



Reclamation of aqueous waste solutions polluted with pharmaceutical and pesticide residues by biological-photocatalytic (solar) coupling in situ for agricultural reuse

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ABSTRACT

This work focuses on the detoxification of aqueous waste solutions polluted with 24 emerging pollutants (13 pharmaceuticals and 11 pesticides) using a coupled biological-photocatalytic facility under natural sunlight for use in crop irrigation. The polluted wastewater (urban, agricultural, and industrial) processed by conventional wastewater treatment plants is in some cases insufficient to reach the degree of purity required. This concern is of particular interest, especially in areas where a low rainfall pattern provides insufficient water resources to meet the demands caused by agriculture, which requires increased reuse of wastewater effluents. For this purpose, polluted water was first subjected to biological treatment followed by a photocatalytic process using the tandem $\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$. Residues of pharmaceuticals and pesticides were isolated by solid phase extraction (SPE) and analysed by HPLC-QqQ-MS². A notorious removal of pharmaceuticals was observed after biological treatment (average removal = 78%), except for diclofenac (31%) and carbamazepine (1%). In a contrary way, biodegradation of pesticides was inconspicuous (average removal = 48%) due to their recalcitrant properties. However, all compounds were rapidly degraded during the photocatalytic treatment because the fluence (H) required to obtain 90% degradation (H_{90}) was $<470 \text{ kJ m}^{-2}$ for the most persistent pollutant (terbutylazine). Single first order kinetic model satisfactorily explained the photooxidation of all micropollutants. Therefore, solar heterogeneous photocatalysis is presented as a promising technology to be incorporated as a tertiary process in wastewater treatment plants to remove biorecalcitrant pollutants. This implementation could be interesting especially in arid and semi-arid areas characterised by water scarcity but receiving many hours of sunshine per year, where a high percentage of reclaimed water is used for crop irrigation.

1. Introduction

Water is an essential and irreplaceable natural resource for life development. However, citizens, politicians, and other people are not capable of adequately managing this valuable resource in many occasions. Since the 1990 s, a large amount of qualitative research has been developed worldwide studying the occurrence and fate of Pollutants of Emerging Concern also called Emerging Pollutants (EPs), in wastewater (WW) and aquatic environments resulting from point and diffuse pollution [46,50,67]. These micropollutants (including microorganisms) mostly reach the environment by anthropogenic activities. The main point sources include wastewater treatment plants (WWTPs), hospitals and industries with agriculture being the main diffuse point

[65]. The occurrence of these compounds (mostly organic in nature) and their detrimental impact on aquatic and terrestrial ecosystems and human health is currently a matter of concern among the scientific community, as the potential ecotoxicological effects on non-target receptors due to their exposure remain unknown [40,68]. A literature review extracted from The Web of Science™ managed by Clarivate Analytics (Philadelphia, PA, USA) using the following keywords: “Emerging Pollutants” OR “Emerging Contaminants” AND “Wastewater”, shows >20,500 publications from the beginning of the 21st century to the present with a marked exponential growth trend in the last decade.

EPs are not necessarily new compounds. They are chemicals and/or microorganisms that have often been present in the environment for a long time but whose presence and significance are now being elucidated.

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EPs can be defined as new chemicals including their intermediate transformation products, which have not been subject to regulatory assessment and whose effects on the environment and human health are not well known. Recent studies on WW composition have drawn attention to the presence in the environment of a wide variety of identified compounds of anthropogenic origin from domestic wastewater, industrial effluents, hospitals, livestock farming, and agricultural activities [40]. Although EPs are usually present in low environmental concentrations (ng L^{-1} to $\mu\text{g L}^{-1}$) it is still unclear whether their levels in the aquatic environment can cause unwanted effects on humans and wildlife, such as endocrine disruption, that disturbs their physiological systems [68]. Therefore, information on their mechanisms of toxicity, their presence in the environment and their characteristics need to be studied in depth to better understand their impact on the environment and human health. Many of them are known to be persistent in water, which puts pressure on WWTPs for their operational removal. In addition to well-known environmental pollutants, more and more EPs are being identified thanks to the development of analytical techniques (mainly LC-MS²) that allow the detection of very low concentrations (ng L^{-1}) although their toxicities, environmental occurrences and characteristics remain less well-known compared to conventional pollutants. According to the substance-database of the NORMAN network (an independent organization for closer collaboration between science and policy), established in 2005 by the European Commission (EC) more than a 1,000 of chemical substances classified into 21 classes have been identified in the European aquatic environment over the last decades [47]. Based on the number of substances listed under the European Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals, established by the European Chemical Agency [21], between 30,000 and 50,000 industrial chemicals have been found of daily-use products and many of them are considered as potential EPs due to their release into the environment. Among them, pesticides (herbicides, insecticides, etc.), pharmaceuticals (antibiotics, legal drugs, analgesics, steroids, beta-blockers, etc.), personal care products (fragrances, insect repellents, UV sunscreen filters, etc.), illicit drugs (opioids, cannabinoids, etc.), life-style compounds (caffeine, nicotine, etc.), industrial compounds and by-products (chlorinated solvents, polyaromatic hydrocarbons, plasticizers, etc.), microplastics, flame retardants, nanomaterials, disinfection by-products and, more recently, microorganisms such as the SARS-CoV-2 virus have been detected in WW worldwide in recent years [1,6,31,55,69].

Specifically, pharmaceuticals (PMs), compounds used in the treatment or prevention of human and animal diseases to restore, correct, or modify organic function, are frequently identified at high level concentrations in the aquatic environment, probably due to their incessant release from WWTPs, which is significantly faster than their removal rates. Thus, they are considered a group of pseudo-persistent pollutants although their slow conversion rate has been evidenced in laboratory tests and field studies [9]. Even though PMs have been present in water for a long time, their levels in the environment have only begun to be monitored and recognised as potentially harmful to ecosystems, becoming in recent years a major public health concern as environmental pollutants. After ingestion, they are partly excreted unchanged and can consequently reach WWTPs via the sewerage network [13,32]. On the other hand, pesticides (PTs) also called plant protection products are substances intended to prevent, destroy, repel, or mitigate any pest on crops either before or after harvest to avoid their deterioration during storage or transport [22]. Although pesticides are beneficial for crop production, their extensive use can have serious costs for human health due to their biomagnification and persistent nature [34]. In fact, many of them have been recognised as endocrine disruptors [45] and can reach WWTPs as a result of livestock farming, and agri-food activities, which generate pesticide-containing WW [11,35,53,61].

Since 2000, the European Union (EU) has had legal instruments in place to prevent and control water pollution. Firstly, through Directive 2000/60/EC, known as the Water Framework Directive (WFD), which

includes measures to assess the chemical status of water resources (lakes, rivers, transitional and coastal surface waters and groundwaters) and to reduce the presence of pollutants [15]. Secondly through the “daughter directives” that have emerged in subsequent years like Directive 2013/39/EU [16], known as Environmental Quality Standard Directive (EQSD). The WFD and EQSD identify so-called priority substances, whose emissions must be reduced or phased out. Currently, according to EQSD, 45 Priority Pollutants are included. Among them, some PTs such as triazine (atrazine, simazine and terbutryn) and phenylurea (diuron and isoproturon) herbicides. This Directive also established the need to create a monitoring list of EPs (Candidate Priority Pollutants). Thus, through different Implementing Decisions (2015/495/EU, 2018/840 and 2020/1161) compounds such as some PMs (diclofenac, macrolide antibiotics, sulfamethoxazole and venlafaxine) and PTs (neonicotinoid insecticides and azoles) were included because their occurrence, persistence and lack of regulation. All this in view of achieving objectives such as the *Zero Pollution Ambition* announced in the European Green Deal [17] related to the Chemical Strategy for Sustainability [19], which aims to join efforts to ensure a more efficient and safer use of water by creating a toxic-free environment. In relation to this initiative, PMs are highlighted in the EU Strategic Approach on Pharmaceuticals in the Environment [18]. Therefore, further measures are needed to prevent pollution from being generated, as well as actions to clean up and remediate it, in order to improve its subsequent reuse while preserving the health of population.

In this sense, the polluted WW (urban, agricultural, and industrial) processed by conventional WWTPs is in some cases insufficient to reach the degree of purity required by law for some of the most persistent pollutants [49]. This fact is evident, as reflected in numerous monitoring studies conducted worldwide on WWTP effluents where a wide range of EPs have been found [64,69]. This concern is of particular interest, especially in areas where a low rainfall pattern provides insufficient water resources to meet the demands caused by agriculture, which requires increased reuse of WWTPs. Water scarcity and uneven geographical distribution of rainfall is a worrying problem in arid and semi-arid areas where water management strategies advocate the reuse of treated effluent in agriculture due to climate change. WW is currently reused worldwide, especially in developing countries. Given the wide variety of EPs entering WWTPs, many substances end up in the receiving environment after with or without alteration. The use of WW and its discharge into waterways exposes the agro-environment to substances, many of them still unknown and unassessed. The EU has also focused on this issue with the revision of the minimum requirements for water reuse in the context of integrated management according to Regulation 2020/741/EU on minimum requirements for water reuse [20]. The aim of this Regulation is to ensure that reclaimed water is safe for agricultural irrigation, promoting the circular economy, supporting resilience to climate change, and contributing to the WFD purposes by controlling water shortage and the subsequent pressure on water resources. When necessary and appropriate, water quality requirements and monitoring in addition to *E. coli*, BOD₅, TSS (total suspended solids), turbidity and others (*Legionella* spp. and intestinal nematodes) include the control of PMs and PTs among others (heavy metals, disinfection by-products, and other EPs such as microplastics) to safeguard the protection of the environment and of human/animal health. The requirements and obligations for risk assessment will include compliance with the environmental quality standards for priority substances and certain other pollutants set out in Directive 2008/105/EC. In short, the growing concern of public administrations about the presence of EPs in both WW and drinking water (DW) is leading to the development of new regulations that will undoubtedly have an impact on the design and operation of WWTPs in the coming years.

It is therefore indispensable to set severe discharge limits for EPs and to develop advanced technologies for their disposal. Although conventional WWTPs are able to remove efficiently some EPs, they are not intended to remove EPs at low concentrations or are ineffective in their

elimination [7]. Hence, conventional WWTPs act as primary barricades against pollution by EPs. Therefore, upgrading the treatment processes of WWTPs could further reduce the environmental release of EPs. Many countries worldwide are studying to upgrade WWTPs by mean of new (advanced) treatment technologies to achieve EPs removal and protect the environment [52,59].

In this context, membrane technology (nano- ultra- microfiltration, reverse osmosis, adsorption dynamics on carbon nanotubes or graphene oxide, aerobic granular sludge or gravity-driven) has been extensively applied during last years to isolate micropollutants from wastewater in reactors (closed system) and in natural water system (open system). They have simple operation, high efficiency, no phase change, great selectivity, and normal operating temperature conditions differing in operation cost, equipment requirements, process management and fouling control. However, during its long-term process, the pollutants gradually accumulate into the adsorption materials, until they reached saturation, then it became inactive. After its inactivation, pollutants removal and membrane filtration efficiency decline [10,12,54,77,79], so that it is usually combined with ozonation, activated carbon, photo-degradation, etc. [73]. In this context, Advanced Oxidation Processes (AOPs) are the most explored in the last years to remove EPs from WW, although they have not yet been implemented on a full-scale [48,60,66]. AOPs have gained great interest and their applications have been recently expanded, especially solar heterogeneous photocatalysis. EPs are oxidised by highly reactive oxidant species, mainly hydroxyl radicals (HO^\bullet , $E^0 = 1.9\text{--}2.7\text{ V vs. NHE}$) and others such as superoxide anion ($\text{O}_2^{\bullet-}$) and hydridodioxigen (HO_2^\bullet). The main advantages of these technologies are that they achieve the removal or at least the reduction of EPs concentration by mineralization, instead of transferring them, as it occurs with conventional processes [44,56]. These technologies are particularly interesting in areas characterised by intensive agriculture and specific climatic pattern, where annual solar radiation levels are very high, and water is scarce. Therefore, there is a clear need to solve this problem through innovative and environmentally friendly technologies developed in WWTPs to efficiently remove EPs. Considering the aforementioned, the aim of this study was to assess the removal of 24 EPs (13 pharmaceuticals and 11 pesticides) residues from aqueous waste solutions. For this purpose, we have used a coupled biological-photocatalytic ($\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$) facility under natural sunlight in a semi-arid area like Murcia (SE of Spain) characterised by a significant water scarcity but receiving $>3,000\text{ h}$ of sunshine per year where $>96\%$ of the reclaimed water is used for crop irrigation.

2. Materials and methods

2.1. Pesticides, pharmaceuticals, reagents and solvents

Analytical standards of PTs (Atrazine, Chlortoluron, Clothianidin, Diuron, Imidacloprid, Isoproturon, Simazine, Thiocloprid, Thiametoxam, Terbutylazine and Terbutryn) and PMs (Atenolol, Carbamazepine, Clarithromycin, Diclofenac, Erythromycin, Furosemide, Ibuprofen, Irbesartan, Ketoprofen, Ofloxacin, Sulfadiazine, Valsartan and Venlafaxine) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Merck Life Science SLU (Madrid, Spain), all of them with purity of $>95\%$. Commercial formulations of pesticides were acquired from FitoDolores SL and Probelte, located in Murcia (Spain), and pharmaceuticals by Fagron and Acofarma, both placed in Tarrasa (Spain). Table SM1 summarises their main physico-chemical properties.

Titanium dioxide (70 anatase/30 rutile, 99.5%, BET $50\text{ m}^2\text{ g}^{-1}$, size $< 21\text{ nm}$) Aeroxide™ P25 was provided by Nippon Aerosil Co Ltd. (Osaka, Japan). TiO_2 was previously characterised by DRS, XRD, FE-SEM, XDS, ATR-FTIR and BET surface [27,28]. H_2O , CH_3CN , CH_3OH (all HPLC-grade) and $\text{Na}_2\text{S}_2\text{O}_8$ (purity $> 98\%$) were supplied by Scharlab (Barcelona, Spain).

2.2. Experimental setup at laboratory scale

The amounts of photocatalyst (TiO_2) and oxidant ($\text{Na}_2\text{S}_2\text{O}_8$) were pre-optimised using pyrex glass vessels (110 mm length \times 80 mm \varnothing) containing 500 mL of water from the *Tagus-Segura Water Transfer*. Water samples were fortified at 0.1 mg L^{-1} of each pollutant with analytical standards and continuously stirred. Water samples were next exposed to direct sunlight for 240 min (from 10 to 14 h). The mean temperature measured during the photoexposure period was $31.1 \pm 2.5\text{ }^\circ\text{C}$. The UV-A and UV-B radiation values during the experiment ranged from 21 to 26 W m^{-2} and 0.9–1.6 W m^{-2} , respectively. The catalyst loading was assessed ranging from 50 to 500 mg L^{-1} of TiO_2 . Next, the effect of the oxidant on the abatement of EPs was tested using different concentrations of $\text{Na}_2\text{S}_2\text{O}_8$ (50–250 mg L^{-1}) keeping the concentration of TiO_2 (200 mg L^{-1}) fixed. Several samples (50 mL) were taken during the illumination period (240 min). Three replications were performed in each case.

2.3. Coupled biological-photochemical facility

The experiments were carried out using a coupled biological-photocatalytic facility located in a sunny area of the Experimental Farm of Torreblanca (Torre Pacheco) at the coordinates $38^\circ 1' 15''\text{ N}$ and $1^\circ 9' 56''\text{ W}$ (Murcia, SE of Spain) from August 2021 to January 2022. Fig. 1 shows a schematic drawing of the coupled systems.

A modular AT-8 WWTP purchased from AugustSpain (Alicante, Spain) was used to carry out the biological treatment of the aqueous waste solutions (polluted influent). Firstly, the influent flows into non-aerated zone, where a mechanical pre-treatment takes place. Several internal walls divide this zone, where there is internal recirculation. Then, by gravity, water flows into anaerobic zone, where is mixed with activated sludge and passed into denitrification zone. From this zone, water overflows into the aeration zone by single-bubble aeration diffusers. Finally, the mixture flows to bottom of sedimentation, where activated sludge is recycled by an airlift and clean water (effluent) is drained into the water reservoir. Figure SM1 shows a detailed description of the system used.

Following this, a solar photocatalytic facility previously described by Kushniarou et al. [38] was used to perform the solar photocatalytic experiments. Briefly, the pilot plant consists of five open reaction tanks (maximum capacity = 1,200 L) linked to water storage tanks and recovery membrane system. Each tank has two integrated PVC rods to keep the water in aeration and agitation, whose duration can be configured through the control unit. Additionally, the facility has an integrated ultrafiltration membrane (pore size = 10–100 nm, operating pressure = 8 bar) to recover TiO_2 nanopowder. Finally, the pilot plant contains a two-tanks system acting as a filter for suspended solid matter and two post-treatment storage tanks to accumulate treated water. A complete description of the facility is shown in Figure SM2.

2.4. Treatment of the aqueous waste solutions

Tagus-Segura Water Transfer (DOC: 1.7 mg L^{-1} ; EC: 0.8 dS m^{-1} ; pH: 7.9; total anions: 488 mg L^{-1} ; total cations: 203 mg L^{-1}) polluted with PTs and PMs to achieve a spiking level below $100\text{ }\mu\text{g L}^{-1}$ each was used to simulate the aqueous waste solution. Table 1 shows the main physico-chemical parameters of the influent and effluent after biological treatment. A total of 12,000 L of polluted water were subjected to biological treatment and temporarily stored in the corresponding tanks, before photocatalytic treatment. Different samples ($n = 24$) were taken from the influent and effluent to check the decay of pollutants during the biological depuration of the aqueous waste solutions.

At the same time as the different effluents were obtained, three photocatalytic treatments (August 2021, September 2021 and December 2021-January 2022) were carried out using the experimental facility described above. The decrease of UV irradiation due to seasonal changes

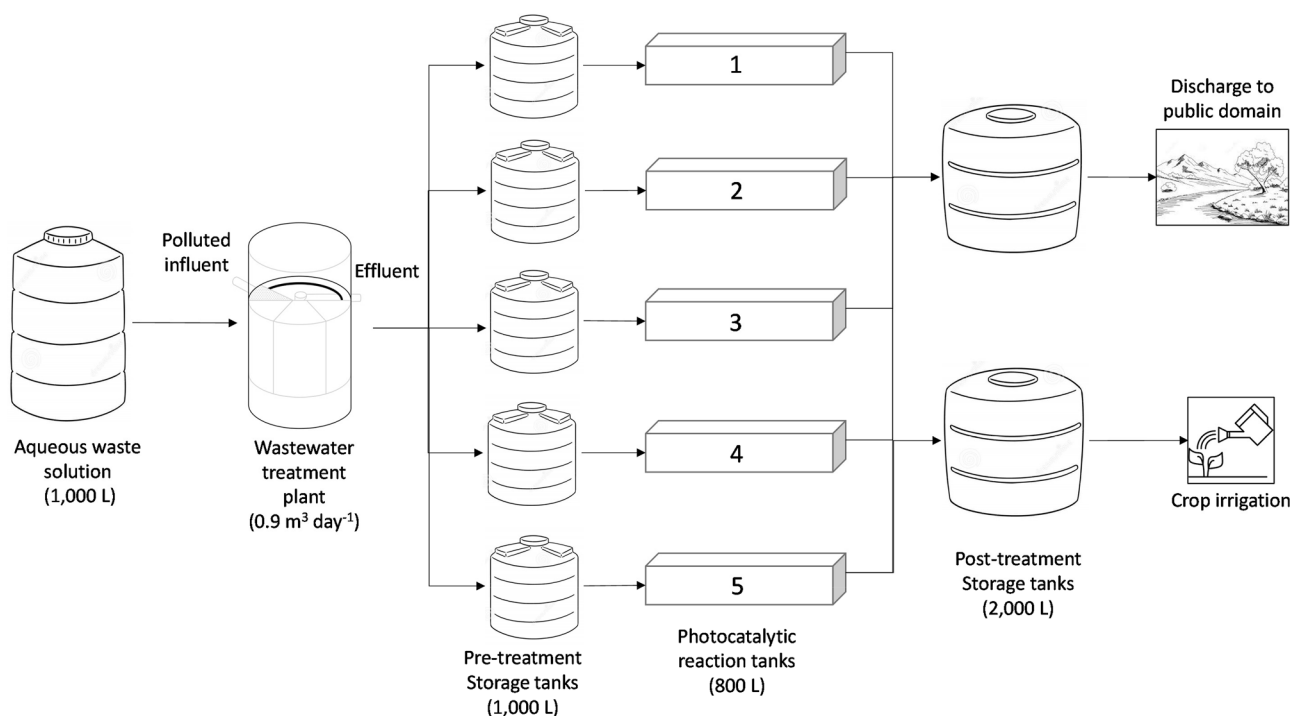


Fig. 1. Schematic drawing of biological-photochemical coupling for water detoxification.

Table 1

Main physico-chemical characteristics of the influent and effluent of aqueous waste solution after biological treatment ($n = 24$).

Parameter	$\bar{X} \pm \text{RSD} (\%)$	
	Influent	Effluent
pH	7.5 ± 1.7	7.7 ± 2.0
EC (dS m^{-1})	1.1 ± 2.3	1.1 ± 3.1
DOC (mg L^{-1})	3.1 ± 4.5	2.6 ± 3.1
TN (mg L^{-1})	2.1 ± 2.9	1.8 ± 2.3
Ca^{2+} (mg L^{-1})	69 ± 6.1	67 ± 7.2
Mg^{2+} (mg L^{-1})	48 ± 6.8	46 ± 6.1
Na^+ (mg L^{-1})	102 ± 5.7	99 ± 8.6
K^+ (mg L^{-1})	7.0 ± 4.3	6.0 ± 5.5
SO_4^{2-} (mg L^{-1})	251 ± 6.9	263 ± 4.8
Cl^- (mg L^{-1})	146 ± 7.3	150 ± 6.2
HCO_3^- (mg L^{-1})	128 ± 8.1	122 ± 9.3
NO_3^- (mg L^{-1})	2.3 ± 2.5	1.9 ± 0.8
NO_2^- (mg L^{-1})	BDL	BDL
PO_4^{3-} (mg L^{-1})	BDL	BDL

RSD: Relative Standard Deviation; BDL: Below Detection Limit.

on the efficacy of the photocatalytic process was assessed by measuring the cumulative mean UV-A and UV-B radiation during the experiment using a pyranometer (Skye Instruments LTD, Powys, UK) equipped with UV-A and UV-B sensors. For this reason, the first two treatments lasted 12 days, while the duration of the third treatment was 35 days. Different samples were taken during each treatment until a cumulative radiation about $4,000 \text{ kJ m}^{-2}$ in all cases (equivalent to $1,120 \text{ Wh m}^{-2}$). Each trial was started with the addition of 200 mg L^{-1} of TiO_2 to the corresponding reaction tank filled with 800 L of water ($n = 5$). The slurries were aerated to maintain TiO_2 in suspension and darkened for 30 min prior to solar exposure to guarantee adsorption equilibrium. After this time, the tanks were uncovered and 200 mg L^{-1} of $\text{Na}_2\text{S}_2\text{O}_8$ were added. From this point, different water samples were collected from each tank at different accumulated UV radiation. Once the treatment was completed, TiO_2 nanopowder was recovered using the ultrafiltration membrane.

According to Liu et al. (2014), the single first order (SFO) kinetic model is frequently suitable for describing the photocatalytic oxidation

rate of many organic pollutants using semiconductor materials when substrate concentration is low. In our case, the degradation rate constant (k) values were obtained using fluence ($H = dE/dA$; i.e., the radiant energy received by a surface per unit area) according to the methodology previously specified by Kushniarou et al. [38], because fluence units are comparable between different studies, while time units depend on the type of photoreactor. Consequently, the fluence required for X percent of pollutant to degrade from the solution can be calculated as follows (Eq. (1)):

$$H_X = \frac{\ln \left[\frac{100}{(100-X)} \right]}{k} \quad (1)$$

2.5. Analytical determinations of pesticide and pharmaceutical residues

Pollutant residues were isolated from water by SPE and analysed by HPLC-TQMS².

2.5.1. Sample preparation

Once the sample was homogenized, 50 mL were passed through an Oasis® HLB 60 μm (500 mg) extraction cartridge (a hydrophilic-lipophilic balanced N-vinylpyrrolidone-divinylbenzene copolymer) purchased from Waters (Milford, MA, USA) using a Visiprep™ SPE Vacuum Manifold (12 port model) supplied by Supelco (Madrid, Spain), at a flow rate of approximately 3 mL min^{-1} . Previously, the extraction cartridge was conditioned with 3 mL of CH_3OH and equilibrated with 3 mL of Milli-Q water (18 m Ω). Once the sample was passed through the cartridge, it was washed with 5 mL of Milli-Q water, discarding the eluate, and drying the column with air. Later, the analytes were eluted with 5 mL of CH_3CN (2 mL min^{-1}), collecting the organic phase in a graduated test tube and recording the total volume. Finally, 2 mL were filtered through a nylon filter (20 μm).

2.5.2. Apparatus and software

Chromatographic separation was performed in an Agilent 1200 HPLC system provided with a Zorbax Eclipse XDB-C₈ analytical column (150 mm \times 4.6 mm) with 5 μm particle size from Agilent Technologies

(Santa Clara, CA, USA). MS/MS detection was performed using an Agilent G6410A triple quadrupole (QQQ) mass spectrometer (MS) running in electrospray (ESI) positive and negative ion mode. Data acquisition was performed using MassHunter software.

2.5.3. HPLC-MS² conditions

Chromatographic determinations were carried out using a gradient elution with eluent A being CH₃CN and eluent B consisting of an aqueous solution of 0.1 % HCOOH. The analysis started with 10% of eluent A, which was increased linearly up to 90% in 5 min and later to 100% in 10 min and held for further 1 min before being returned to 10% of eluent A in 5 min to give a total run time of 20 min and followed by a re-equilibration time of 5 min. The flow rate was set at 0.7 mL min⁻¹ and column temperature 20 °C. 10 µL of water extract were injected into the chromatographic system.

For MS/MS detection, the ionization source parameters in positive mode were as follows: capillary voltage 4 kV, source temperature 120 °C, desolvation temperature of 350 °C, nebulizer (50 psi), and nitrogen gas flow 9 L min⁻¹. The ionization source parameters in negative ion mode were the same except the capillary voltage, which was set at 3 kV. The optimum MS/MS conditions of the pollutants were performed by column injection of individual standards at 100 µg L⁻¹. Full-scan mass spectra (50–1000 *m/z*) and product ion scans were acquired to obtain one precursor and two product ions for each compound for both identification and quantification purposes. The most abundant product ion was selected for quantification and the second one for confirmation. The multiple reaction monitoring (MRM) transitions and the applied fragmentor (FV) and collision energies (CE) are summarized in Table 2.

2.5.4. Validation study for pollutants

The specificity was assessed by examining blank water samples (n = 5) to control the absence of interferences. Linear calibration curves were obtained for all pollutants from 0.1 to 50 µg mL⁻¹. The linearity range was assessed as a function of positive results for different tests (R² > 0.99, normality and Durbin-Watson). Recovery and precision (n = 5) were assessed by spiking blank samples at two fortification levels (5 and 20 ng mL⁻¹). LODs and LOQs were determined as the lowest concentration of the pollutants producing a chromatographic peak at signal to noise ratio (S/N) of 3 and 10, respectively. The matrix effect (ME) was quantitatively evaluated (n = 5) by comparing the response of the pollutant in standard solution (CH₃CN) to that of a post-extract spiked with each pollutant at the same concentration according to the following formula (Eq. (2)):

$$ME (\%) = \left(\frac{X - Y}{X} \right) \cdot 100 \quad (2)$$

where *X* is the peak area of a compound in pure solvent and *Y* is the peak area of the analyte in the post-extract spiked sample. To confirm the accuracy, calibration standards were run on multiple times during analytical measurements.

2.6. Measurements of cations, anions, Ti⁴⁺ and total organic carbon

Anion concentrations were measured using a Thermo Scientific Dionex ICS-2100 ion chromatograph (Waltham, MA, USA) with an AS19 column. For cation measurements, an Agilent 5110 ICP-OES was used. For Ti⁴⁺ determination, an Agilent 7900 ICP-MS was used. Dissolved organic carbon (DOC) and total nitrogen (TN) content were determined by means of an Analytic Jena Multi N/C 3100 TOC Analyzer (AG, Jena, Germany) after filtering of samples through a nylon filter (0.45 µm).

2.7. Statistical analysis

The statistical software SigmaPlot (Systat, Software Inc., San Jose, CA, USA) v.14 was used to fit the experimental data. To assess the

Table 2
Retention times (R_T) and MS/MS parameters of the studied pollutants.

Pollutant ^a	R _T (min) ^b	SRM ₁ / SRM ₂ (<i>m/z</i>) ^c	FV ₁ / FV ₂ (V) ^d	CE ₁ / CE ₂ (V) ^e	Polarity
Atenolol ^{PM}	2.94	267 → 145	110	20	+
		267 → 190	110	10	
Ofloxacin ^{PM}	5.18	362 → 261	150	30	+
		362 → 318	150	20	
Sulfadiazine ^{PM}	5.35	251 → 156	120	10	+
		251 → 92	120	30	
Venlafaxine ^{PM}	5.70	278 → 58	90	20	+
		278 → 260	90	5	
Erythromycin ^{PM}	5.81	735 → 158	150	30	+
		735 → 83	150	50	
Thiamethoxam ^{PT}	5.83	292 → 211	90	5	+
		292 → 181	90	20	
Clarithromycin ^{PM}	6.07	749 → 158	150	30	+
		749 → 590	150	20	
Clothianidin ^{PT}	6.11	250 → 169	90	5	+
		250 → 132	90	10	
Imidacloprid ^{PT}	6.24	256 → 209	120	10	+
		256 → 175	120	10	
Irbesartan ^{PM}	6.60	429 → 207	150	20	+
		429 → 195	150	20	
Thiachloprid ^{PC}	6.68	253 → 126	110	20	+
		253 → 186	110	10	
Furosemide ^{PM}	6.77	329 → 285	90	10	-
		329 → 205	90	20	
Carbamazepine ^{PM}	6.83	237 → 194	120	20	+
		237 → 179	120	40	
Simazine ^{PT}	7.06	202 → 104	110	30	+
		202 → 132	110	20	
Chlortoluron ^{PT}	7.33	213 → 72	110	20	+
		213 → 140	110	20	
Terbutryn ^{PT}	7.41	242 → 186	110	20	+
		242 → 91	110	30	
Ketoprofen ^{PM}	7.50	255 → 77	110	50	+
		255 → 209	110	10	
Isoproturon ^{PT}	7.50	207 → 72	110	20	+
		207 → 165	70	10	
Valsartan ^{PM}	7.54	436 → 207	110	20	+
		436 → 291	110	10	
Diuron ^{PT}	7.54	233 → 72	110	20	+
		233 → 160	110	10	
Atrazine ^{PT}	7.57	216 → 174	110	10	+
		216 → 96	110	20	
Terbuthylazine ^{PT}	8.16	230 → 174	130	20	+
		230 → 132	130	20	
Diclofenac ^{PM}	8.19	296 → 214	83	30	+
		296 → 250	83	5	
Ibuprofen ^{PM}	8.40	207 → 161	110	0	+
		207 → 119	110	20	

^a PM (Pharmaceutical); PT (Pesticide); ^b Retention time; ^c Single reaction monitoring transition; ^d Fragmentor; ^e Collision energy.

differences between means on the disappearance of pollutants from water a One-Way Analysis of Variance (ANOVA) was performed by means of software IBM-SPSS Statistics (Armonk, NY, USA) v.28 followed by Tukey's Honest Significant Difference test (*p* < 0.05).

3. Results and discussion

3.1. Analytical validation

Specificity was confirmed, with no other interferences observed at the retention time of the targeted analytes. The curves obtained showed linearity through the calibration range (R² > 0.99). Pollutant recovery from spiked samples varied from 70% to 123% with RSD < 8% and an intra- and inter-day RSD < 6%. The LODs ranged from 0.003 µL⁻¹ to 0.3 µg L⁻¹ and the LOQs varied from 0.01 µg L⁻¹ to 1 µg L⁻¹ for terbutryn and ibuprofen, respectively. According to Zhou et al. [78], when LC-MS is used in ESI mode, ME can be responsible for ion suppression (loss in response, ME < 0%) or ion enhancement (increase in response, ME >

0%). If ME is close to 0%, no ME exists. In our case, the values obtained for ME ranged from -3.1% to $+4.2\%$, indicating a small ME. With an appropriate sorbent like N-vinylpyrrolidone-divinylbenzene copolymer, the SPE technique used lead to small matrix effects as the interfering components in the matrix are significantly reduced as compared to other methods (e.g., liquid-liquid extraction). To get more unflinching results, the ME can also be evaluated by comparing the calibration curve slope for standard solutions vs matrix matched standard solutions. Thus, a lower slope specifies ion-suppression, while a higher slope indicates ion enhancement.

3.2. Outcome of primary and secondary treatment technologies on EPs removal

The removal of EPs studied during the primary (mechanical) treatment was negligible ($<2\%$) in all cases. Sorption is the main process during this stage, while sedimentation and flocculation are stated to be of lesser importance [2]. As demonstrated by Alvarino et al. [7], sorption includes both, absorption of EPs onto lipid portion of the primary sludge (hydrophobic interaction) and adsorption on the particles surface of the sludge (electrostatic interaction). In our case, this process was practically nil since the influent had a value of TSS of 1.3 mg L^{-1} and DOC = 3.1 mg L^{-1} because irrigation water from *Tagus-Segura Water Transfer* was used to obtain waste solutions. Fig. 2 shows the concentrations found in the influent and effluents after secondary (biological) treatment on the removal of PMs. The removal efficiency (RE) of the pollutants was calculated considering their respective concentrations in the influent [C_i] and effluent [C_e], according to the following equation (Eq. (3)):

$$RE(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3)$$

As can be observed in Table 3, a notorious removal was observed except for diclofenac and carbamazepine. $>95\%$ of influent amount for atenolol, ibuprofen, ketoprofen, ofloxacin, clarithromycin, erythromycin, valsartan and sulfadiazine was removed during biological treatment and consequently, they can be considered as highly biodegradable (biodegradation $\geq 75\%$). Furosemide (71%), irbesartan (65%) and venlafaxine (63%) showed medium biodegradability (biodegradation = 35–75%), while diclofenac (32%) and carbamazepine (1%) can be classified as low biodegradable compounds (biodegradation $\leq 35\%$). According to their biodegradation rate constant (K_{bio}) expressed as L g^{-1}

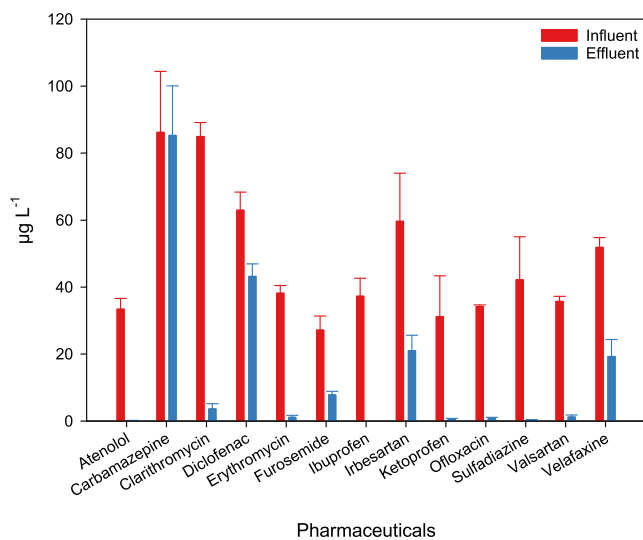


Fig. 2. Concentration of PMs found in the influent and effluent after primary and secondary biological treatment. Error bars denote standard deviation ($n = 24$).

Table 3

Removal efficiency (RE) for the studied EPs during biological treatment of waste solutions ($n = 3$).

Pollutants (RE \pm RSD)					
Pharmaceutical	RE (%)	RSD (%)	Pesticide	RE (%)	RSD (%)
Atenolol	99.7	14.8	Atrazine	11.9	3.7
Carbamazepine	1.0	19.2	Chlortoluron	60.6	11.6
Clarithromycin	95.8	24.7	Diuron	36.3	27.5
Diclofenac	31.5	8.6	Imidacloprid	87.8	29.3
Erythromycin	97.1	30.3	Isoproturon	83.6	10.5
Furosemide	71.2	14.2	Simazine	20.6	22.3
Ibuprofen	99.7	7.2	Thiacloprid	89.1	30.8
Irbesartan	64.8	23.0	Thiametoxam	11.1	21.9
Ketoprofen	98.4	29.6	Terbutylazine	26.5	30.5
Ofloxacin	97.7	20.1	Terbutryn	49.4	20.3
Sulfadiazine	99.2	29.6			
Valsartan	96.6	27.2			
Venlafaxine	62.8	15.8			

RSD: Relative standard deviation.

MLSS (mixed liquor suspended solids) d^{-1} , clarithromycin (386–1200), erythromycin (386–1200), diclofenac (1.9–321), ibuprofen (6–103), ketoprofen (16–226), atenolol (6–95) and carbamazepine (8–314) can be classified as moderate ($K_{bio} = 1-10$) to highly ($K_{bio} > 10$) biodegradable [60].

The main mechanisms for EPs removal during secondary treatment are sorption on the sludge and biodegradation (the breakdown of the parent compounds into intermediates by hydroxylation, carboxylation, ring cleavage, etc. by microorganisms) as demonstrated for ibuprofen [60], while other processes such as photodegradation and volatilization have minimal impacts on pharmaceuticals removal efficiency [33,76]. Biodegradation of PMs and other EPs depends on their structural complexity and the type and activity of biomass in the sludge.

On the other hand, the effectiveness of biodegradation on the removal of PTs is shown in Fig. 3. As general rule, detoxification of water polluted with PTs is not compatible with classical biological treatments owing to their high toxicity for microorganisms and resistance to biodegradation (recalcitrant characteristics) [66]. As can be observed, following the same criteria as for the PMs (Table 3), isoproturon (84%), imidacloprid (88%) and thiacloprid (89%) show high biodegradability; diuron (36%), terbutryn (49%) and chlortoluron (61%), can be considered as moderate biodegradable, while thiametoxam (11%), atrazine (12%), simazine (21%) and terbutylazine (27%) can be catalogued as

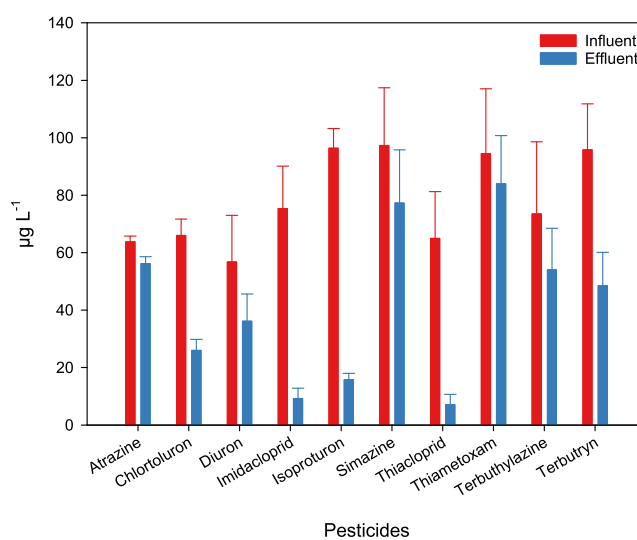


Fig. 3. Concentration of PTs found in the influent and effluent after primary and secondary biological treatment. Error bars denote standard deviation ($n = 24$).

low biodegradable compounds.

Biodegradation of organic pollutants can occur through natural attenuation or intrinsic degradation, where the resident microorganisms diminish the pollutant amount without stimulation, biostimulation (where oxygen, nutrients, electron acceptors and donors are used to improve the process) and bioaugmentation as results of the addition of capable strain of microorganisms [14]. Biodegradation of EPs such as PMs (nonprimary substance) in the presence of a main substrate (primary substrate) occurs via two different mechanisms: Co-metabolism and competitive mechanism. A co-metabolic pathway needs a primary substrate for the growth of biomass, which is required for the transformation of the nonprimary substrate. Regarding competitive mechanism, both the primary and nonprimary substrate compete for the active sites on the biomass. Thus, the degradation of the EPs is faster when the primary substrate concentration is moderately low and vice versa. A comparative study on the biodegradation efficiency of some PMs (diclofenac, ibuprofen, and sulfamethoxazole) reported higher efficiency by the co-metabolic method using glucose as carbon source as compared to metabolic mechanism where PMs were used as main carbon source [23]. Regarding PTs biodegradation, common mechanisms include mineralization, co-metabolism, bioconcentration, or cumulative effects. Some studies have shown that mineralization and co-metabolism are the main mechanisms for the further degradation of the parent compounds and their intermediate reaction products [8].

Especially important are the redox conditions. As general rule, we have observed a higher biodegradation for both classes of EPs in aerobic conditions as compared to anaerobic conditions because dissolved oxygen favours biodegradation as pointed by Rout et al. [60]. Several research papers studying the aerobic biological treatment of PMs in WW have showed a noteworthy decrease in the chemical (COD) and biological oxygen demand (BOD) [23]. However, it has been also demonstrated that the combination of aerobic/anaerobic conditions increase the biomass of active microorganisms during biological treatment, improving the efficacy of the biodegradation process for some PTs [62].

As result, conventional WWTPs are not so effective on the EPs removal, especially PTs. Hence, other methods, such as the use of membrane bioreactors (micro-, ultra-, nanofiltration and reverse osmosis), activated carbon adsorption (high porosity and large surface area), or AOPs (ozonation, photo-Fenton, heterogeneous photocatalysis, etc.) should be applied to deal with this environmental concern before the water is reused [58,60,61,66]. Different organic and inorganic species present in water can modify the photocatalytic degradation of EPs because i) compete with EPs and scavenge HO[•] radicals, ii) act as UV filter and attenuate light, and iii) foul catalytic surface by occupying active sites of the catalyst [71]. However, no significant differences were found in our study in the main physico-chemical parameters of the influent and effluent after biological treatment as shown in Table 1.

To assess the ecotoxicological potential of the effluent, the Toxicity Estimation Software Tool (TEST, v. 5.1) based on QSAR (Quantitative Structure Activity Relationship) models was used [72]. Results are included in Table SM2, where predicted ecotoxicological parameters are shown. As general rule, the concentrations of the EPs studied are below the *Daphnia magna* LC₅₀ (48 hr) and *Tetrahymena pyriformis* IGC₅₀ (48 hr) thresholds. However, it is very important to consider the possible synergistic effect caused by the concentration summation. In addition, many of them can develop toxicant effects and neonicotinoids insecticides and some PMs, such as diclofenac, ofloxacin and valsartan are catalogued as mutagenic.

3.3. Assessment of the photocatalytic process as tertiary treatment for EPs removal

Currently, solar photocatalysis based on chemical reactions generated after the absorption of solar photons over the reactants and/or catalysts surface is a demonstrated technology for EPs removal (especially PTs) from WW [30]. The major limitation of AOPs is the relatively

high-cost process due to the use of chemicals and energy consumption. However, it has been demonstrated that photocatalyst can be reused several cycles [4,28]. In addition, the use of sunlight, a renewable and cost-free source of energy makes the process very attractive, especially in areas that receive a large number of hours of sunshine per year [63]. Among various semiconductor materials, TiO₂ is the most widely studied for environmental applications mainly due to its non-toxicity, photostability, biological and chemical inertness, resistance to corrosion, availability, and chemical and thermal stability. On the other hand, sulfate radical-based processes (SO₄^{•-}-AOPs) have been achieving attention as an operative tool to eliminate different emerging pollutants in water. Particularly, persulfate is a strongest oxidizing agent capable of effectively degrading micropollutants [51].

Some PMs such as atenolol, ibuprofen, ketoprofen, ofloxacin and sulfadiazine were not included in this section of the study because their concentrations in the effluent obtained from the WWTP were lower than 1 µg L⁻¹ (biodegradation > 98%). For the rest of PMs, the initial levels ranged from 1.1 ± 0.6 µg L⁻¹ to 85.8 ± 14.8 µg L⁻¹ for erythromycin and carbamazepine respectively (Fig. 2). In the case of PTs, those values varied from 7.1 ± 3.6 µg L⁻¹ (thiacloprid) to 84.0 ± 16.8 µg L⁻¹ (thiametoxam) according to the data shown in Fig. 3. The evolution of EP residues during the three photocatalytic treatments carried out are shown in Figures SM3 (PMs) and SM4 (PTs) as a function of accumulated H (kJ m⁻²).

According to SFO kinetic model, the main parameters calculated are shown in Table 4. As can be observed, SFO model satisfactorily explains de photooxidation of all EPs. R² values ranged from 0.93 to 0.99, with a relationship C_H/C₀ very close to 1 in all cases and S_{Y/X} ≤ 0.1 in the most unfavourable case. As function of the rate constants calculated, the values of H₅₀ varied from 19 kJ m⁻² to 139 kJ m⁻² for diclofenac and terbuthylazine, respectively. Although all compounds were rapidly degraded because the fluence necessary to obtain 90% degradation (H₉₀) was lower than 470 kJ m⁻² (equivalent to 2–4 days of exposition) for the most persistent compound (terbuthylazine) we have established two terciles to include the compounds in three groups (low persistent, moderately persistent and persistent) as a function of their degradation rates. As general rule, the most persistent compounds were neonicotinoid insecticides and triazine herbicides except for terbuthryn (moderately persistent), which is due to this herbicide is a methylthio-triazine while atrazine, simazine and terbuthylazine are chlorotriazines, more persistent compounds [39]. On the other hand, antibiotics (macrolides) anti-hypertensives (valsartan and irbesartan) and phenylurea herbicide (diuron) are catalogued as moderately persistent compounds. Finally, diclofenac (anti-inflammatory), furosemide (diuretic), venlafaxine (anti-depressant), carbamazepine (anti-convulsant) isoproturon and chlortoluron (phenylurea herbicides) were rapidly degraded (H₉₀ < 112 kJ m⁻²). The main difference between phenylurea herbicides studied is the number of chlorine atoms in their structures (0, 1 and 2 for isoproturon, chlortoluron and diuron, respectively). Consequently, the photooxidation effectivity was in the order: diuron < chlortoluron < isoproturon. In addition, diuron has a lower Henry's Law constant (Table SM1). Similar findings have been pointed for the photocatalytic oxidation of triazine [24], phenylurea [25] and neonicotinoids [26] under sunlight irradiation. No significant differences (p < 0.05) were observed when comparing the mean values of rate constants for PMs (Table SM3), while significant differences (p < 0.05) were detected between isoproturon and neonicotinoids (imidacloprid, thiacloprid and thiametoxam) and triazines (atrazine, simazine and terbuthylazine) as can be observed in Table SM4. As shown in Figure SM5, clothianidin, a transformation intermediate product of thiametoxam, was detected with a maximum concentration of 3.3 ± 1.8 after 200–300 kJ m⁻² were accumulated although it had a quick disappearance. As a consequence of the mineralization of the EPs studied, a reduction in the DOC content was measured during the experiments (Figure SM6).

Table 4

Kinetic parameters for the photocatalytic degradation of EPs in water (n = 3) after photocatalytic treatment.

Compound	R ² ± SD	C _H /C ₀ ± SD	k ± SD	S _{y/x} ± SD	H ₅₀	H ₉₀	Tercile
Diclofenac	0.9492 ± 0.0726	0.9860 ± 0.0233	0.0360 ± 0.0189	0.0632 ± 0.0610	19	64	T1
Furosemide	0.9722 ± 0.0329	0.9911 ± 0.0086	0.0347 ± 0.0115	0.0491 ± 0.0389	20	66	Low persistent
Isoproturon	0.9933 ± 0.0102	1.0151 ± 0.0232	0.0327 ± 0.0188	0.0258 ± 0.0257	21	70	
Venlafaxine	0.9954 ± 0.0014	1.0088 ± 0.0044	0.0280 ± 0.0136	0.0263 ± 0.0053	25	82	
Carbamazepine	0.9886 ± 0.0039	1.0260 ± 0.0195	0.0209 ± 0.0099	0.0432 ± 0.0088	33	110	
Chlortoluron	0.9642 ± 0.0220	1.0535 ± 0.0421	0.0207 ± 0.0108	0.0800 ± 0.0343	34	111	
Erythromycin	0.9620 ± 0.0230	0.9972 ± 0.0411	0.0178 ± 0.0091	0.0687 ± 0.0200	39	129	T2
Terbutryn	0.9821 ± 0.0105	1.0327 ± 0.0180	0.0169 ± 0.0069	0.0543 ± 0.0204	41	137	Moderately persistent
Diuron	0.9595 ± 0.0245	1.0715 ± 0.0402	0.0130 ± 0.0059	0.0884 ± 0.0348	53	178	
Valsartan	0.9916 ± 0.0046	1.0101 ± 0.0222	0.0110 ± 0.0061	0.0370 ± 0.0078	63	210	
Irbesartan	0.9349 ± 0.0460	1.0325 ± 0.0485	0.0106 ± 0.0024	0.0931 ± 0.0280	65	217	
Clarithromycin	0.9271 ± 0.1182	0.9855 ± 0.0474	0.0099 ± 0.0032	0.1077 ± 0.0649	70	232	
Imidacloprid	0.9876 ± 0.0127	1.0186 ± 0.0152	0.0082 ± 0.0032	0.0428 ± 0.0234	85	282	T3
Thiachloprid	0.9786 ± 0.0092	1.0382 ± 0.0291	0.0077 ± 0.0031	0.0626 ± 0.0135	90	298	Persistent
Simazine	0.9890 ± 0.0059	1.0319 ± 0.0193	0.0059 ± 0.0029	0.0453 ± 0.0112	117	388	
Thiamethoxam	0.9788 ± 0.0164	1.0342 ± 0.0412	0.0059 ± 0.0020	0.0611 ± 0.0257	117	390	
Atrazine	0.9816 ± 0.0107	1.0492 ± 0.0293	0.0057 ± 0.0023	0.0601 ± 0.0161	122	404	
Terbutylazine	0.9882 ± 0.0042	1.0331 ± 0.0341	0.0050 ± 0.0016	0.0492 ± 0.0099	139	461	

R²: coefficient of determination; C_H: Residual concentration of pollutant at a certain H value; C₀: Initial concentration of pollutant; k: Apparent rate constant (m² kJ⁻¹); S_{y/x}: Standard error of estimate; H₅₀ and H₉₀ (kJ m⁻²) are the necessary radiant energy received by a surface to obtain 50% and 90% of degradation, respectively.

3.4. Impact of water matrix composition

The surface charge of the photocatalyst and the ionization (pK_a) of the pollutants may be strongly affected by the solution pH. Electrostatic attraction or repulsion between the photocatalyst surface and EPs could take place according to the point of zero charge (PZC) of TiO₂ P25 (6.3) [37]. Thus, the surface of the photocatalyst will remain positively charged (pH < PZC) or negatively charged (pH > PZC). Consequently, the pH of the solution may enhance or inhibit the photodegradation rate. The holes (h⁺) are considered as the major oxidation specie at low pH, whereas HO[•] are considered as the predominant species in neutral or alkaline media [43]. Despite this, some authors have shown that the rate of photocatalytic degradation does not usually depend closely on pH values in the 4–10 range [41]. In our case, initial pH values ranging from 6 to 8 did not show significant effects on the process efficiency. Thus, the pH of the water (7.7) was not adjusted. As photodegradation progressed, there was a weak decrease in pH. Regarding temperature, photocatalytic systems do not require heating and operate at room temperature because of photonic activation [41].

On the other hand, several studies have confirmed that water components, especially anions such as, bicarbonate, phosphate, nitrate, sulphate, chloride, and dissolved organic compounds can affect the photodegradation rate of EPs since they can be adsorbed onto the surface of TiO₂ [5,57]. Figure SM7 shows the evolution of Cl⁻, SO₄²⁻ and HCO₃⁻ during the photocatalytic treatments. As can be seen, no significant changes were observed for Cl⁻ concentration, while an increase in SO₄²⁻ and a decrease in HCO₃⁻ were observed. The decrease of HCO₃⁻ is due to its transformation in CO₂ while the increase of SO₄²⁻ is due to the conversion of S₂O₈²⁻ (S₂O₈²⁻ + UV → 2SO₄^{•-}; SO₄^{•-} + H₂O → SO₄²⁻ + HO[•] + H⁺; SO₄^{•-} + OH⁻ → SO₄²⁻ + HO[•]). Consequently, a weak increase in electrical conductivity was observed at the end of irradiation time. However, the known data do not recognize a level of SO₄²⁻ in drinking water that may cause adverse human health effects. For this reason, the World Health Organization (WHO) does not propose a health-based guideline for SO₄²⁻ in drinking water. The data from tap water studies with human volunteers indicate a laxative effect at concentrations ranging from 1000 to 1200 mg L⁻¹. Thus, because of gastrointestinal effects it is recommend to notify when SO₄²⁻ concentrations exceed 500 mg L⁻¹ [75]. In addition, SO₄²⁻ has no major impact on the soil beyond contributing to the total salt content. Irrigation water containing a high concentration of SO₄²⁻ (>400 mg L⁻¹) may interfere with plant uptake of other nutrients like phosphorus. Thus, no significant differences (p < 0.05) were found when comparing grown broccoli [74], lettuce [3] and pepper [4] using unreclaimed and persulfate-reclaimed water. If

necessary, SO₄²⁻ can be eliminated from water by the ion exchange technique, the most appropriate method due to its effectiveness and simplicity [29]. On the other hand, dissolved organic matter (DOM) can produce two contradictory effects (sensitization, contributing to free radical generation or quenching, producing a strong filter effect) in the photocatalytic process depending on its concentration [36]. In our case, due to the low DOM value (2.6 mg L⁻¹) in the effluent of WWTP, the quenching effect can be considered negligible. Finally, the concentration of Ti⁴⁺ dissolved at the end of the photocatalytic treatments (n = 15) was < 2.1 ± 1.3 μg L⁻¹.

4. Conclusions

Water shortage and uneven geographical distribution of rainfall is a progressively persistent problem in arid and semi-arid regions worldwide, where water management strategies call for the reuse of treated effluents in agriculture, especially in developing countries due to the challenge caused by climate change. Considering the large variety of EPs entering WWTPs, many transformation products and their parent compounds end up in the receiving environment. The use of WW for crop irrigation is exposing the agricultural environment to hundreds of substances, whose impact is currently unknown.

Generally, a notorious removal was observed for PMs after biological treatment, except for diclofenac and carbamazepine. However, primary (physical) and secondary (biological) treatments were not effective in removing more biorecalcitrant micropollutants, like PTs. Hence, other methods, such as AOPs (especially solar heterogeneous photocatalysis) constitute an important tool to detoxify polluted WW. As function of the rate constants calculated, the values of H₅₀ varied from 19 kJ m⁻² to 139 kJ m⁻² for diclofenac and terbuthylazine, respectively. All compounds were rapidly degraded during the photocatalytic treatment because the time necessary to obtain 90% degradation of the more recalcitrant compound (terbuthylazine) was achieved from 2 to 4 days, after 470 kJ m⁻² were recovered. This finding is correlated with the decrease in the DOC content of the waste solutions, indicating the mineralization of the EPs. The major limitation of AOPs is their relatively high cost due to energy consumption. However, it has been demonstrated that the use of sunlight, a renewable and cost-free energy source in combination with a photocatalyst (TiO₂) and an oxidant (Na₂S₂O₈) makes the process very attractive to reclaim water for crop irrigation, especially in those areas suffering water shortage but receiving many hours of sunshine per year. This research should be continued to find out the possible reaction intermediates originated from the parent compounds for both PMs (antibiotics, anti-

inflammatory, diuretics, anti-depressants and anti-convulsant) and PTs (insecticides and herbicides) as well as their reaction mechanisms.

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CRediT authorship contribution statement

G. Pérez-Lucas: Methodology, Writing – original draft. **A. El Aatik:** Methodology, Data curation. **M. Aliste:** Visualization, Methodology, Data curation. **V. Hernández:** Resources, Validation, Formal analysis. **J. Fenoll:** Supervision, Conceptualization, Validation. **S. Navarro:** Supervision, Conceptualization, Data curation, Funding acquisition, Writing – review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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