl (3.0 eV), the photocatalytic activity of At is higher than that of Rl. This can be explained because At has a higher surface adsorption capacity to hydroxyl groups and a lower charge carrier recombination rate than Rl [68]. Also, the lower photocatalytic activity of Rl is due to its larger grain size [69], lower specific surface areas and less capacity for surface adsorption. In addition, the lifetime of photo-generated e^- and h^+ in Rl is about an order of magnitude smaller than that of At. Consequently, the chance of participation of photoexcited e^- and h^+ of At in surface chemical reactions is greatly enhanced. According to Zhang et al. [70], Rl and Bk

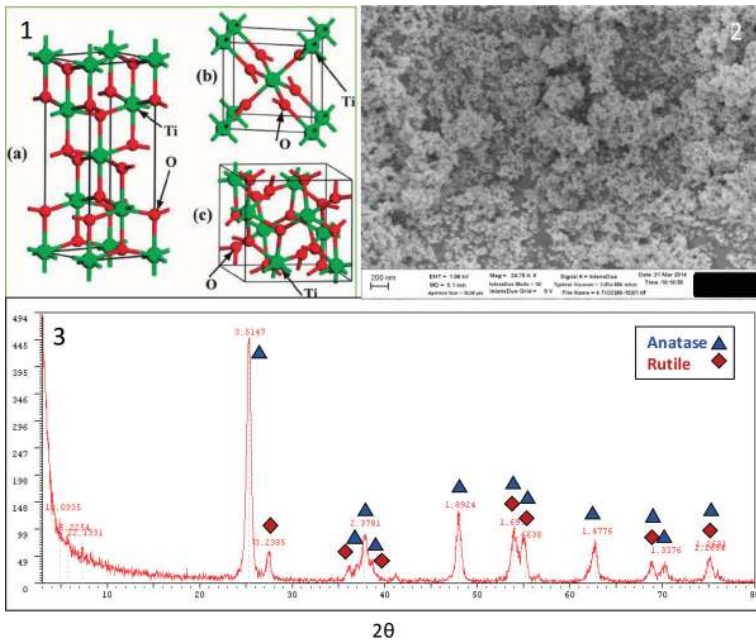


Figure 4. (1) The schematic conventional cells for anatase (a), rutile (b) and brookite (c) phases [73]; (2) SEM image of TiO_2 P25 and (3) XRD pattern of TiO_2 P25.

belong to the direct band-gap SC category, while At appears to be an indirect band-gap SC. As a consequence, At exhibits a longer lifetime of photoexcited e⁻ and h⁺ than Rl and Bk because the direct transition of photo-generated electrons from the conduction band to valence band of At is not possible. Moreover, At has the lightest average effective mass of photo-generated e⁻ and h⁺ than Rl and Bk suggesting the fastest migration of photo-generated e⁻ and h⁺ from the interior to the surface of At. This results in the lowest recombination rate of photo-generated charge carriers within At. Therefore, it is not surprising that Rt and Bk show a smaller photocatalytic activity than At.

TiO₂ can use natural sunlight because it has an appropriate energetic separation between its valence and conduction bands which can be surpassed by the energy content of a solar photon (380 nm > λ > 300 nm). The sunlight puts 0.2–0.3 mol photons of m⁻² h⁻¹ in the 300–400 nm range with a typical UV flux of 20–30 W m⁻². In addition, photons can be generated by artificial irradiation although it is the most important source of costs during the treatment of wastewater [65]. Different available TiO₂ catalysts (with different surface areas, crystal sizes and compositions) such as Degussa P25, Hombikat UV100, PC500, PC10, PC50, Rhodia and others have been tested for the photolytic degradation of pesticides in aqueous environments [39]. From them, Degussa P25 has been the most used because it has good properties (i.e. typically a 70:30 At:Rl composition, non-porous, Brunauer, Emmett and Teller (BET) around 55 m² g⁻¹ and average particle size 30 nm) and a substantially higher photocatalytic activity than other commercial TiO₂ [65]. The higher photocatalytic activity of P25 has been attributed to its crystalline composition of Rl and At. It is known that the smaller band gap of rutile absorbs the photons and generates e⁻/h⁺ pairs. Then, the electron transfer takes place from the rutile to electron traps in the At phase. Thus, the recombination is inhibited and allows the hole to move to the surface of the particle to react [71].

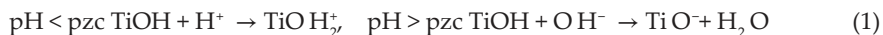
2.2.2. Operating conditions

The e⁻/h⁺ formation in the photochemical reaction is strongly dependent on the light intensity at a given wavelength [72]. Therefore, the dependency of pollutant degradation rate on the light intensity has been studied in numerous investigations of various organic pollutants. According to Herrmann [73], the reaction rate is proportional to the radiant flux (φ) < 25 mW cm⁻², while above this value, the rate varies as φ^{1/2}, which indicates a too high value of the flux increasing the e⁻/h⁺ recombination rate. When the intensity is high, the reaction rate does not depend on light intensity because at low intensity, reactions involving e⁻/h⁺ formation are predominant, while e⁻/h⁺ recombination is not significant [74].

Several authors have indicated that when the level of the target pesticide increases, a large number of molecules of the compound are adsorbed on the photocatalyst surface and, consequently, the reactive species (•OH and O₂•⁻) required for pesticide degradation also increase. However, the formation of •OH and O₂•⁻ on the catalyst surface remains constant for a given catalyst amount, light intensity and irradiation time. Hence, at higher concentrations the available •OH is inadequate for pollutant degradation. Therefore, as the concentration increases, the pollutant degradation rate decreases [75]. In addition, an increase in pesticide concentration leads to the generation of intermediates (metabolites), which may be adsorbed on the surface of the catalyst.

Because TiO_2 is often used as suspension, the photocatalytic degradation rate initially increases with catalyst loading and then decreases at high concentrations due to light scattering and screening effects. Although the number of active sites in solution will increase with catalyst loading, light penetration is compromised because of excessive particle concentration. The interaction between particles (agglomeration) increases at high concentration, and, consequently, the surface area available for light adsorption is reduced and photocatalytic activity decreases. The optimum catalyst loading has to be found in order to avoid excess catalyst and ensure the maximum absorption of photons. Although the results in the literature are very different, it may be deduced that the incident radiation and path length inside the photoreactor are of special interest in determining the optimum catalyst mass.

Waste water, surface water, groundwater and drinking water pHs vary significantly and play an important role in the photodegradation of pesticides since it determines the size of aggregates it forms and the surface charge of the photocatalyst. The surface charge of the photocatalyst and the ionisation or speciation ($\text{p}K_a$) of a pesticide can be seriously affected by the solution pH. Electrostatic interaction between the surface of the semiconductor, substrate, solvent molecules and radicals formed during photocatalytic oxidation strongly depends on the solution pH. At pH below its $\text{p}K_a$ value, an organic compound exists as neutral state. Above this $\text{p}K_a$ value, organic compounds attain a negative charge, which can significantly influence their photocatalytic degradation. The point of zero charge (PZC, the pH at which the surface has a neutral net electrical charge) of TiO_2 is not very sensitive to the crystallographic structure (At vs Rl) and the experimental method used. The common value is pH 5.9 for both phases. Although the PZC of TiO_2 depends on the production method, the most frequent value for TiO_2 P25 is 6.3 [76]. Below or above this value, the charge of the catalyst surface is positive or negative, respectively, according to the following reactions:

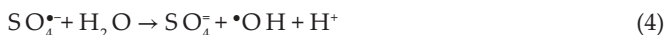


At low pH, the positive holes are considered as the major oxidation step, whereas at neutral or high pHs, $\cdot\text{OH}$ is the predominant species [77]. It is expected that the generation of $\cdot\text{OH}$ will be higher due to the presence of more available OH^- on the TiO_2 surface. Thus, the degradation efficiency of the process will be enhanced at high pH. A very important feature of the photocatalytic process is that in many cases, a great number of different metabolites are produced, which may behave in a different way depending on the pH of the solution. As regards temperature, photocatalytic systems do not require heating and operate at room temperature because of photonic activation [65].

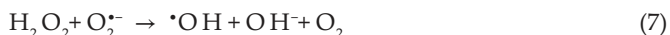
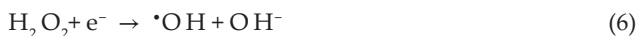
The e^-/h^+ recombination is one of the main drawbacks in the application of semiconductor photocatalysis as it causes waste of energy. In the absence of suitable electron acceptor, recombination step is predominant, and thus, it limits the quantum yield [39]. In HP reactions, O_2 is generally used as electron acceptor. Addition of exogenous oxidant/electron acceptors into a semiconductor suspension has been shown to improve the photocatalytic degradation of many pesticides because they can eliminate the e^-/h^+ recombination by accepting the conduction band electron, increase the $\cdot\text{OH}$ concentration and oxidation rate of intermediate compound and produce more radicals and oxidising species to accelerate the degradation

efficiency of intermediate compounds. Because $\bullet\text{OH}$ plays an important role in photodegradation, several researchers have investigated the effect of addition of different electron acceptors (i.e. H_2O_2 , KBrO_3 or $\text{Na}_2\text{S}_2\text{O}_8$) on the photocatalytic degradation of many pesticides [75, 78].

The ability of peroxydisulfate is not only attributed to the promotion of charge separation but also to the production of sulphate radicals ($\text{SO}_4^{\bullet-}$), which are very strong oxidising agents ($E_0 = 2.6 \text{ V}$), and the appearance of more hydroxyl radicals ($\bullet\text{OH}$) according to the following reactions:



Besides, the addition of H_2O_2 enhances the degradation due to the increase in the $\bullet\text{OH}$ concentration as follows:



The quantum yield of $\text{S}_2\text{O}_8^{2-}$ ($1.8 \text{ mol Einstein}^{-1}$) is much larger than that of H_2O_2 ($1 \text{ mol Einstein}^{-1}$), which can be related to the rate of recombination of $\bullet\text{OH}$ ($5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{SO}_4^{\bullet-}$ ($8.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [79].

As reviewed by Ahmed et al. [39], many studies have demonstrated that water components like Ca^{2+} , Mg^{2+} , Fe^{2+} , Zn^{2+} , Cu^{2+} , HCO_3^- , PO_4^{3-} , NO_3^- , SO_4^{2-} and Cl^- and dissolved organic matter (DOM) can affect the photodegradation rate of organic pollutants since they can be adsorbed onto the surface of TiO_2 [80, 81]. These dissolved components can compete with the pesticide for the active sites depending on the solution pH, reducing the formation of $\bullet\text{OH}$. Anions result in corresponding anion radicals scavenged by $\bullet\text{OH}$. However, they have lower oxidation potential. In addition, DOM, ubiquitously present in storm and wastewater effluent, also plays an important role regarding pesticide degradation. The observed slowdowns are related to the inhibition (surface deactivation), competition and light attenuation effects. Moreover, the presence of humic acids in the reaction solution has been reported to significantly reduce light transmittance and consequently the photooxidation rate.

As usual, two types of photoreactors are used for photocatalytic wastewater treatment processes: (i) slurry photoreactors and (ii) fixed-bed photoreactors [82]. The slurry photoreactors utilise suspended photocatalyst particles, while the other type utilises immobilised photocatalyst particles on a surface. Currently, the catalysts are applied in the form of a slurry in most cases. However, the separation of catalyst after the reaction in the slurry systems is an expensive

and tedious stage, which adds to the overall running costs of the plant. Therefore, immobilised catalyst systems are preferred in order to avoid an increase in cost and time. However, the immobilised catalyst systems have low interfacial surface areas and consequently a very low activity, being also difficult to scale [83]. It is noted that configuration of photoreactor has an important role in the efficiency of the photocatalytic wastewater treatment processes.

2.2.3. Bare, doped and immobilised application of TiO_2

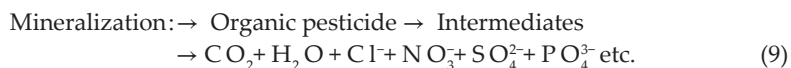
Generally, the use of TiO_2 slurries has been demonstrated to have higher photocatalytic activity as compared to the same immobilised catalyst. This is due to changes on the surface of the catalyst by blocking pores and the appearance of by-products causing the loss of active sites on its surface. Usually, TiO_2 is prepared in the form of nanopowders, crystals, thin films, nanotubes and nanorods. As a rule, the immobilisation of TiO_2 onto supporting material has been carried out via one of two major routes: (i) physical (thermal treatment) and (ii) chemical (sol-gel, electrodeposition, etc.). The evolution of different supports and the benefits and drawbacks of various immobilisation techniques to obtain a high-surface-area TiO_2 can be seen in the reviews by Shan et al. [84] and Dahl et al. [85]. Nonetheless, the interest for the development of TiO_2 supported on different materials is growing because the use of the bare TiO_2 phases presents some drawbacks as (i) necessity of irradiation with UV light due to the small amount of photons absorbed in the Vis region, (ii) high recombination rate for the photoproduced e^-/h^+ pairs, (iii) difficulty to improve the performance by doping with some materials that often act as recombination centres, (iv) deactivation in the absence of H_2O vapour when aromatic molecules must be abated and (v) difficulty to support powdered TiO_2 on some materials [45]. Consequently, the research line in HP has been driven to modify some electronic and morphological properties of TiO_2 to enhance its photoefficacy. In this context, nanosized particles and films on glasses or other supports and powdered samples with high specific surface areas have been obtained to increase the possibility for the involved species to avoid the separation step [86]. Doping, loading and sensitisation of TiO_2 are methods aimed to shift the light absorption towards visible light and/or to increase the lifetime of the photoproduced e^-/h^+ pairs.

A number of approaches have been suggested in recent years to enhance photocatalytic activity of TiO_2 in the visible light region for its use in water detoxification [87]. Metal ion doping and co-doping with non-metals can improve trapping of the photoexcited conduction band electrons at the surface, thereby minimising charge carrier recombination. Several dopants used (e.g. Sn, Ag, Pd, Re, Bi, V, Mo, Th or Pt among others), have been shown to enhance photocatalytic activity for the systems examined. However, the photoactivity of the metal-doped TiO_2 photocatalyst significantly depends on the dopant ion nature and concentration, preparation method and operating conditions [88]. The deposition of metal ions on TiO_2 can modify the photoconductive properties by increasing the charge separation efficiency between electrons and holes, which will enhance the formation of both free hydroxyl radicals and active oxygen species [89]. Recent research indicates that the desired narrowing on the band gap of TiO_2 can be achieved using non-metal elements such as N, F, S and C. Thus, modified TiO_2 showed a significant improvement on the absorption in the Vis light region due to band-gap narrowing and enhancing the degradation of pesticides under Vis light irradiation, mainly

under sunlight [90, 91]. Also, it is possible to produce coupled colloidal structures using TiO₂ such as TiO₂-SnO₂, TiO₂-CdS, TiO₂-Bi₂S₃, TiO₂-WO₃ or TiO₂-Fe₂O₃, in which illumination of one semiconductor produces a response in the other at the interface between them by increasing the charge separation and extending the energy range of photoexcitation. On the other hand, the coating of one semiconductor or metal nanomaterial on the surface of another semiconductor or metal nanoparticle core is called capping. Semiconductor nanoparticles of TiO₂ can be coated with another semiconductor (i.e. SnO₂) with a different band gap to enhance its emissive properties [92].

2.3. Heterogeneous photocatalytic degradation of pesticide residues in water over titanium dioxide

A desirable feature in the photodegradation of pesticides in water is the transformation of the parent compounds in order to avoid their toxicity. However, the main objective is the mineralisation of the pesticides. As previously commented, [•]OH is the main species involved for organic substrate oxidation, but the free radical HO₂[•] and its conjugate O₂^{•-} also play an important role although those radicals are much less reactive than [•]OH. All these free radicals react with pesticides by hydrogen abstraction or electrophilic addition to double bonds. Further, the radicals react with O₂ to give organic peroxy radicals (ROO[•]) initiating different oxidative reactions that may lead to the complete mineralisation of the pesticides. Since [•]OH is non-selective, numerous and different transformation products (intermediates) can be formed at low concentrations being in certain cases more persistent and toxic than the parent compounds.



The presence of pesticide residues in water is usually monitored using chromatographic techniques such as gas chromatography (GC) and liquid chromatography (LC) coupled to mass spectrometry (MSⁿ) and time-of-flight (TOF) detection systems. However, since identification of all the transformation products generated during the photooxidation is not possible, the measure of total organic carbon (TOC) and more specifically dissolved organic carbon (DOC) is crucial in the process because determination of CO₂ must be stoichiometric with the organic carbon in the parent pesticide. This determination can be carried out in a simple and rapid way to know the mass balance and the remaining amount of metabolites. As example, **Figure 5** shows the photodegradation pathways proposed for chlorantraniliprole [93] and tebuconazole [94] dissolved in water when illuminated in the presence of TiO₂.

In the case of chlorantraniliprole, a new class of anthranilic diamide insecticide, several transformation products are generated during irradiation as a result of different reactions such as hydroxylation, deamination, hydrolysis of the amide bridge and rearrangement followed by cyclisation, methyl amine transfer and fragmentation. For tebuconazole, a common triazole fungicide with numerous agricultural and urban uses, the transformation pathway was found to proceed through tert-butyl chain cleavage, hydroxylation, oxidation and dechlorination and showed that its degradation mechanism was mainly driven by [•]OH and h⁺.

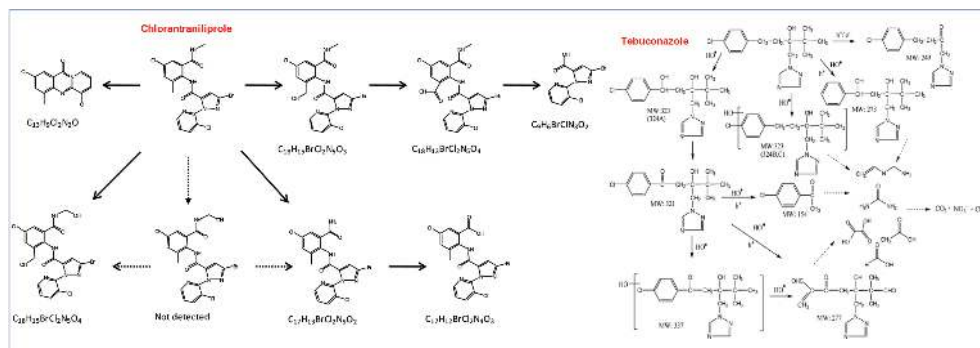


Figure 5. Photometabolic pathways proposed for chlorantraniliprole (insecticide) and tebuconazole (fungicide) in water slurries when illuminated in the presence of TiO_2 .

The use of HP has showed a powerful growth in recent years. Today, pesticides constitute an important group concerning pollutant treatment. The large number of papers published in the last years proves this interest. A review to the literature extracted from the Web of Science™ (formerly ISI Web of Knowledge, www.isiknowledge.com) managed by Thomson Reuters (Philadelphia, USA) using the following keywords, TiO_2 , pesticides and water, shows 463 papers only in the period 2005–2016.

Table 1 shows some of the most popular journal publishing on the topic “photocatalysis and pesticides” according to the following criteria: impact factor > 2 and Eigenfactor score > 0.01 (Journal Citation Reports (JCR) Science Edition 2015).

The *Journal Impact Factor* is defined as all citations to the journal in the current JCR year to items published in the previous 2 years, divided by the total number of scholarly items (these comprise articles, reviews and proceeding papers) published in the journal in the previous 2 years. The *Eigenfactor* score calculation is based on the number of times articles from the journal published in the past 5 years have been cited in the JCR year, but it also considers which journals have contributed these citations so that highly cited journals will influence the network more than lesser cited journals. References from one article in a journal to another article from the same journal are removed, so that *Eigenfactor* scores are not influenced by journal self-citation.

Following the criteria above, some of the most representative publications are presented in this summary (**Table 2**). Results show that sunlight photoalteration (photolysis) processes are well now to play an important role in the degradation of pesticides and other contaminants in the aquatic environment. These technologies allow the removal of pesticides by mineralisation. When the exciting energy used comes from the Sun, the process is called *solar photocatalysis* [95]. Photocatalytic oxidation by semiconductor oxides is an area of environmental interest for the treatment of polluted water, particularly relevant for Mediterranean agricultural areas, where solar irradiation is highly available making this process quite attractive. An ideal photocatalyst is characterised by photostability, biologically and chemically inert

Journal title (ISO)	Editorial/country	ISSN ^a	IF ^b	5Y-IF ^c	ES ^d
Chemical Reviews	American Chemical Society (USA)	0009-2665	37.369	51.560	0.24503
Journal of Photochemistry and Photobiology C: Photochemistry Reviews	Elsevier Science BV (Japan)	1389-5567	12.162	15.268	0.00442
Applied Catalysis B: Environmental	Elsevier Science BV (The Netherlands)	0926-3373	8.328	8.142	0.05714
Journal of Catalysis	Academic Press INC Elsevier Science (USA)	0021-9517	7.354	7.482	0.03438
Water Research	Pergamon-Elsevier Science Ltd. (England)	0043-1354	5.991	6.769	0.08394
Environmental Science and Technology	American Chemical Society (USA)	0013-936X	5.393	6.396	0.20232
Chemical Engineering Journal	Elsevier Science SA (Switzerland)	1385-8947	5.360	5.439	0.09715
Catalysis Science and Technology	Royal Society of Chemistry (England)	2044-4753	5.287	5.547	0.02367
Journal of Hazardous Materials	Elsevier Science BV (The Netherlands)	0304-3894	4.836	5.641	0.09715
Solar Energy Materials and Solar Cells	Elsevier Science BV (The Netherlands)	0927-0248	4.732	5.016	0.04275
Catalysis Today	Elsevier Science BV (The Netherlands)	0920-5861	4.312	4.105	0.03376
Applied Catalysis A: General	Elsevier Science BV (The Netherlands)	0926-860X	4.012	4.403	0.03476
Science of the Total Environment	Elsevier Science BV (The Netherlands)	0048-9697	3.976	4.317	0.08394
Journal of Molecular Catalysis A: Chemical	Elsevier Science BV (The Netherlands)	1381-1169	3.958	4.045	0.01727
Chemosphere	Pergamon-Elsevier Science Ltd. (England)	0045-6535	3.698	4.068	0.06483
Solar Energy	Pergamon-Elsevier Science Ltd. (USA)	0038-092X	3.685	4.414	0.02277
Journal of Environmental Management	Academic Press-Elsevier Science Ltd. (England)	0301-4797	3.131	4.049	0.03326
Catalysts	MDPI AG (Switzerland)	2073-4344	2.964	3.194	0.16915

Journal title (ISO)	Editorial/country	ISSN ^a	IF ^b	5Y-IF ^c	ES ^d
Journal of Agricultural and Food Chemistry	American Chemical Society (USA)	0021-8561	2.857	3.308	0.08776
Environmental Science and Pollution Research	Springer Heidelberg (Germany)	0944-1344	2.760	2.876	0.02617
Journal of Chemical Technology and Biotechnology	Wiley-Blackwell (England)	0268-2575	2.738	2.744	0.01051
Journal of Photochemistry and Photobiology A: Chemistry	Elsevier Science SA (Switzerland)	1010-6030	2.477	2.573	0.01025
Photochemical and Photobiological Science	Royal Society of Chemistry (England)	1474-905X	2.235	2.673	0.01040
Journal of Environmental Science	Science Press (Mainland China)	1001-0742	2.208	2.699	0.01282

^aInternational Standard Serial Number.

^bImpact factor.

^c5-Year impact factor.

^dEigenfactor score.

Table 1. Some of the main and influential journals of interest to readers where the authors usually publish their works about 'photocatalytic degradation of pesticides in water' (source: JCR, 2015).

Pesticides	Photocatalysts	Light source	Main findings	References
Pyrimethanil	TiO ₂ P25 and home made	Solar	Similar photoefficiencies in mineralisation	[81]
Acephate, omethoate, methyl parathion	Fe ₃ O ₄ @SiO ₂ @mTiO ₂ nanomicrospheres	UV	Disappearance after 45–80 min	[96]
Imidacloprid	TiO ₂ and TiO ₂ -based hybrid	Solar	TiO ₂ + fly ash is 2–3 times less active than sol-gel TiO ₂	[97]
Spirotetramat, spirodiclofen, spiromesifen	ZnO, TiO ₂ P25, TiO ₂ Kronos vlp 7000, Zn ₂ TiO ₄ and ZnTiO ₃	UV	ZnO > TiO ₂ P25 > TiO ₂ Kronos vlp 7000 > Zn ₂ TiO ₄ > ZnTiO ₃	[98]
Flubendiamide	ZnO/Na ₂ S ₂ O ₈ and TiO ₂ P25/Na ₂ S ₂ O ₈	UV	ZnO and TiO ₂ oxides strongly enhance the degradation rate	[99]
Thiamethoxam, imidacloprid, acetamiprid	ZnO/Na ₂ S ₂ O ₈ and TiO ₂ P25/Na ₂ S ₂ O ₈	UV/solar	Solar irradiation was more efficient compared to artificial light for the removal of these insecticides (t _{1/2} = 0.3–2 min)	[100]
Chlorantraniliprole	ZnO, TiO ₂ P25, TiO ₂ Kronos vlp 7000, Zn ₂ TiO ₄	UV	Half-lives of 53 and 71 min for ZnO/Na ₂ S ₂ O ₈ and TiO ₂ /Na ₂ S ₂ O ₈ systems, respectively	[93]

Pesticides	Photocatalysts	Light source	Main findings	References
Metamitron, metribuzin	Different TiO ₂ nanopowders	UV	t _{1/2} lower than 8 min using TiO ₂ P25	[101]
Dichlorvos	TiO ₂ supported on zeolites	UV	Complete degradation in 360–540 min	[102]
Atrazine	N-Doped TiO ₂ supported by phosphors	UV	Enhanced performance compared to either pure N-TiO ₂ nanoparticles or bare phosphors microparticles	[103]
Spinosad, indoxacarb	ZnO/Na ₂ S ₂ O ₈ and TiO ₂ P25/Na ₂ S ₂ O ₈	UV	95% degradation rate was observed for both spinosyns after 2 min when using Na ₂ S ₂ O ₈	[104]
Methabenzthiazuron	ZnO, TiO ₂ P25	UV	Half-lives of 2 and 7 min for ZnO and TiO ₂ , respectively	[105]
Monocrotophos, endosulfan, chlorpyrifos	TiO ₂ coated on polymeric beads	Solar	Rapid photodegradation using immobilised bead photoreactor	[106]
Isoproturon	TiO ₂ coated on inert cement beads	UV	85% degradation rate after 6 h	[107]
Diazinon	TiO ₂ doped with N, NS and FeFNS	UV LED	The FeFNS-doped TiO ₂ was found to be an efficient catalyst (96% degradation after 100 min)	[108]
Methyl oxidemeton, methidathion, carbaryl, dimethoathe	TiO ₂ P25, Hombikat UV 100, Millennium PC (50, 100, 105), Kronos 7101	UV	TiO ₂ P25 was the most effective for pesticide degradation. Removal of pesticides in less than 300 min	[109]
30 sulfonylurea herbicides	ZnO and TiO ₂ P25 in tandem with Na ₂ S ₂ O ₈	UV	Average time required for 90% degradation about 3 and 30 min for ZnO/Na ₂ S ₂ O ₈ and TiO ₂ /Na ₂ S ₂ O ₈ systems, respectively	[110]
Chlorotoluron, diuron, fluometuron, isoproturon, linuron	ZnO, TiO ₂ , WO ₃ , SnO ₂ and ZnS	Solar	The time required for 90% degradation ranged from 23 to 47 min for isoproturon and linuron, respectively, when using the tandem ZnO/Na ₂ S ₂ O ₈	[111]
Carbofuran	ZnO, TiO ₂ P25 Degussa	Solar	Half-lives ranging from 6 to 385 min	[112]
Malathion	WO ₃ /TiO ₂		2% WO ₃ /TiO ₂ exhibited the best photocatalytic activity achieving abatement of 76% TOC after 300 min	[113]
Ethoprophos, isoxaben, metalaxyl, metribuzin, pencycuron, pendimethalin, propanil, tolclofos-methyl	ZnO, TiO ₂ , WO ₃ , SnO ₂ , ZnS	Solar	Half-lives for ZnO ranged from 9 to 38 min (t _{30W} 0.3–1.7 min), while in the presence of TiO ₂ , ranged from 41 to 260 min (t _{30W} 1.9–16.3 min)	[114]
Simazine, prometryn, terbutryn, atrazine, terbuthylazine, propachlor, S-metolachlor, alachlor	ZnO, TiO ₂	Solar	Degradation rate >70% after 240 min in the ZnO/Na ₂ S ₂ O ₈ system	[115]

Pesticides	Photocatalysts	Light source	Main findings	References
Fenamiphos	ZnO, TiO ₂ , WO ₃ , SnO ₂	Solar	Half-life <3 min for ZnO, TiO ₂ in tandem with Na ₂ S ₂ O ₈	[116]
Cyprodinil, fludioxonil	ZnO, TiO ₂	Solar	DT _{75%} referred to the normalised illumination time (t _{30W}), was lower than 40 and 550 min (t _{30W} = 2 and 40 min) for both fungicides using ZnO and TiO ₂ , respectively	[117]
Methyl parathion, dichlorvos	N-doped and P25 TiO ₂	UV/solar	N-doped TiO ₂ showed higher photocatalytic activity under solar radiation compared to UV and visible light	[118]
MCPA, clopyralid, mecoprop	Fe- and N-doped TiO ₂	UV	Lowering of the band gap of titanium dioxide by doping is not always favourable for increasing photocatalytic efficiency of degradation	[119]
2,4-D, Diuron, ametryne	TiO ₂ slurry	Solar	Results showed that the overall model fitted the experimental data of herbicides mineralisation in the solar CPC reactor satisfactorily for both cloudy and sunny days	[120]
Carbendazim	TiO ₂ slurry	UV	More than 90% of fungicide was degraded after 75 min	[121]
Glyphosate	TiO ₂ slurry	UV	Addition of Fe ³⁺ , Cu ²⁺ , H ₂ O ₂ , K ₂ S ₂ O ₈ or KBrO ₃ enhances the photodegradation	[122]
Alachlor, atrazine, chlorfenvinphos, diuron, isoproturon, pentachlorophenol	TiO ₂ slurry and Fe ²⁺	Solar	Photo-Fenton treatment was found to be shorter than TiO ₂ and more appropriate for these compounds	[123]
Triclopyr, dantinozid	Different types of TiO ₂ slurries in tandem with electron acceptors	Solar	The photocatalyst Degussa P25 was found to be more efficient as compared with other photocatalysts	[124]
Cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil, telone	TiO ₂ slurry and Fe ²⁺	Solar	Total disappearance of the parent compounds and nearly complete mineralisation were attained with all pesticides tested	[125]
Dimethoate	ZnO, TiO ₂	UV	Both catalysts were unable to mineralise dimethoate, but the addition of oxidants improved the efficiency of the processes	[126]
Dichlorvos, monocrotophos, parathion, phorate	TiO ₂ :SiO ₂ beads	Solar	After 420 min illumination by sunlight, 0.65 × 10 ⁻⁴ mol dm ⁻³ of four organophosphorus pesticides can be completely photocatalytically degraded into PO ₄ ³⁻ .	[127]

Table 2. A brief summary of recent research studies in which TiO₂ was used for treating pesticide-polluted waters in the period 2005–2016.

nature, low cost and availability and capability to adsorb reactants under efficient photonic activation. Due to these characteristics, titanium dioxide (TiO₂) has been demonstrated to be an excellent catalyst, and its behaviour is very well documented for the photodegradation of pesticide residues in water.

2.4. Environmental impact and treatment cost

As previously stated, there is a very extensive literature (at laboratory and pilot plant scale) on the photocatalytic degradation of organic pollutants in water. However, there are not many works devoted to the study of the impact of the process from an environmental and economic point of view. In this context, the well-known life cycle impact assessment (LCIA) tool has been successfully used to assess the environmental impact of chemical processes. This tool finds the potential impacts associated with the entire life cycle of a product or a process. This methodology has been devised to study and compare processes at the industrial level but can be perfectly used at the laboratory level. On the other hand, there are several methods of estimating the costs of implementing each of the different AOPs. In general, the following items are proposed: (i) facility cost, (ii) project contingency, (iii) engineering project and (iv) replacement costs. The sum of these four concepts is the total installed cost, based on which the yearly economic impact can be evaluated. Then, operating costs have to be calculated. These costs are normally yearly and consist of the following items: (i) personnel, (ii) maintenance, (iii) electricity and (iv) materials and services. These costs added to the annual facility costs are the total annual costs [128].

3. Conclusion

Currently, population growth, technology development, inadequate agricultural practices and land use have created unprecedented water pollution problems. Agricultural wastewater is characterised by high organic matter content and traces of organic pollutants, mainly pesticides. In addition, effluents from the agro-food and other industries have a potentially environmental risk that requires appropriate and comprehensive treatment. The most often used methods for the treatment of the industrial wastewaters, including membrane filtration, chemical coagulation/flocculation, ion exchange, precipitation, adsorption, biological degradation and ozonation, are not efficient enough and have important limitations to remove bio-recalcitrant compounds as many pesticides. In recent years, advanced oxidation processes (AOPs) have been proposed as a most promising way for degradation of various pollutants. Among them, heterogeneous photocatalysis technology is an interesting route among AOPs, which can be conveniently used for the complete degradation of different hazardous compounds including pesticides. Results show that sunlight photoalteration processes are well now to play an important role in the degradation of pesticides and other contaminants in water. These technologies allow pesticides to be removed by mineralisation. Photocatalytic oxidation by semiconductor oxides is an area of environmental interest for the treatment of polluted water, particularly relevant for Mediterranean agricultural areas, where solar irradiation is highly available (more than 2800 h of sunshine per year on average) making this process

quite attractive. Due to its specific characteristics, titanium dioxide (TiO_2) has been demonstrated to be an excellent catalyst, and its behaviour is very well documented for the photodegradation of pesticide residues in water. Recently, many authors have also developed combined AOP and biological systems to implement in wastewater treatment plants. In addition to the experimental and modelling work, the aspect most lacking of this combination systems for the treatment of bio-recalcitrant specific industrial wastewater is the performance of complete economic studies, which could present this innovative technology as a cost-competitive one.

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Abbreviations

POPs	Persistent organic pollutants
EDCs	Endocrine-disrupting chemicals
OC	Organochlorine
EWFD	European Water Framework Directive
AOPs	Advanced oxidation processes
HP	Heterogeneous photocatalysis
E_g	Band-gap energy
D	Donor
A	Acceptor
cb	Conduction band
e^-	Electron
h^+	Hole
vb	Valence band
SC	Semiconductor
At	Anatase
Bk	Brookite
Rl	Rutile
SEM	Scanning electron microscopy
XRD	X-ray diffraction
UV	Ultraviolet

BET	Brunauer, Emmett and Teller
PZC	Point of zero charge
TOC	Total organic matter
DOM	Dissolved organic matter
GC	Gas chromatography
LC	Liquid chromatography
MS	Mass spectrometry
TOF	Time of flight
JCR	Journal Citation Reports
LCIA	Life cycle impact assessment
EU	European Union
ISSN	International Standard Serial Number
IF	Impact factor
5Y-IF	5-year impact factor
ES	Eigenfactor score

Author details

Nuria Vela¹, Gabriel Pérez-Lucas², José Fenoll³ and Simón Navarro^{2*}

*Address all correspondence to: snavarro@um.es

1 Applied Technology Group to Environmental Health, Faculty of Health Science, Catholic University of Murcia, Murcia, Spain

2 Department of Agricultural Chemistry, Geology and Pedology, Faculty of Chemistry, University of Murcia, Murcia, Spain

3 Sustainability and Quality Group of Fruit and Vegetable Products, Murcia Institute of Agri-Food Research and Development, Murcia, Spain

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