

Article

Photocatalytic Oxidation of Chlorantraniliprole, Imidacloprid, Pirimicarb, Thiamethoxam and Their Main Photoreaction InterMediates as Impacted by Water Matrix Composition under UVA-LED Exposure

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Abstract: Processes on wastewater treatment plants (WWTP) are not always efficient for pollutant removal. A new, low-cost, and effective technology is needed. In this work, the photocatalytic degradation of four insecticides, chlorantraniliprole, imidacloprid, pirimicarb, and thiamethoxam, has been examined in different water matrices (irrigation water, leaching waters, and WWTP effluent). Lab experiments were conducted with TiO₂ and ZnO, as photocatalysts, with and without Na₂S₂O₈ as an oxidant, exposed to UVA irradiation with LED lamps. Previously, different loadings of TiO₂ and ZnO were assessed on the disappearance kinetics of the different insecticides to know the optimal efficiency. The effect of water matrices, susceptible to being contaminated with the target insecticides, was discussed when the photocatalytic system TiO₂/Na₂S₂O₈ was applied. The abatement of their main transformation products (TPs) was also monitored during the studied photoperiods. A total of 13 TPs were detected in the different water matrices studied. All of them were formed and eliminated during the photoperiod, except thiamethoxam urea which was present from the beginning of the experiments due to its hydrolysis in water. In conclusion, UVA-LED lamps are a good source to carry out heterogeneous photocatalysis in WWTP, since its high efficiency, low-cost, long lifetime, and effectiveness on pollutant removal.

Keywords: insecticides; heterogeneous photocatalysis; UV-LED lamps; irrigation water; leaching water; WWTP effluent



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1. Introduction

In addition to water scarcity, the presence of a wide range of pollutants in wastewater have triggered the search of new, low-cost, and effective technologies that allow for reusing and recycling these waters in many countries [1]. Wastewater treatment plants (WWTP) use different processes, such as sedimentation, coagulation, volatilization, biodegradation, or sorption, to eliminate toxic contaminants, including pathogens, nutrients, or suspended solids, from wastewater [2]. However, these processes are not always efficient to remove pesticides and others organic biorecalcitrant pollutants [3]. The physicochemical properties of pesticides and the composition of water matrix are key factors having an important impact on the removal of these compounds in water [3,4].

AOPs are the most studied and applied processes for the depletion of organic contaminants in water. Advanced oxidation processes (AOPs) are based on the formation of hydroxyl radicals (HO[•]) that have the ability to oxidize (E₀ = 2.8 eV) organic molecules by a non-selective attack [5,6]. Among AOPs, heterogeneous photocatalysis using semiconductor materials such as TiO₂ and ZnO has received the attention of the scientific community

due to their photochemical properties and low cost [7,8]. Thus, Teixeira et al. [8], for instance, reused TiO₂ and ZnO nanoparticles through an ecofriendly and cost-effective process for water treatment. Semiconductor materials can be irradiated by photons of energy equal or higher to its band gap energy (E_g), generating electron/hole pairs (e^-/h^+) on the catalyst surface. The e^-/h^+ formed can generate hydroxyl (HO•) and others, such as superoxide anion (O₂•⁻) and hydridodioxygen (HO₂•), radicals that have the ability to mineralize almost any organic molecule [7]. The E_g of TiO₂ and ZnO is approximately 3.0 and 3.1 eV, respectively, therefore, the activation of these pure photocatalysts can only be carried out under UV light [9]. In addition to this, the use of oxidants improves the efficiency of the catalysts in these reactions. Persulfate (S₂O₈²⁻) is a powerful oxidizing agent, since it decomposes in SO₄•⁻ radicals by the action of UV light and the electrons formed by the photocatalyst. This radical anion has a high oxidation potential ($E_0 = 2.6$ eV) similar to HO• [7]. The semiconductor based photocatalytic degradation of pesticides has been described in the recent literature thoroughly [10]. This process contributes efficiently to remove biorecalcitrant pesticides from water, which are chemically stable and resistant to biodegradation. It is considered as a promising and environmentally friendly technique for many researchers [11]. The photocatalytic oxidation process is known to be an eco-friendly tool used for the transformation of toxic and hazardous pollutants, like pesticides, into CO₂, H₂O, and inorganic mineral salts by mineralization of the parent compounds; instead of relocating them as it occurs with conventional (physical, chemical and/or biological) processes used for the treatment and reuse of water [12].

Medium and low-pressure mercury lamps are the UV radiation sources commonly used for photocatalytic oxidation of organic pollutants [13–17]. However, the toxicity of mercury has led the search for alternatives mercury-free UV sources, such as UV light emitting diodes (UV-LED) [18]. LED is a semiconductor device that transform energy into light. Different semiconductors, like GaN with an emitting central wavelength of 356 nm, or InGaN for longer UV wavelength, have been used [19].

In the last years, UV-LED lamps have been used for the photocatalytic degradation of various organic contaminants in water [16,18,20–22]. It is due to the advantages of this type of UV source, such as the absence of mercury, low cost, long lifetime, high quantum efficiency, monochromatic emission in a range of wavelength, easy handling, small volume and high stability, robustness and flexibility [23–28]. Heterogeneous photocatalysis using TiO₂ and UVA-LED is the most frequently applied method for the degradation of organic pollutants, mainly dyes, pharmaceutical compounds, and pesticides [18,29]. However, ZnO has been little investigated [30,31].

Bearing in mind the above mentioned, more research is necessary to find an efficient, suitable, and eco-friendly alternative for tackling the elimination of organic pollutants in water. We have assessed in this work the photocatalytic degradation of four insecticides, chlorantraniliprole (anthranilic diamide), imidacloprid (neonicotinoid), pirimicarb (carbamate), and thiamethoxam (neonicotinoid), widely used for crop protection and found in surface- and groundwater resources [32,33]. For this purpose, TiO₂ and ZnO have been used as photocatalysts in tandem with Na₂S₂O₈ and UVA-LED lamps in different type of waters (irrigation, leaching and wastewater effluent). The abatement of their main transformation products (TPs) has been also monitored during the studied photoperiod.

2. Results and Discussion

2.1. Assessment of the Optimum Catalysts Loading for the Photocatalytic Degradation in Pure Water

The impact of catalyst concentration on the degradation rates of the studied insecticides for the election of the most appropriate loading to be used in the incoming experiments was previously evaluated. The catalyst and oxidant load, photoreactor geometry, and light irradiation condition the photocatalytic efficiency [34]. In this paper, these parameters were fixed, except the catalysts load, which was studied. A battery of tests was performed separately for TiO₂ (0–500 mg L⁻¹) and ZnO (0–500 mg L⁻¹). As observed in previous works [7,29,35,36], the evolution of rate constants, with the addition of the

different catalyst loads, follow similar behavior. Degradation rates of the four insecticides were increasing as the catalyst loading increased. The greater catalyst load, the freer active sites available for photons [37]. There was a point where a maximum value of rate constant is reached (200 and 350 mg L⁻¹ for TiO₂ and ZnO, respectively) and, next, the efficiency of the process started to decrease fairly. An excess of catalyst in the reaction medium causes a light scattering and screening effect that inhibits the effectiveness of the systems [7,10]. For TiO₂ assays, rate constants ranged from 0.007 min⁻¹ for CH (without TiO₂ load) to 1.721 min⁻¹ for PI (with 200 mg L⁻¹ of TiO₂). In the case of experiments with ZnO, rate constants ranged from 0.007 min⁻¹ for CH (without ZnO load) to 1.554 min⁻¹ for PI (with 350 mg L⁻¹ of ZnO). The greater rate constants were reached with 200 mg L⁻¹ of TiO₂ and 350 mg L⁻¹ of ZnO, when 200 mg L⁻¹ of PS were fixed, for the four insecticides. The rate constant order was: PI > IM ≥ TH > CH (Figure S1, Supplementary material).

Figure 1 shows a comparison between the optimized systems TiO₂/PS and ZnO/PS and the simple systems with TiO₂, ZnO and PS alone or only UV radiation (photolysis). First, only PI seems to be slightly affected by the UV radiation. PI suffers a fast degradation when is irradiated with UVA lamps [38]. At the end of the photolysis experiment 26% of PI removal was achieved, while for the rest of the insecticides UV radiation removed less than 4% after 60 min of reaction. When we focused on the simple systems, degradation curves of insecticides did not follow a clear pattern. For CH, the three degradation curves had a similar shape, for IM and PI the order was TiO₂ > PS > ZnO while, for TH the degradation rate with PS was noticeable better than with TiO₂ or ZnO. This tells us that the chemical structure of each compound can affect to the degradation in a same studied system.

Those systems in which catalysts and oxidant were combined, the degradation rates improved significantly for all insecticides compared with those systems where only catalysts or oxidant were used. The use of electron acceptors such as persulfate (S₂O₈²⁻) or peroxymonosulfate (HSO₅⁻) enhance the formation of HO• and inhibit the e⁻/h⁺ pair recombination [39]. The principle of AOPs is the generation of strongly oxidizing radical species, such as HO• (E₀ = 1.9–2.7 V vs. NHE), in the presence of a semiconductor oxide. In addition, when an oxidant as Na₂S₂O₈ is also used, sulfate radical anion SO₄^{•-} (E₀ = 2.5–3.1 V vs. NHE) and more HO• are generated, among other. Both radical species take part equally in reactions at neutral pH [40,41]. The scientific literature presents a large number of rigorous research works related with the activation of PS [40–43]. Degradation rate constants (Table S1, Supplementary Material) shows the system ZnO/PS being slightly faster than TiO₂/PS for CH, IM, and TH. As has been already discussed in previous works [29,44–47], TiO₂ offers more advantages from the economic and environmental point of view than ZnO, despite producing faster insecticides abatement. If advantages of using TiO₂ are added to those using UV-LED lamps, an attractive and eco-friendly method would be developed. TiO₂/PS was the chosen photocatalytic system to carry out the discussion in different water matrices susceptible to being contaminated with the target insecticides.

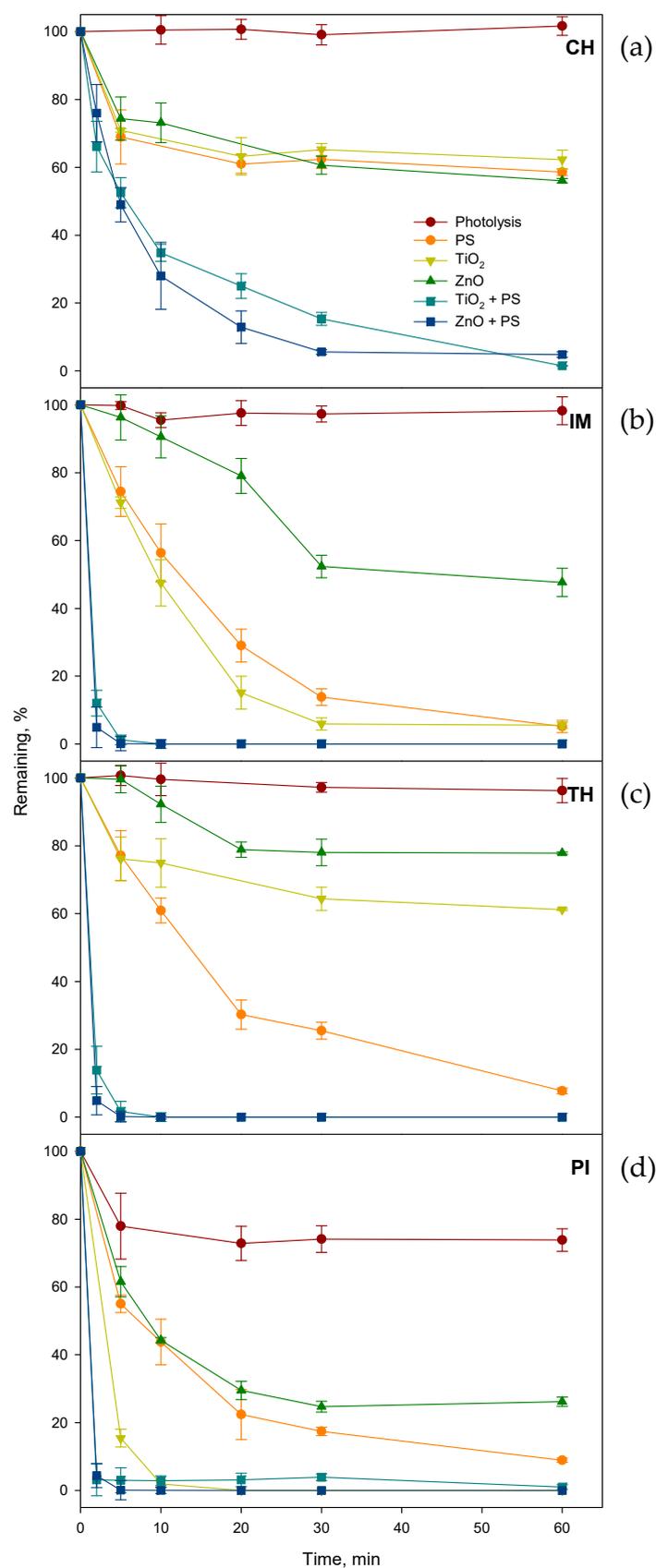


Figure 1. Photocatalytic processes comparison in pure water spiked at 1 mg L^{-1} of target compounds ($[\text{PS}] = 200 \text{ mg L}^{-1}$; $[\text{TiO}_2] = 200 \text{ mg L}^{-1}$; $[\text{ZnO}] = 350 \text{ mg L}^{-1}$). (a) Chlorantraniliprole; (b) Imidacloprid; (c) Thiamethoxam; (d) Pirimicarb.

2.2. Photocatalytic Activity in Real Matrices

Insecticides photocatalytic removal (CH, IM, PI, and TH) was studied in different water matrices. Those waters, which were spiked with the studied insecticides at 1.0 mg L^{-1} , were irrigation water (IW), leaching water with high (LW-H), and low DOC (LW-L) content and an effluent from a wastewater treatment plant (WWTPe). The combined system TiO_2/PS , above chosen, was used for the experiments with UV-LED exposure. In addition, the main TPs derived from the studied insecticides (Table S2, Supplementary Material) were also monitored.

The half-life data of each insecticide (calculated as $t_{1/2} = \ln 2/k_{\text{app}}$) are a good parameter to compare their removal in different water matrices. Compared to distilled water (where $t_{1/2}$ were less than 1 min; except for CH which was 11 min), LW-H was the most affected by the matrix effect with half-lives 163, 245, 430 and 396 times higher for CH, IM, PI, and TH, respectively (Table 1). We noticed a full shortage of efficiency in the essays conducted in LW-H. As expected, we observed lower pesticide decrease on the processes carried out in those water matrices with higher DOC. The general trend in the degradation efficiency of insecticide studied followed the order: $\text{IW} > \text{WWTPe} > \text{LW-L} > \text{LW-H}$, which could be associated to the complexity of real tested water.

Table 1. Degradation rate constant (k_{app} , min^{-1}) and half-lives ($t_{1/2}$, min) of each insecticide in each tested water ($n = 3$).

Water	Chlorantraniliprole		Imidacloprid		Pirimicarb		Thiamethoxam	
	k_{app}	$t_{1/2}$	k_{app}	$t_{1/2}$	k_{app}	$t_{1/2}$	k_{app}	$t_{1/2}$
DW	0.065	11	1.027	0.7	1.721	0.4	0.951	0.7
IW	0.007	105	0.053	13	0.123	6	0.049	14
LW-H	0.000	1733	0.004	165	0.004	173	0.002	289
LW-L	0.004	161	0.025	28	0.020	35	0.020	35
WWTPe	0.004	193	0.024	29	0.054	13	0.023	30

Lado Ribeiro et al. [4] listed the effect of those components (organic and/or inorganic) that affect the degradation processes: (1) light attenuation by solid suspended, (2) consumption of HO^\bullet (among others oxidizing species) by natural organic matter (NOM), (3) scavenging from formatted radicals, with lower oxidation potential, from those anions present in waters (bicarbonate, sulfate, chloride or nitrate), and (4) competition for active sites on catalyst surface between all organic and inorganic species present in water. To sum up, the presence of non-target compounds can compete with target compounds in the degradation process. As showed Table S3 (Supplementary Material), NO_2^- and PO_4^{3-} were below detection limit in all cases. All target compounds have chlorine and nitrogen atoms on their chemical structure, except PI that does not have chlorine (Table S4, Supplementary Material). Thus, a weak increase in Cl^- and NO_3^- concentrations was observed during the experiment as a consequence of mineralization. The increase in EC observed in all experiments is mainly correlated with the increase in SO_4^{2-} appeared because the $\text{S}_2\text{O}_8^{2-}$ added ($\text{SO}_4^{\bullet-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{HO}^\bullet + \text{H}^+$) [32], additionally to the weak increase in Cl^- and NO_3^- . HCO_3^- concentration was reduced due to its conversion into CO_2 , from 19.6% to 92.0% with WWTPe and IW, respectively (Table S3, Supplementary Material). A weak decrease on pH values was observed likely due to the formation of some organic acids during the treatment. However, no significant differences ($p < 0.05$) were observed in pH value, which was circumneutral during the photo-processes.

Some inorganic ions, mainly SO_4^{2-} , Cl^- , NO_3^- , and HCO_3^- , have a detrimental effect due to their capability to act as HO^\bullet scavengers. Consequently, the oxidizing capacity of the solution is decreased. Considering the water composition, the scavenging of HO^\bullet by these anions could cause the corresponding radicals but all of them with lower E_0 than HO^\bullet [4,7,32,48]. On the other hand, high concentration of DOC can decrease insecticide photodegradation. The sensitization effect is shadowed by the forceful filter effect (quench-

ing) of some recalcitrant organic compounds such as humic substances [49]. They can operate as one of the most important absorbers of sunlight, especially in the UV-range and rapidly reacting with HO^\bullet . In addition, humic substances can be easily adsorbed onto the semiconductor surface, competing for the reaction sites with target pollutants [50].

The aim of AOPs is not only the removal of the parent compounds, but also the degradation of reaction intermediates originated, because they can be more hazardous in some cases and their complete mineralization to CO_2 , H_2O and mineral salts is difficult at certain times. What is expected of the TPs is that they form and disappear, completely, during the photoperiod. Figure 2 depicts the photocatalytic abatement found for each insecticide, in all water tested, and the behavior of their detected TPs. At the end of the photoperiod, 85.2, 61.8, 60.1 and only 10.9% of CH removal in IW, WWTPe, LW-L and LW-H, respectively, were achieved (Figure 2a). CH removal in LW-H was so slow that it was not possible to identify more than one TP: CH-1, whose reduction could not be reached. However, in water matrices, with less than 10 mg L^{-1} of DOC, CH-2, CH-6 and CH-7 were additionally detected. On the contrary, CH-3 was only detected when the degradation took place in LW-L, being all of them partially eliminated. Regarding to IM, PI and TH removal (Figure 2b–d), once finished the photoperiod, a complete elimination (>99.7%) in IW, LW-L and WWTPe matrices was noted. However, in LW-H, removal percentages were 61.0, 58.9, and 44.9% for IM, PI, and TH, respectively. Only IM-2 (hydroxy imidacloprid) was detected on IM removal in all tested waters (Figure 2b). In the same way that happened with CH, IM-2 appeared since the beginning of the photoperiod, reached a high and decreased until its almost complete disappearance at 240 min of reaction. However, in LW-H, the high of IM-2 was not achieved at the end of the experiment and its decrease was not noted. Five TPs from PI described in Table S2 (Supplementary Material) were detected, at different amounts, in all studied water matrices; except PI-4 in LW-H, which was not detected (Figure 2c). PI-1 (desmethyl-formamido) was the most abundant in all cases, following by PI-5 (desmethyl). This suggests that the preferred degradation pathway starts forming the carbamate with a successive N-dealkylation of the 2-dimethylamino group, as proposed Fenoll et al. [9]. For TH abatement, two TPs were detected: TH-1 and TH-2 (Figure 2d). TH-1 (clothianidin) appeared and disappeared during the photoperiod, except in LW-H, in consonance with TPs above mentioned. Exceptionally, TH-2 (thiamethoxam urea) was present from time zero in all water matrices ($9528 \pm 425 \text{ u.a.}$) and disappeared with the same shape than its parent compounds. It was probably generated during the homogenization time in darkness before UV-A LED exposure because it is described as a mayor hydrolysis product of TH [51]. Regarding to DOC data, IW and LW-L suffered a decrease due to abatement of target pesticides and their main detected TPs, from 17.5 and 30.2 (0 min) to 13.1 and 24.1 mg L^{-1} (240 min), respectively. DOC concentration evolution in WWTPe suffered a slightly not significant increase (from 12.8 at initial time to 13.3 mg L^{-1} at final time). In the case of LW-H, DOC concentration increases from 102.7 to 104.4 mg L^{-1} (initial and final reaction time, respectively) due to the no reached reduction of CH-1, IM-2 and TH-1 at the end of the experiments. To sum up, DOC data are a good complementary tool to indicate if an abatement of organic pollutants have been reached successfully.

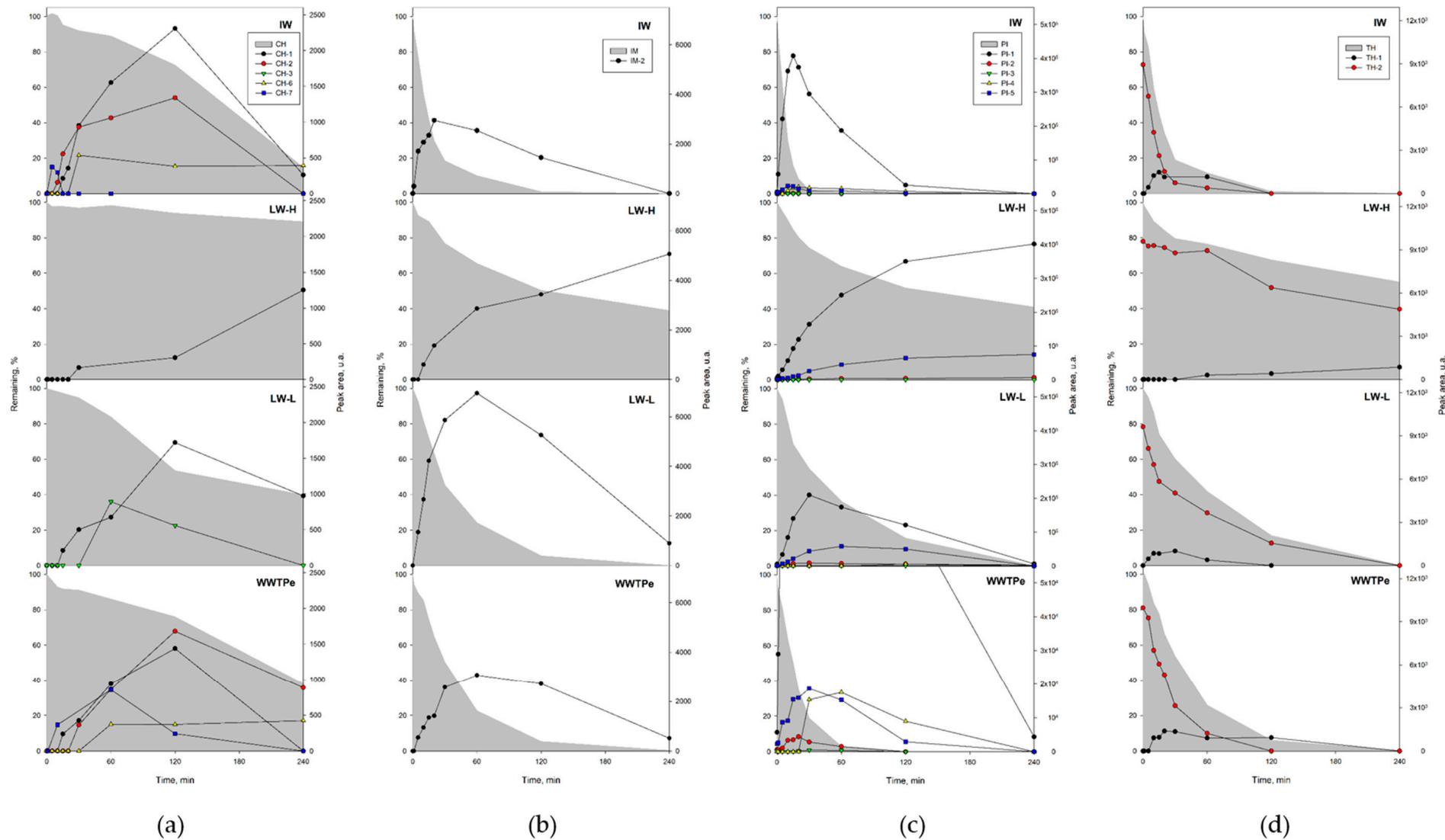


Figure 2. Degradation kinetics of (a) chlorantraniliprole; (b) imidacloprid; (c) pirimicarb; (d) thiamethoxam, spiked at 1 mg L^{-1} , and their TPs (peak area data) during the UVA-LED photocatalytic process, in the studied water matrices.

3. Materials and Methods

3.1. Reagents

Chlorantraniliprole (CH), imidacloprid (IM), pirimicarb (PI), and thiamethoxam (TH) analytical standards, all with purity >97%, were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Their main physicochemical properties are summarized in Table S4 (Supplementary Material) [52]. Commercial formulations of CH, IM, PI, and TH were supplied by FitoDolores S.L. (Murcia, Spain). TiO₂ Aeroxide P25 (99.5% purity) and ZnO (99.9% purity) catalysts, previously characterized by [53] were purchased from Nippon Aerosil Co Ltd. (Osaka, Japan) and Alfa Aesar (Karlsruhe, Germany), respectively. Different solvents, such as acetonitrile, and reagents, such as Na₂S₂O₈ and NaCl were purchased from Scharlab (Barcelona, Spain).

3.2. Water Sources

Irrigation water (IW; pH: 7.2; EC: 0.49 dS m⁻¹; DOC: 3.7 mg L⁻¹) was collected from the Tagus-Segura Water Transfer. Leaching water samples were generated by washing a clay-loam textured soil (30% clay, 43% silt, 27% sand; pH 8.1, OC: 0.96%; EC: 4.8 dS m⁻¹; alkalinity: 456 mg CaCO₃ kg⁻¹) through a disturbed polyvinyl chloride column (30 cm × 5 cm id) by washing it with deionized water. Two leachates of 900 mL of each one were collected. The first leachate (LW-H; pH: 7.4; EC: 1.13 dS m⁻¹; DOC: 92.0 mg L⁻¹) had a higher DOC content and EC than the second one (LW-L; pH: 7.3; EC: 0.35 dS m⁻¹; DOC: 21.1 mg L⁻¹). Finally, a real sample of wastewater effluent (WWTPE; pH: 7.2; EC: 2.69 dS m⁻¹; DOC: 7.2 mg L⁻¹) was collected from a WWTP placed in Murcia (SE of Spain).

3.3. Photochemical Experiments

Photocatalytic processes under lab-conditions were carried out using a photochemical reactor Photolab LED365-16/450-16c (APRIA Systems S.L., Cantabria, Spain), as formerly described Aliste et al. [29] (Figure S2, Supplementary Material). The total radiation intensity was 656.4 W m⁻², at 365 nm of used source. Firstly, the effect of catalyst load on the photo-oxidation process of these insecticides was studied in pure water (EC < 1 μS cm⁻¹; pH 6.9 and DOC < 30 μg L⁻¹). In each experiment, water was spiked with analytical standards of each insecticide at 1 mg L⁻¹ and different concentrations of TiO₂ (0–500 mg L⁻¹) and ZnO (0–500 mg L⁻¹) were added to the solutions. The slurries were homogenized in darkness for 20 min. After this time, 200 mg L⁻¹ of Na₂S₂O₈ (PS) were added and slurries were exposed to UV-LED lamps for 60 min. Different samples were collected during each photo-process and the experiments were replicated three times. Additionally, both photolysis and only photocatalysis (without oxidant), experiments were carried out to compare with the experiments above mentioned.

The photochemical reactor was used, secondly, to perform photocatalytic removal of insecticides in different water matrices: irrigation-leaching water (at two level of dissolved organic carbon, DOC), and a WWTP effluent. All the water samples were spiked at 1 mg L⁻¹, with the commercial formulations of the target insecticides. For the photocatalytic treatments with the different kinds of water using UV-LED lamps on the removal of four insecticides, 200 mg L⁻¹ of TiO₂ were added. 20 min of homogenization in darkness were needed before PS addition (200 mg L⁻¹). Subsequently, samples were collected for 240 min of reaction time where they were exposed to UV irradiation. Each experiment was replicated three times.

3.4. Analytical Measurements

CH, IM, PI, and TH residues from water were analyzed following the methodology proposed by Fenoll et al. [54]. Table S2 (Supplementary material) details the analytical conditions for each insecticide and their TPs already described by Fenoll et al. [9,44,55].

DOC content was measured after filtering of water samples (0.45 μm nylon filter) using a Multi N/C 3100 TOC Analyzer (Analytic Jena AG, Jena, Germany) connected to a NDIR detector (950 °C). Anions (Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, CO₃²⁻, and HCO₃⁻) were

analyzed using ion chromatography by means of an ion chromatograph, Dionex ICS-2100 (Thermo Scientific, Waltham, MA, USA), as previously specified [32].

3.5. Determination of Kinetic Parameters

Kinetic parameters of insecticide degradation were determined with the software Sigmaplot v.14.0 administered by Systat Software Inc. (San José, CA, USA). They were estimated using a single first-order kinetics [56] (1), where C_0 and C_t are the insecticide concentration at initial time (t_0) and a given time t , respectively, and k_{app} is the apparent rate constant (min^{-1}).

$$C_t = C_0 e^{-k_{app} t} \text{ or } \ln(C_0/C_t) = k_{app} t, \quad (1)$$

4. Conclusions

High amounts of pesticide residues have been found in different wastewaters. The presence of these can considerably affect living beings and the environment, which is why it is necessary to eliminate them from the environment. What a good tool for an efficient photocatalytic system is a good quality of light. LED technology has revolutionized AOPs due to its significant advantages over conventional lamps, from an economic, useful, and environmentally friendly point of view. In this work, we studied the abatement of four insecticides and their transformation products in different water matrices by heterogeneous photocatalysis ($\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$) assisted by UV-LED radiation. The findings suggest that the degradation rates of pollutants will depend on the chemical composition of water matrices, the organic matter content being the greatest scavenger. Finally, the studied technology is necessary and possible to improve water quality, especially in WWTPs.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11050609/s1>, Figure S1. Optimization of the photocatalytic process using different concentrations of TiO_2 and ZnO ($0\text{--}500 \text{ mg L}^{-1}$), with 200 mg L^{-1} of $\text{Na}_2\text{S}_2\text{O}_8$, Figure S2: Schematic drawing for the photochemical reactor Photolab LED365-16/450-16c (APRIA Systems S.L. Cantabria, Spain) used in experiments [29], Table S1: Kinetic parameters estimated for the photocatalytic degradation of insecticides at 1 mg L^{-1} ($n = 3$), Table S2: Analytical conditions of the studied insecticides and their transformation products by HPLC-MS² [9,44,55], Table S3. Evolution of electric conductivity (EC, $\mu\text{S cm}^{-1}$) and concentrations of inorganic anions (mg L^{-1}) in different water matrices during the photochemical period, Table S4: Main physico-chemical properties of the insecticides studied.

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