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Impact of Inorganic Anions on the Photodegradation of Herbicide Residues in Water by UV/Persulphate-Based Advanced Oxidation

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Impact of Inorganic Anions on the Photodegradation of Herbicide Residues in Water by UV/Persulphate-Based Advanced Oxidation

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Abstract: For some persistent pollutants, such as recalcitrant pesticides, the polluted water (urban, agricultural and/or industrial) treated by conventional wastewater treatment plants is in some cases insufficient to achieve the legally required level of purity. This issue is of particular concern in areas where low rainfall does not provide sufficient water resources to meet the needs of agriculture, requiring increased reuse of water from wastewater treatment plants. In this context, Advanced Oxidation Processes (AOPs) hold great promise for the removal of organic pollutants. This study first evaluates the effectiveness of UV/$S_2O_8^=$ compared to heterogeneous photocatalysis using UV/TiO_2 processes on the degradation of two commonly used herbicides (terbutylazine and isoproturon) in aqueous solutions using a photoreactor. In addition. the effect of UV wavelength on the degradation efficiency of both herbicides was investigated. Although degradation rate was higher under UV-254/$S_2O_8^=$ nm than under UV-365/$S_2O_8^=$ nm, complete degradation of the herbicides (0.2 mg L^{-1}) was achieved within 30 min under UV-366 nm using a $Na_2S_2O_8$ dosage of 250 mg L^{-1} in the absence of inorganic anions. To assess the impact of water matrix, the individual and combined effects of sulphate, bicarbonate and chloride were evaluated. They can react with hydroxyl and sulphate radicals formed during AOPs to form new radicals with a lower redox potential. The results showed negligible effects of sulphate, while the combination of bicarbonate and chloride seemed to be the key for the decrease in herbicide removal efficiency found when working with complex matrices. Finally, the main intermediates detected during the photodegradation process were identified and the likely pathways are proposed and discussed.

Keywords: matrix effect; herbicides; water treatment; persulphate; titanium dioxide; photooxidation

1. Introducción

Pesticides constitutes an issue of considerable political interest in the fields of environment, agriculture and human health under European Legislation. The Directive on the Sustainable Use of Pesticides (2009/128/EC) [1] aims to reduce the risks and impacts of pesticide use on human health and the environment, and to promote the use of integrated pest management and alternatives such as non-chemical approaches. In this context, water quality legislation is key to protecting public health and the environment in the EU. The Green Deal [2] and its associated strategies aim to reduce pesticide use and risks by 50% by 2030, with a focus on protecting ecosystems and enhancing biodiversity. For this purpose, the Water Framework Directive (WFD) 2000/60/EC [3] and its "*daughter directives*" such as the Groundwater Directive (GWD) 2006/118/EC [4] and the Environmental Quality Standard Directive (EQSD) 2013/39/EU [5] help to protect European waters from pesticide and chemical pollution. In line with advances in science and technology over the past decades, on 26 October 2022, the EU Commission published its proposal to amend the WFD and EQSD [6].

These directives focus largely on so-called priority substances. The Commission now proposes a simpler and more general definition of priority substances as chemicals that "*present a significant risk to or via the aquatic environment in a high proportion of Member States*", leaving open how many water bodies and Member States would be considered a "*high proportion*". Priority hazardous substances are "*priority substances that are also identified as hazardous on the basis that they are recognised in scientific reports, relevant Union legislation or relevant international agreements as being toxic, persistent and liable to bio-accumulate, or as giving rise to an equivalent level of concern where this concern is relevant to the aquatic environment*". The first list of 33 priority substances in the field of water policy was published in 2001 [7]. Subsequently, Directive 2008/105/EC [8] established Environmental Quality Standards (EQS) for these priority substances and certain other pollutants, which were subsequently updated by the EQSD Directive, covering 46 substances and groups of substances. Article 8 of the EQSD establishes a "*watch list*" of substances for which EU-wide monitoring data will be collected to provide adequate data for possible future inclusion in the priority list. The watch list was updated by the Commission in a series of implementing decisions, first in 2015 [9], then in 2018 [10], 2020 [11] and finally in 2022 [12]. These monitoring activities have led to the identification of several new priority substances, but not all of the substances originally included in a watch list are of EU-wide concern. Indeed, for the identification of new priority substances, the watch list mechanism seems to act as a filter. The updating of the list of priority substances and compounds on the watch list by delegated acts could speed up the process and make it less cumbersome. This argument, together with the "*one substance, one assessment*" argument, is used to justify transferring future work on priority substances and the setting of EQS values to the European Chemicals Agency (ECHA). In addition, the new Drinking Water Directive (DWD) 2020/2184 [13] sets quality objectives for pesticides at the tap and includes a "*risk-based approach*", provisions for the protection of raw water and the consideration of pesticide metabolites.

On the other hand, since the adoption of the EU Urban Wastewater Treatment Directive (UWWTD) 91/271/EEC [14] in 1991, the quality of Europe's rivers, lakes and seas has improved dramatically. EU countries have used EU funding to build collection systems and wastewater treatment plants. However, there is still pollution that needs to be tackled and is not covered by current legislation. According to the European Environment Agency (EEA), a report based on data from Member States shows that only 38% of EU surface water bodies are in good chemical status, 46% are not in good chemical status and 16% are in unknown chemical status [15]. Another recent EEA technical report provides an overview of the occurrence of pesticides and their main metabolites (breakdown or reaction products) in surface water (lakes and rivers, 180 pesticides) and groundwater (159 pesticides) focusing on the European level (up to 39 European countries) from 2007 to 2017 [16]. This report shows exceedance rates of 5 to 15 % for herbicides and 3 to 8 % for insecticides in surface water, while in groundwater the percentages were around 7 % for herbicides and less than 1 % for insecticides. Fungicides appeared to be less frequently exceeded for both surface water and groundwater. In order to achieve maximum crop yields, herbicides are widely used. Agricultural activities, cleaning of herbicide containers and equipment, and agricultural and herbicide manufacturing effluents are the main sources of herbicide water pollution. Two herbicides, isoproturon and terbuthylazine, are among the most frequently reported pesticides in surface and groundwater in Europe. More recently, another study proposes a protocol for a systematic review and meta-analysis to know the prevalence of pesticides in European water resources (watersheds, aquifers, rivers, sea and springs), wastewater (influent and effluent) and drinking water [17].

To address water pollution, the Commission has proposed an update of the Directive [18] to enable a significant reduction in the discharge of pollutants into the EU's lakes, rivers and seas. In this sense, for some of the most persistent pollutants, such as recalcitrant pesticides, the polluted water (urban, agricultural and industrial) treated by conventional wastewater treatment plants (WWTPs) is in some cases insufficient to achieve the legally required level of purity [19]. This issue is of particular concern in areas where low rainfall does not provide sufficient water resources to meet the needs of agriculture, requiring increased reuse of wastewater treatment plants. Water scarcity and the uneven geographical distribution of rainfall are concerns in arid and semi-arid areas where water management strategies advocate the reuse of treated wastewater in agriculture due to climate change. The EU has also addressed this issue by revising the minimum requirements for water re-use in the context of integrated management under Regulation 2020/741/EU on minimum requirements for water re-use [20]. The aim of this Regulation is to ensure the safety of recycled water for agricultural irrigation, promote circularity, support resilience to climate change and contribute to the objectives of the WFD by addressing water scarcity and related pressures on water resources. Growing public concern about the presence of pesticides in both wastewater and drinking water is leading to the development of new regulations that will undoubtedly have an impact on the design and operation of wastewater treatment plants in the coming years.

As stated in the EQSD, the sources of pollution must be identified, and the emissions of pollutants must be treated at source in the most economic, environmental and sustainable way. Concerns have increased, as has the need to identify them and apply new and effective techniques for their reduction and elimination. Conventional water treatment processes and technologies reduce pollution significantly, but not as much as current regulations require. The refractory nature of some pesticides, which can be toxic to the micro-organisms used, often renders biological treatments ineffective [21]. In addition, approaches based on adsorption, flocculation and ion exchange are not fully effective because they do not destroy the contaminant, but rather transfer it to a solid phase that requires subsequent treatment. Membrane technology has been used extensively in recent years to remove micropollutants from wastewater, but during the long-term process, the pollutants gradually accumulate in the adsorption materials until they reach saturation, after which they become inactive and consequently the pollutant removal and membrane filtration efficiency decreases [22], so it is usually combined with other techniques such as ozonation, activated carbon or photooxidation [23].

Advanced Oxidation Processes (AOPs) have been the most studied in recent years for the removal of pesticides and other micropollutants from wastewater [24-26]. Pesticides are oxidised by highly reactive oxygen species (ROS), mainly hydroxyl radicals ($HO^{\bullet}/OH^{-}$, E^0 = 1.9-2.7 V vs. NHE) and others such as superoxide anion ($O_2^{\bullet-}$) and hydridodioxygen ($HO_2^{\bullet}$). The main advantage of these technologies is that they achieve the removal, or at least the reduction, of pesticide levels by mineralisation rather than by transfer, as happens in conventional processes [27]. These technologies are particularly interesting in areas characterised by intensive agriculture and specific climatic patterns, where annual solar radiation is very high and water is scarce. More recently, AOPs based on sulphate radical anion ($SO_4^{\bullet-}$) have received increasing attention as an alternative to conventional $HO^{\bullet}$ based AOPs [28-30]. $SO_4^{\bullet-}$ has similar redox potential ($SO_4^{\bullet-}/SO_4^{=}$, E^0 = 2.6-3.1 V vs. NHE) compared to $HO^{\bullet}$, higher selectivity and, in some cases, longer half-lives ($t_{1/2}$ = 30-40 μs) than the $HO^{\bullet}$ ($t_{1/2} \leq$ 1μs), allowing more contact and transfer mass between radical and organic compounds [31]. $SO_4^{\bullet-}$ are typically generated from peroxydisulphate ($S_2O_8^{=}$, PDS), henceforth persulphate (PS) or peroxymonosulphate (HSO_5^{-}, PMS) that can be activated by energy (photochemical, sonochemical and thermal), carbonaceous materials, electrochemical activation, alkaline conditions, transition metal ions and various other oxidants such as ozone, hydrogen peroxide and calcium peroxide [32,33]. PMS has a smaller bond length (1.460 Å) than PS (1.497 Å), which explains its higher dissociation energy of the O-O bond (377 kJ mol^{-1}) compared to PS (92 kJ mol^{-1}) [28]. In most cases, UV/PS showed a better ability to oxidise organic pollutants than UV/PMS. This can be attributed to the quantum yield of radical formation, as the quantum yield of PS_{254} is about 1.8 M Einstein^{-1}, which is much higher than that of PMS_{254} (0.5 M Einstein^{-1}) [28]. As a result, more energy is required for PMS to generate a radical during the homolytic cleavage of the peroxide bond [34]. In the thermal/photochemical decomposition pathway of PS, two mols of $SO_4^{\bullet-}$ are formed per mole of $S_2O_8^{=}$ as a result of the cleavage of the peroxide bond (Eq. 1). $SO_4^{\bullet-}$ reacts with H_2O at all pHs to form $HO^{\bullet}$ (Eq. 2) which is the primary reactive species under basic conditions (Eq. 3). At acidic (pH < 7) and basic (pH > 9) pHs, $SO_4^{\bullet-}$ and $HO^{\bullet}$ are the dominant reactive species, respectively, while both radicals participate similarly in reactions at circumneutral pHs [28,35]. Finally, $SO_4^{\bullet-}$ promotes the mineralisation of pesticides to CO_2 and H_2O (Eq. 4) according to the following reactions:

$$S_2O_8^{2-} + h\nu(UV) \rightarrow 2SO_4^{\bullet-} \qquad k = 5.8 \times 10^{-5}\ M^{-1}\ s^{-1} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} + H^+ \qquad k = 200\ \mathrm{M^{-1}\,s^{-1}} \tag{2}$$

$$SO_4^{\bullet-} + HO^{-} \rightarrow HO^{\bullet} + SO_4^{2-} \qquad k = 6.5 \times 10^{7}\ \mathrm{M^{-1}\,s^{-1}} \tag{3}$$

$$SO_4^{\bullet-} + Pesticides \rightarrow Intermediates \rightarrow SO_4^{2-} + CO_2 + H_2O \tag{4}$$

However, both ($SO_4^{\bullet-}$ and $HO^{\bullet}$) undergo rapid and unwanted reactions (Eq. 5-7) where they are consumed, which may be limitations to their effectiveness [36]:

$$2SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \qquad k = 8.1 \times 10^{8}\ \mathrm{M^{-1}\,s^{-1}} \tag{5}$$

$$SO_4^{\bullet-} + HO^{\bullet} \rightarrow HSO_5^{-} \qquad k = 1.0 \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}} \tag{6}$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \qquad k = 6.1 \times 10^{9}\ \mathrm{M^{-1}\,s^{-1}} \tag{7}$$

As general rule, $SO_4^{\bullet-}$ is more susceptible to electron transfer reactions than $HO^{\bullet}$. In contrast to $SO_4^{\bullet-}$, $HO^{\bullet}$ is more prone to hydrogen abstraction or addition [31,37]. Thus, $SO_4^{\bullet-}$-based oxidation is presented as an alternative oxidative treatment to AOPs based on $HO^{\bullet}$ generation. $SO_4^{\bullet-}$ has some unique properties, such as being a very strong electron acceptor, which allows the degradation of persistent pesticides that are refractory to the $HO^{\bullet}$. In addition, $S_2O_8^{=}$, an environmentally friendly nontoxic oxidizer, avoids the problems of transport limitations because it is relatively stable and can be produced in high quantities.

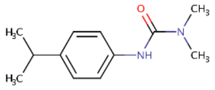
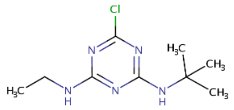
Overall, the elimination of pesticides and other micropollutants by $HO^{\bullet}$ and SO4$^{\bullet-}$ based-AOPs is largely influenced by the quality of the water matrix (dissolved constituents), which can have neutral, inhibitory or promoting, depending on the process and the mechanism by which these water constituents react [28,38]. In addition to organic species, inorganic species such as Cl^-, HCO_3^-/CO_3^{2-}, NO_3^-/NO_2^-, PO_4H^{3-} and/or SO_4^{2-}, among others, can also acts as inhibitors either by scavenging and generating radicals such as $ClOH^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$, $CO_3^{\bullet-}$, $HCO_3^{\bullet-}$, $Br^{\bullet}$, $Br_2^{\bullet-}$, $NO^{\bullet}$, and/or $H_2PO_4^{\bullet}$, which have a lower E^0 than $HO^{\bullet}$ and $SO_4^{\bullet-}$ or by promoting the formation of ROS, as in the case of NO_3^-, which is capable of generating $HO^{\bullet}$ and $NO_2^{\bullet}$ radical species that promote the photodegradation of pesticides, especially those for which indirect photolysis is the main reactive pathway. For all the above mentioned, the aim of this work has been to evaluate the impact of inorganic ions on the removal of two herbicides (isoproturon and terbuthylazine) commonly found in wastewater using UV/persulphate-based advanced oxidation under laboratory conditions.

2. Materials and Methods

2.1. Herbicides, solvents and reagents

Analytical standards of the herbicides, isoproturon (ISP), terbuthylazine (TBZ) and their main metabolites were purchased from Dr. Ehrenstorfer GmBh (Augsburg, Germany), all with purity greater than 95%. The main physical-chemical characteristics of the herbicides studied are shown in Table 1. Titanium dioxide (70 anatase/30 rutile, 99.5%, BET 50 m^2 g^{-1}, size <21 nm) Aeroxide™ P25 was supplied by Nippon Aerosil Co Ltd. (Osaka, Japan). Solvents (H_2O, CH_3CN, CH_3OH, CH_2O_2), all HPLC-grade and reagents ($Na_2S_2O_8$, NaCl, Na_2SO_4 and $NaHCO_3$) with purity > 98.5% were provided by Scharlab (Barcelona, Spain).

Table 1. Main physico-chemical properties of the herbicides studied.

Herbicide[1]	Structure	Formula	MW[2]	S_{H2O}[3]	log K_{ow}[4]	*H*[5]
Isoproturon[PU]		$C_{12}H_{18}N_2O$	206.3	70	2.5	1.5×10^{-5}
Terbuthylazine[TZ]		$C_9H_{16}ClN_5$	229.7	7	3.4	2.3×10^{-3}

[1] PU: Phenulurea; TZ: *s*-Triazine; [2] Molecular weight; [3] Water solubility (mg L^{-1}); [4] Partition coefficient n-octanol/water; [5] Henry Law Constant (Pa m^3 mol^{-1}).

2.2. Experimental setup

The degradation of the herbicides was carried out by the UV/$S_2O_8^=$ or UV/TiO_2 process in a 2 L (10 cm Ø x 25 cm long) Pyrex batch cylindrical photoreactor (SBS, Barcelona, Spain) equipped with a magnetic stirrer, as previously described [39]. The study was carried out in batch circulation mode at a flow rate of 600 mL min^{-1}. The UV light source was two Philips LIT 8 W low-pressure mercury lamps with peak emission at 254 and 366 nm. Typical irradiance of approximately 10 mW cm^{-2} was measured using a Delta Ohm HD 2102.2 radiometer (Caselle di Selvazzano, Italy). Nitrogen was continuously fed into the photoreactor at a flow rate of 0.5 L min^{-1} to ensure that oxygen did not interfere with the process. The system was thermostatically controlled by circulating water to maintain a constant temperature of 23±1 ^{0}C. The photochemical reactor was filled with 2000 mL of Type II analytical grade water (pH 6.7, ORP 220 mV, conductivity < 20 µS cm^{-1}, TOC < 30 µg L^{-1}) and spiked with 0.2 mg L^{-1} of each herbicide. After the addition of 250 mg L^{-1} $Na_2S_2O_8$ or 250 mg L^{-1} of TiO_2, the two UV lamps (1 x 254 nm + 1 x 366 nm or 2 x 366 nm) were switched on and degradation was studied for 120 min. All experiments were replicated three times (n = 3). Table 2 summarises the test carried out.

2.3. Sample preparation and analytical determinations

Sample (25 mL) was passed through an Oasis® HLB 60 µm (500 mg) extraction cartridge purchased from Waters (Milford, MA, USA) using a Visiprep™ SPE vacuum manifold supplied by Supelco (Madrid, Spain) at a flow rate of approximately 3 mL min^{-1}. The extraction cartridge was previously conditioned with 3 mL of CH_3OH and equilibrated with 3 mL of acidified ultrapure water (pH = 3). After passing through the cartridge, the sample was washed with 5 mL of Milli-Q water (18.2 MΩ·cm), the eluate was discarded and the column was dried with air. The analytes were then eluted with 5 mL CH_3OH and the extracts were evaporated to dryness. Finally, the residues were dissolved in 500 µL of CH_3CN and filtered through 0.22 µm polytetrafluoroethylene (PTFE) syringe filters prior to the chromatographic analysis.

Table 2. Summary of the trials carried out.

	Trials	pH	[a]CE	[b]$SO_4^=$	[b]Cl^-	[b]HCO_3^-
1	UV (1 x 254 nm + 1 x 366 nm)	6.7	< 5	-	-	-
2	UV (2 x 366 nm)	6.7	< 5	-	-	-
3	$Na_2S_2O_8$	5.1	240	-	-	-
4	$Na_2S_2O_8$/UV (254/366 nm)	5.1	242	-	-	-
5	$Na_2S_2O_8$/UV (366 nm)	5.0	246	-	-	-
6	TiO_2/UV (366 nm)	5.3	< 5	-	-	-
7	$Na_2S_2O_8$/UV (366 nm)	4.7	760	250	-	-
8	$Na_2S_2O_8$/UV (366 nm)	8.3	377	-	-	125

9	$Na_2S_2O_8$/UV (366 nm)	5.2	610	-	150	-
10	$Na_2S_2O_8$/UV (366 nm)	8.4	1200	250	150	125

[a] µS cm^{-1}; [b] mg L^{-1}.

The determination of herbicide residues was carried out using an HPLC system consisting of a Waters e2695 separation module (Waters, Mildford, USA) equipped with a quaternary pump and an autosampler and coupled to a Waters 2998 photodiode array detector (PDA). Data were processed using Water Empower software (version 3). Separation was performed on a 100 mm × 4.6 mm, 5 µm, Phenomenex Kinetex XB-C_{18} analytical column (Madrid, Spain) with a mobile phase consisting of CH_3CN (solvent A) and an aqueous solution of HCOOH (0.1%) (Solvent B) under gradient mode, with the temperature of the column oven set to 25 °C. The following gradients were used: 30% of A for 1 min, linearly increased to 90% of A for 9 min, held for 1 min and decreased to 30% of A for 2 min to allow equilibration before the next injection (5 min). The flow rate was maintained (0.5 mL min^{-1}) and the volume injected was 50 µL. Confirmation criteria were retention times and recovered spectra (190-400 nm). The detection wavelengths were 222 nm and 241 nm for TBZ and ISP, respectively. Standard solutions containing the herbicides were used to construct calibration curves (0.1-1000 µg L^{-1}). The limits of detection (LOD) and limits of quantitation (LOQ) were obtained by dividing the signal-to-noise ratios of 3 and 10 times, respectively, by the angular coefficients of the calibration curves. In addition, HPLC-MS^2 analysis of the intermediates generated during the UV/PS process was performed on an Agilent 1200 HPLC system equipped with the same analytical column as previously described and coupled to an Agilent G6410A triple quadrupole (QqQ) mass spectrometer (MS) operating in electrospray (ESI) positive ion mode. The most abundant fragment ion was selected for quantification and the second for identity confirmation. Data acquisition was performed using MassHunter software.

Dissolved organic carbon (DOC) content was determined using a Multi N/C 3100 TOC Analyzer (Analytic Jena AG, Jena, Germany) after passing the samples through a nylon syringe filter (0.45 mm) prior to analysis to remove particulate OC from the sample. A GLP 21 pH-meter and GLP 31 conductivity-meter both of Crison Instruments (Barcelona, Spain) were used for pH and conductivity measurements, respectively. The statistical software SigmaPlot (Systat, Software Inc., San Jose, CA, USA) v.15 was used to fit the experimental data.

3. Results and Discussion

3.1. Photodegradation of herbicides by UV, $Na_2S_2O_8$ and UV/$Na_2S_2O_8$

The efficiency of degradation of the herbicides has been defined according to the following equation (Equation 8):

$$R_r(\%) = \left(\frac{H_0 - H_t}{H_0}\right) x\ 100 \quad (8)$$

where R_r is the removal rate, H_0 is the initial concentration of herbicide and H_t is the concentration of herbicide at time t.

UV radiation has been proposed as an effective method of removing herbicides from water [40]. Most herbicides are photoactive because their structure generally contains aromatic rings, heteroatoms and other functional groups that make them susceptible to absorbing UV-vis radiation (direct photolysis) or to reacting with photosensitive species capable of inducing photodegradation of herbicides in water (indirect photolysis). The results of herbicide degradation using UV (254/366 nm), UV (366 nm), PS alone, UV (254/366 nm)/PS and UV (366 nm)/PS combined (trials 1-5) are shown in Figure 1.

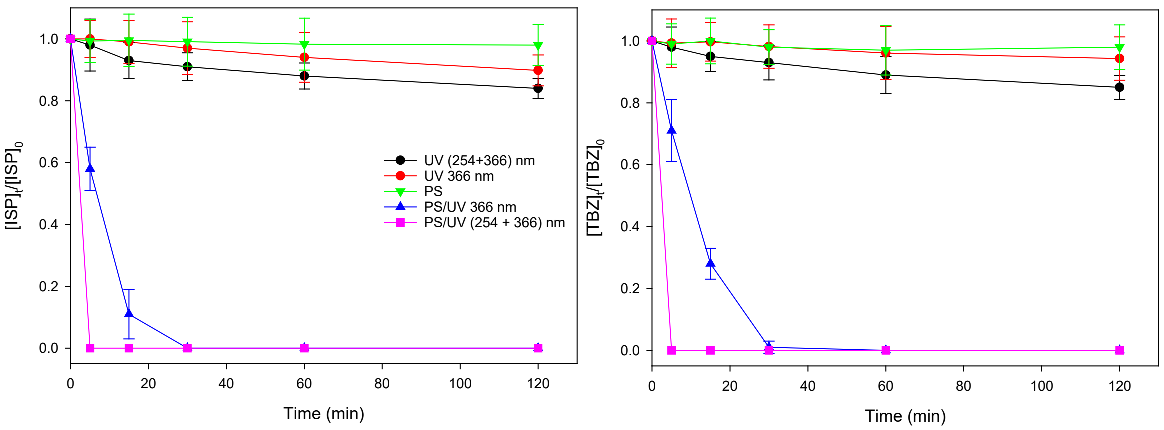


Figure 1. Evolution of herbicide residues over time in photolytic, PS and UV/PS tests.

Minimal degradation (R_r about 2%) was observed for both herbicides when PS was used in the dark. When UV irradiation (254 or 366 nm) was used, the R_r of ISP was increased to 16% (254 nm +366 nm) and 10% (366 nm only), while TBZ removal was 15% (254 nm +366 nm) and 7% (366 nm only) after 120 min photoperiod. Some studies showed that TBZ undergoes limited photodegradation and is considered photolytically and hydrolytically stable under at environmentally relevant temperatures and pH conditions [41]. However, photodegradation was drastically increased in both cases when PS was activated with UV, either at a combined wavelength (254 + 366 nm) or at 366 nm only. After 5 min of irradiation (254 + 366 nm), the levels of both herbicides in absence of inorganic anions were below the LOD, whereas after 30 min of irradiation with 366 nm only, both herbicides practically disappeared. Similar results were obtained by Lin and Wu [42], who compared the effectiveness of PS activation under two wavelengths (254 nm and 365 nm) on the photodegradation of polyvinyl alcohol. PS Activation by UV light might not be a promising method in industrial applications because of the high cost and the requirement of complex equipment. Although the activation of PS by UV/254 nm improve the efficiency of the process, it is important to remark that of the total radiant energy emitted by the Sun, only the part with a wavelength between 280-3000 nm, known as short-wave radiation, reaches the surface of our planet. This includes UVB (280-315 nm) and UVA (315-400 nm), but not UVC (100-280 nm). Therefore, and considering that the UVC fraction does not reach the earth's surface, this fraction cannot be used in solar treatments for water purification because the spectrum of sunlight at earth’s surface begins around 300 nm. The UV-365 nm/PS can therefore be considered as a clearly economical and effective process for the degradation of the herbicides studied using natural sunlight. For this reason, the UVA fraction (366 nm) was used in the subsequent tests, in view of the satisfactory results obtained.

3.2. Comparing UV/TiO_2 and UV/$Na_2S_2O_8$ efficiency

To compare the effectiveness on the degradation of the two herbicides, UV/PS (test 5) and heterogeneous photocatalysis using UV/TiO_2 as catalyst (test 6) were compared. Figure 2 shows the evolution of the residues of both herbicides under these conditions. As can be seen, in both cases a higher efficacy was observed for UV/PS than for UV/TiO_2, which is more notorious in the case of TBZ.

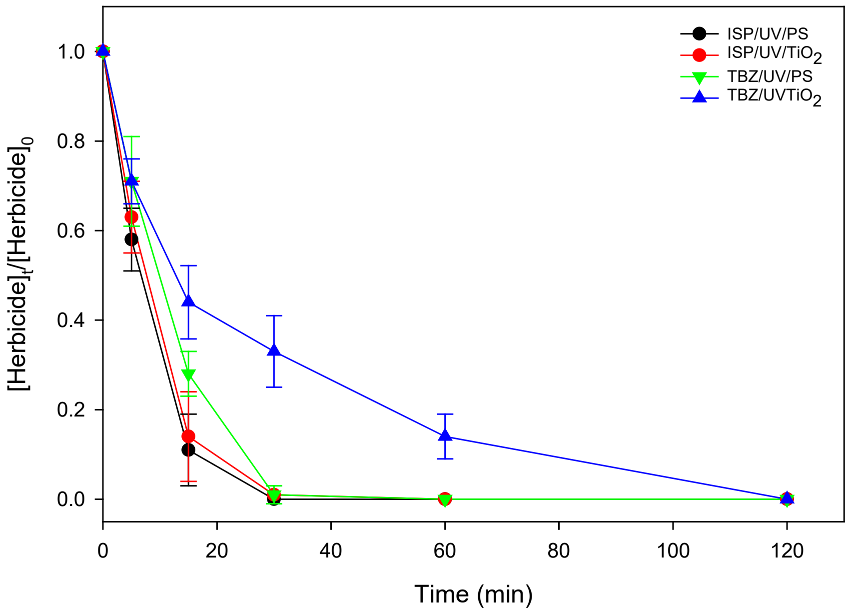


Figure 2. Herbicide photodegradation in UV/PS and UV/TiO_2 systems.

According to the law of mass action, the photodegradation of the herbicides could be modelled assuming pseudo-first order kinetics [43]. The kinetic study of the experimental results showed that the degradation process of both herbicides under UV basically conformed to the single first-order (SFO) kinetic model according to the following equations (Equation 9-11):

$$-\frac{d[H]}{dt} = kt \tag{9}$$

$$[H]_t = [H]_0\, e^{-kt} \tag{10}$$

$$\ln[H]_t = \ln[H]_o - kt\ \frac{\ln[H]_o}{\ln[H]_t} = kt \tag{11}$$

where $[H]_t$ is the concentration of herbicide in solution at time t, $[H]_0$ is the initial herbicide concentration in solution, t is the time (min), and k is the apparent reaction rate constant (min^{-1}). The slope of $\ln(C_0/C)$ plotted against time gives the value of k. From the above equation, the time required for X% disappearance of herbicides (disappearance time) from the water can be calculated according to Equation 12:

$$DT_x = ln\left(\frac{100}{100-x}\right)/k \tag{12}$$

The fit to the selected model of the experimental data obtained is shown in Table 3. Consistent with the data shown in this table, the SFO model fitted the exponential decay curve realistically with $R^2 \geq 0.97$ in all cases and standard error of estimation ($S_{y/x}$) < 0.05. The ratio between the apparent rate constants (k_{PS}/k_{TiO2}) was > 1 in both cases, 1.1 for ISP and 3.3 for TBZ, indicating a higher reaction rate for both herbicides using UV/PS compared to UV/TiO_2. For this reason, UV/PS was used to study the impact of inorganic anions on the photodegradation on the herbicides studied.

Table 3. Kinetic parameters obtained following SFO model for the photocatalytic degradation of herbicides in water in absence of inorganic anions.

Test	Terbuthylazine					Isoproturon				
	R	**C/C_0**	**^{1}k**	**$^{2}S_{y/x}$**	**$^{3}DT_{50}$**	**R**	**C/C_0**	**^{1}k**	**$^{2}S_{y/x}$**	**$^{3}DT_{50}$**
UV/PS	0.9952	1.01	0.1257	0.03	5.51	0.9953	1.01	0.1267	0.03	5.47
UV/TiO_2	0.9736	0.94	0.0409	0.07	16.94	0.9935	1.02	0.1137	0.04	6.09

[1] (min^{-1}); [2] Standard Error of Estimation; [3] (min).

3.3. *Effect of inorganic anion content on herbicide photodegradation using $Na_2S_2O_8$/UV*

The composition of the water on the photodegradation process is critical to the assessment of its suitability for real wastewater treatment, and its impact can be complex in some cases. In addition to dissolved organic matter, the unfavorable effects of some inorganic ions (mainly anions) such as Cl^-, HCO_3^-/CO_3^{2-}, NO_3^-/NO_2^-, PO_4H^{3-} and/or SO_4^{2-}, among others can be explained by the fact that they reduce the oxidising power of the solution. The scavenging of $HO^\bullet$ and $SO_4^{\bullet-}$ by various anions generates the corresponding radicals such as $ClOH^{\bullet-}$, $Cl^\bullet$, $Cl_2^{\bullet-}$, $CO_3^{\bullet-}$, $HCO_3^\bullet$, $Br^\bullet$, $Br_2^{\bullet-}$, $NO^\bullet$, and/or $H_2PO_4^\bullet$, which have a lower E^0 than $HO^\bullet$ and $SO_4^{\bullet-}$ or by promoting the formation of ROS, as in the case of NO_3^-, which is capable of generating $HO^\bullet$ and $NO_2^\bullet$ radical species, which promote the photodegradation of pesticides, especially those for which indirect photolysis is the main reaction pathway [28,38,44]. Some anions and cations present in water are transparent to solar radiation, while nitrate (λ = 303 nm) and nitrite (λ = 355 nm) show some adsorption. Both absorb light and undergo homolysis to form $HO^\bullet$ and nitrogen reactive species such as $NO^\bullet$, $NO_2^\bullet$, N_2O_3, and/or N_2O_4 such as leading to the herbicide degradation, although $HO^\bullet$can be further scavenged by NO_2^- to form $NO_2^\bullet$ [45]. However, the concentrations of NO_3^-/NO_2 in real wastewater is usually low (< 5 mg L^{-1}). For this reason, we have assessed the influence of SO_4^{2-}, Cl^- and HCO_3^-, which are present at much higher concentrations.

As shown in Figure 3, the removal efficiency of the herbicides was not affected by the presence of sulphate at the concentration studied. Even, the presence of SO_4^{2-} in the solution (test 7) has a positive effect on the photodegradation of both herbicides, especially for ISP, because higher values of *k* were obtained according to the results shown in Table 4. $SO_4^=$ is not a strong scavenger of $HO^\bullet$ such as Cl^-, HCO_3^- and CO_3^{2-}. On the contrary, it has been shown to promote the oxidative degradation of the antibiotics chloramphenicol [46] and ciprofloxacin [47] or polyvinyl alcohol [42], as occurs in our case. According to Cabrera-Reina et al. [48], the removal efficiency of acetamiprid, carbamazepine and caffeine was also unaffected by sulphate concentration in the range 0-550 mg L^{-1}. Therefore, sulphate impact on activated PS processes, summarized in Equation 13-14, is very low.

$$SO_4^{2-} + HO^{\cdot} \rightarrow \ SO_4^{\cdot-} + \ OH^- \tag{13}$$

$$SO_4^{2-} + \ SO_4^{\cdot-} \ \rightarrow S_2O_8^{2-} + \ e^- \tag{14}$$

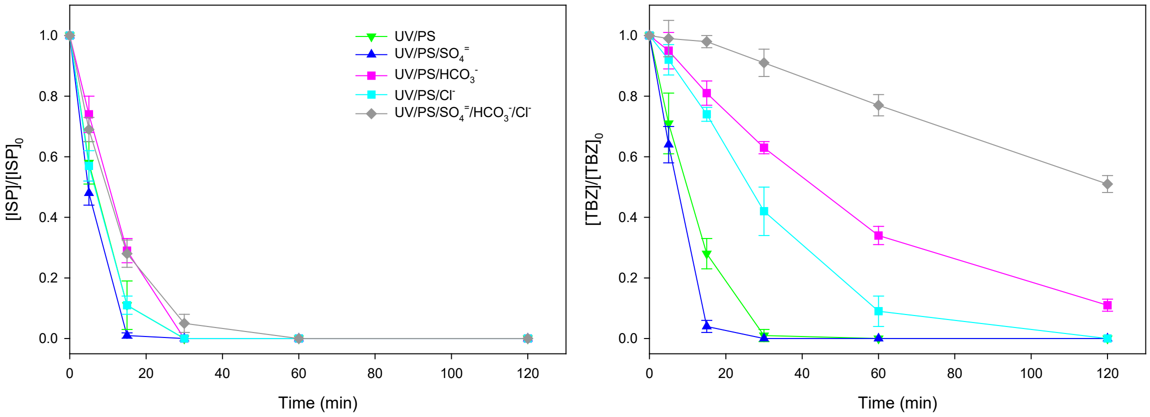


Figure 3. Anion-influenced UV/PS herbicide degradation.

Chloride ion (Cl^-) is one of major inorganic anions in natural water. The adverse effect of Cl^-, especially at high concentration on the degradation of many organic micropollutants has been reported by some authors [28]. In the case of ISP, a minimal influence was observed when chloride ions (150 mg L^{-1}) are present in the solution because $k_{PS}/K_{PS/Cl}$ is 0.98 (Table 4). However, a significant influence was observed for TBZ where the ratio $k_{PS}/K_{PS/Cl}$ was 4.1 as can be seen in Figure 3. The adverse effects of high Cl^- concentrations could favour the scavenging of $HO^\bullet$ and $SO_4^{\bullet-}$ according to the following reactions (Equation 15-18):

$$Cl^- + SO_4^{\cdot -} \rightarrow SO_4^{2-} + Cl^{\cdot} \tag{15}$$

$$Cl^- + HO^{\cdot} \rightarrow ClOH^{\cdot} \tag{16}$$

$$ClOH^{\cdot} + H^+ \rightarrow H_2O + Cl^{\cdot} \tag{17}$$

$$Cl^- + Cl^{\cdot} \rightarrow Cl_2^{\cdot -} \tag{18}$$

Table 4. Kinetic parameters obtained following SFO model for the photocatalytic degradation of herbicides in saline waters.

Anion	**Terbuthylazine**				**Isoproturon**			
	R	**^{1}k**	**^{2}S$_{y/x}$**	**^{3}DT$_{50}$**	**R**	**^{1}k**	**^{2}S$_{y/x}$**	**^{3}DT$_{50}$**
UV/PS	0.9952	0.1257	0.03	5.5	0.9953	0.1267	0.03	5.5
UV/PS/$SO_4^{=}$	0.9755	0.1287	0.08	5.4	0.9917	0.1672	0.04	4.1
UV/PS/HCO_3^-	0.9963	0.0175	0.02	40	0.9875	0.0844	0.05	8.2
UV/PS/Cl^-	0.9829	0.0307	0.06	23	0.9961	0.1284	0.03	5.4
UV/PS/$SO_4^{=}$+HCO_3^-+Cl^-	0.9755	0.0054	0.03	128	0.9979	0.0849	0.03	8.2

^{1} (min^{-1}); ^{2} Standard Error of Estimation; ^{3} (min).

Compared to $HO^{\bullet}$-based AOPs, radical scavenging by Cl^- in $SO_4^{\bullet-}$-based AOPs is a major challenge. The reaction between Cl^- and $HO^{\bullet}$ gives $ClOH^{\bullet-}$ (Equation 16), but this is a reversible reaction that mostly returns to $HO^{\bullet}$ [49]. In contrast, $SO_4^{\bullet-}$ produces $Cl^{\bullet}$ (E^0 = 2.4 V) by one-electron abstraction from Cl^- (Equation 15), which is often reflected in lower efficiencies in organic pollutant removal as well as higher generation of reactive chlorine species such as $Cl_2^{\bullet-}$ (E^0 = 2.1 V), $ClO_2^{\bullet}$ (E^0 = 0.9 V), ($ClO^{\bullet}$ E^0 = 1.4 V) and $ClOH^{\bullet-}$ (E^0 = 1.9) V, all of them with lower E^0 than $HO^{\bullet}$ and $SO_4^{\bullet-}$ [50].

An overall negative effect of HCO_3^- and CO_3^{2-} anions on the $SO_4^{\bullet-}$-based AOPs has traditionally been assumed [51]. The alkalinity of a water body is mainly contributed by $CO_3^{2-}$and HCO_3^- ions, which are generally present in natural waters ranging from 50-250 mg L^{-1}. Both $CO_3^{2-}$and HCO_3^- are known to be radical scavengers in AOPs [28]. Among them, the radical scavenging ability of CO_3^{2-} is stronger than that of HCO_3^- due to its higher reaction rate constant with $OH^{\bullet}$ (3.9×10^8 M^{-1} s^{-1} *vs* 8.5×10^6 M^{-1} s^{-1}) [52].

However, depending on the chemical structure of the pesticides, the HCO_3^-/CO_3^{2} effect will be neutral, positive or negative for their degradation rate, which makes it very difficult to predict due to the complex mixtures of pollutants always present in wastewater [53,54]. Although $CO_3^{\bullet-}$ have low redox potential than $HO^{\bullet}$, it could exhibit better removal performing in degrading organic micropollutants, which could be due to its high selectivity and longer survival time in solution [55].

When HCO_3^- was added, the initial pH of the aqueous solution changed to about 8.3, rather than pH 6.7 without the addition of any anions, and the basic conditions reduced the efficiency of degradation of both herbicides, as discussed by some authors [56]. CO_2, CO_3^{2-} and HCO_3^- are present in aqueous media at pH > 4. CO_3^{2-} and HCO_3^-, responsible of water alkalinity, can compete with herbicides for $HO^{\bullet}$ and $SO_4^{\bullet-}$ to generate other weaker radicals, such as $CO_3^{\bullet-}$ and/or $HCO_3^{\bullet}$. Above pH = 10.3, CO_3^{2-} is the prevalent specie, but at pH below 8.3 all CO_3^{2-} has been converted to HCO_3^- [57]. As pH decreases, HCO_3^- also decreases and dissolved CO_2 increases (Figure 4). The relationship between CO_3^{2-}/HCO_3^- and solution pH is represented as follows (Equation 19):

$$pH = pK_a - log\frac{[HCO_3^-]}{[CO_3^{2-}]}\ pK_a = 10.3 \tag{19}$$

The high concentration (125 mg L^{-1}) of HCO_3^- strongly scavenges $HO^{\bullet}$ and $SO_4^{\bullet-}$, generating electrophilic $CO_3^{\bullet-}$, a more selective and less reactive reaction radical with a lower electrode potential (E^0 = 1.6 V) than $HO^{\bullet}$ and SO_4 [58]. Detailed reaction mechanisms between $CO_3^{\bullet-}$ and micropollutants are still largely unclear. In previous studies, the single electron transfer was determined to be the dominant pathway [52]. The nature of $CO_3^{\bullet-}$ makes it more selective towards electron-rich moieties such as such as -NH_2, -OH and aromatic rings. $HCO_3^{\bullet}$ has lower reaction rate with organic pollutants than $HO^{\bullet}$. For $SO_4^{\bullet-}$, it has lower reaction rate with CO_3^{2-} (6.1×10^6 M^{-1} s^{-1}) and similar reaction rate with CO_3^{2-} (9.1×10^6 M^{-1} s^{-1}) compared to $HO^\bullet$ [59]. Nevertheless, the presence of CO_3^{2-}/HCO_3^- can cause the transformation of $HO^\bullet$ and $SO_4^{\bullet-}$, which can further affect the performance of AOPs. In radical-based treatment processes, $CO_3^{\bullet-}$ and $HCO_3^\bullet$ can be formed by oxidation of CO_3^{2-} and HCO_3^- with highly reactive radical species, such as $HO^\bullet$ and $SO_4^{\bullet-}$ (Equation 20-23) [60]:

$$CO_3^{2-} + HO^{\cdot} \rightarrow CO_3^{\cdot-} + OH^- \tag{20}$$

$$CO_3^{2-} + SO_4^{\cdot-} \rightarrow CO_3^{\cdot-} + SO_4^{2-} \tag{21}$$

$$HCO_3^- + HO^{\cdot} \rightarrow H_2O + CO_3^{\cdot-} \tag{22}$$

$$HCO_3^- + SO_4^{\cdot-} \rightarrow SO_4^{2-} + HCO_3^{\cdot} \rightarrow SO_4^{2-} + H^+ + CO_3^{\cdot-} \tag{23}$$

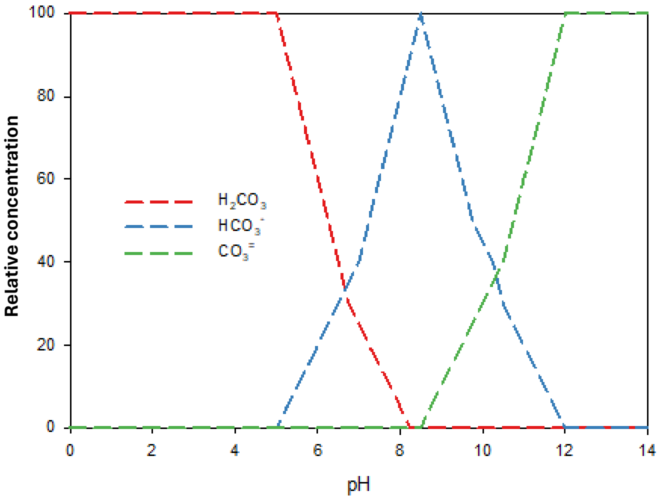


Figure 4. Speciation of carbonate species in water as function of pH. Adapted from Manaham [57].

In addition, the carbonate precipitation can result in fouling on the membrane surface, which further affects the removal efficiency of micropollutants [61].

After studying the individual effects of $SO_4^=$, Cl^- and HCO_3^- on the UV/PS process, their combined effect was then assessed (test 10). The R_r of both herbicides is presented in Figure 3. As can be seen, Cl^- (150 mg L^{-1}) and HCO_3^- (125 mg L^{-1}) generally had a negative effect on herbicide R_r, although the magnitude depended on the chemical structure of each herbicide. As can be observed in Table 4 the R values ranged from 0.976 to 0.996 for TBZ and 0.988 to 0.998 for ISP, with standard errors of estimation less than 0.08 and 0.05, respectively, indicating good fit. The time to 50% disappearance (DT_{50}) for ISP was slightly higher in the presence of anions (8.2 min) than in the corresponding experiment carried out in the absence of anions (5.5 min). However, a substantial effect was observed for TBZ, as the DT_{50} was approximately 23 times higher than in the absence of anions, mainly due to the impact of HCO_3^-.

The initial pH of the aqueous solution of herbicides in absence/presence of inorganic anions decreased in all cases during the photoperiod (Table 5). The acidification may be caused by the formation of acidic products as consequence of the herbicide degradation, and acidic photoproducts derived from $S_2O_8^=$, such as HSO_4^-, with release of H^+ (Equation 24, 25) as reported by Yang et al. [28]:

$$SO_4^{\bullet-} + H_2O \rightarrow HO^\bullet + HSO_4^- \tag{24}$$

$$HSO_4^- \rightarrow SO_4^{2-} + H^+ \tag{25}$$

Table 5. Evolution of pH in the different tests.

Time (min)	pH									
	Trial									
	1	2	3	4	5	6	7	8	9	10
0	6.70	6.74	5.09	5.11	5.04	5.33	4.69	8.29	5.20	8.39
5	6.53	6.56	4.97	5.02	5.00	5.15	4.60	8.20	4.79	8.36
15	6.42	6.41	4.81	4.88	4.84	4.93	4.46	8.23	4.46	8.39
30	6.29	6.33	4.58	4.60	4.64	4.84	4.29	8.24	4.20	8.40
60	6.15	6.19	4.23	4.34	4.38	4.75	4.01	8.21	3.93	8.35
120	6.07	6.14	3.86	3.88	3.95	4.61	3.77	8.07	3.66	8.25

In addition, the concentration of SO_4^{2-} increased significantly throughout the process (Equation 25), as can be seen from the EC values shown in Table 6, due to the transformation of the initially added $S_2O_8^{2-}$ into SO_4^{2}. Various methods have been proposed to remove $SO_4^{=}$ from water over the past decades, such as adsorption on activated carbon, neutralisation with calcium carbonate, biological treatment, reverse osmosis and dialysis, and ion exchange. The choice of wastewater treatment method is usually based on the type of wastewater, the removal rate, the waste concentration and the cost of treatment. Of these, adsorption on an ion exchange resin is the most popular method for removing $SO_4^{=}$ from water and wastewater and shows good potential for industrial wastewater treatment [62].

Table 6. Evolution of EC in the different tests.

Time (min)	EC (µS cm^{-1})									
	Trial									
	1	2	3	4	5	6	7	8	9	10
0	< 5	< 5	242	238	242	< 5	760	377	610	1200
5	< 5	< 5	248	245	249	7	764	380	620	1234
15	< 5	< 5	255	252	254	10	769	383	644	1253
30	< 5	< 5	261	263	260	12	773	386	662	1259
60	< 5	< 5	273	270	266	18	795	389	674	1262
120	< 5	< 5	285	287	280	23	825	395	700	1265

Figure 5 shows the evolution of DOC during the different tests carried out. It is important to monitor the process using this tool because only DOC values close to zero guarantee that recalcitrant pollutants or intermediates with greater persistence and toxicity than the initial ones do not persist. In the absence of any ions (test 5) and in the presence of $SO_4^{=}$ (test 7) a high mineralisation rate was observed because the remaining DOC after 120 min was less than 5%. However, in the presence of HCO_3^- (test 8) and Cl^- (test 9), the residual DOC concentration after 120 min was 20% and 10% respectively, while in the presence of all anions in the reaction solution (test 10), the residual DOC concentration at the end of the experiment was significantly increased (37%). These residual DOC fraction may be due to the partial removal of herbicides in aqueous solution and the formation of non-degradable organic intermediates produced during the irradiation time.

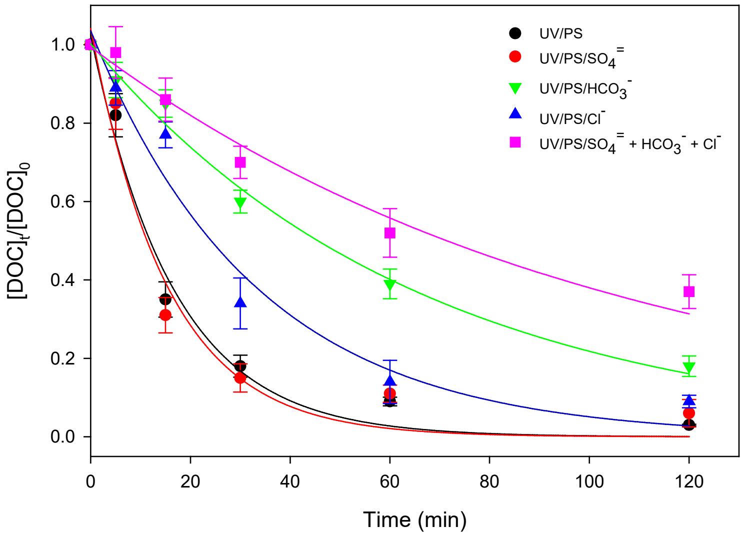


Figure 5. Evolution of DOC in UV/PS system as a function of the anionic content.

3.4. Degradation pathway of herbicides with UV/$Na_2S_2O_8$

To gain a better understanding of the reaction mechanisms involved in the photodegradation of both herbicides, the evolution of key intermediates during the irradiation experiment was also followed by comparison with authentic analytical standards using quantitative HPLC-MS^2 analysis. Figure 6 shows the proposed degradation pathways for both herbicides. The metabolic pathway involved in the degradation of ISP mainly involves two successive *N*-demethylations followed by hydrolysis to the aniline-based metabolite which can then be further degraded. Photooxidation of TBZ leads to dealkylation of the amine groups, dechlorination and subsequent hydroxylation [66].

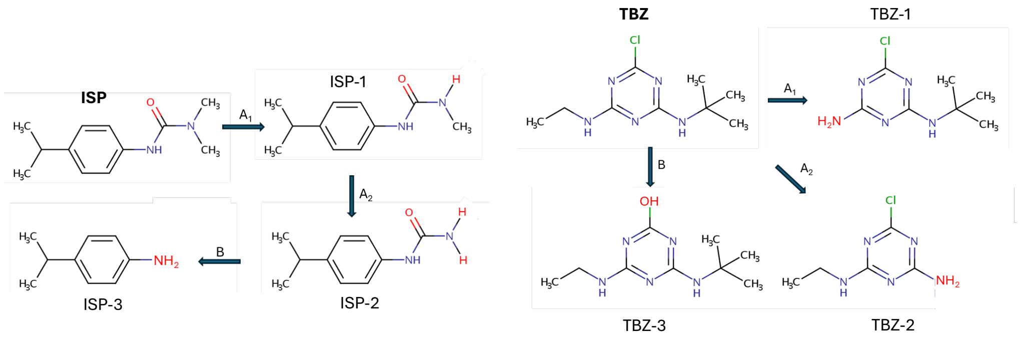


Figure 6. Proposed degradation pathways for ISP including *N*-dealquilations (A1 and A2) and hydrolysis to aniline derivative (B) and TBZ involving dealkylations (A1 and A2), dechlorination and subsequent hydroxylation (B).

Three transformation products of ISP, 1-(4-Isopropylphenyl)-3-methylurea (ISP-1), 1-(4-isopropylphenyl)urea (ISP-2) and 4-isopropylaniline (ISP-3) were identified during experiment 10, although their concentrations were below their LOQs (<-2 µg L^{-1}) at the end of the photoperiod (120 min). The maximum concentration peak was found after 30 min from the start, reaching levels between 4 and 8 µg L^{-1}. These intermediates were also isolated by other authors in aqueous suspensions of TiO_2 and ZnO under UV light [63,64]. In the case of TBZ, the photooxidation of the parent compound was accompanied by the appearance of desethyl-terbuthylazine (TBZ-1), deisopropyl-atrazine (TBZ-2) and terbuthylazine-2-hydroxy (TBZ-3), whose residual levels after 120 min were in the range of 0.5-1.2 µg L^{-1}, respectively. Fenoll et al [65] found TBZ-1 and TBZ-3 intermediates using TiO_2 and ZnO as photocatalysts. The presence of these degradants confirms the behaviour observed in the evolution of DOC indicating that there is no total mineralisation of the herbicides in the presence of anions. It should be remembered that for mineralisation of the pollutant to occur, not only must it disappear, but all the organic carbon must be converted into inorganic carbon in the form of CO_2, since the DOC value is independent of the oxidation state of the compounds present in the aqueous solution.

4. Conclusions

The need to increase the supply of water is linked to both the scarcity of the quantity available and the deterioration of its quality. There are many families of chemical compounds, many of which are organic in nature, that can have a negative impact on natural ecosystems and adversely affect water quality, thus posing a risk to human health. Among these, pesticides stand out for their toxicity and persistence, and their control is currently a priority at institutional level. Many of them are carcinogenic, endocrine disrupting or even teratogenic and highly persistent in the environment due to their complex structures and resistance to degradation. As a result of the current water scarcity, more emphasis should be placed on the 3*R*s (*R*ecover, *R*ecycle and *R*euse) approach to wastewater treatment, both industrial and agricultural.

Each water treatment method has its own drawbacks, including those related to feasibility, availability of equipment or space, disposal efficiency, environmental impact, sludge and by-product generation, operational difficulties and/or pre-treatment requirements. For this reason, it is now essential to develop remediation techniques that favour the total elimination of all traces of pollutants in water, both of natural and anthropogenic origin, in order to promote its subsequent reuse, all with the aim of achieving the zero-pollution goal announced in the European Green Deal in relation to the Chemicals Sustainability Strategy.

The need for treatment technologies that minimise environmental hazards at a reasonable cost has been driven by increasingly stringent environmental regulations regarding the presence of emerging contaminants in wastewater and natural systems. Conventional water treatment processes and technologies reduce the level of water pollution to a significant extent, but not to the extent required by current legislation. In addition, approaches based on adsorption, flocculation and ion exchange are not fully effective. Rather than destroying the contaminant, they transfer it to a solid phase that requires subsequent treatment. Due to the refractory nature of contaminants, biological treatments are often ineffective, which can be toxic to the microorganisms used. The use of artificial UV light in photochemical processes may not be a promising method for environmental applications due to high costs and the need for complex equipment. However, in the case of solar-powered applications, the process is not expensive because of the use of solar radiation.

AOPs, usually applied after biological processes, have recently emerged as effective tertiary treatments for the removal of pesticides and other micropollutants, but the oxidation rates of individual compounds can be strongly influenced by the constituents of the water matrix. Overall, the removal of the herbicides studied (isoproturon and terbuthylazine) by $HO^{\bullet}$ and $SO4^{\bullet -}$-based AOPs is largely influenced by the quality of the water matrix (dissolved constituents), which can be neutral, inhibitory or promoting, depending on the process and the mechanism by which these water constituents react. In addition to organic species, inorganic species, mainly chloride and carbonate/bicarbonate ions can also act as inhibitors either by scavenging or by generating new radicals that have a lower E^0 than $HO^{\bullet}$ and $SO_4^{\bullet -}$. Herbicide photodegradation by UV/PS treatment is faster in the absence of inorganic compounds, largely due to the absence in pure water of organic and inorganic compounds that can absorb UV radiation and generate other ROS with lower oxidation potential.

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Reference

1. EU. 2009. Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides. *Off. J. Eur. Union*, L309, 71-86. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32009L0128.
2. EC. 2019. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions - the European Green Deal, COM/2019/640. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM%3A2019%3A640%3AFIN.
3. EU. 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Off. J. Eur. Union*, L327, 1-73. https://eur-lex.europa.eu/eli/dir/2000/60/oj.
4. EU. 2006. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *Off. J. Eur. Union*, L372, 19-31. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32006L0118.
5. EU. 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. *Off. J. Eur. Union*, L226, 1-17. https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:en:PDF.
6. EU. 2022. Proposal for a Directive of the European Parliament and of the Council amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, Directive 2006/118/EC on the protection of groundwater against pollution and deterioration and Directive 2008/105/EC on environmental quality standards in the field of water policy. COM/2022/540. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52022PC0540.
7. EU. 2001. Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. *Off. J. Eur. Union*, L331, 1-5. https://faolex.fao.org/docs/pdf/eur36180.pdf.
8. EU. 2008 Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/ EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. *Off. J. Eur. Union*, L348, 84-97. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0105.
9. EC. 2015. Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. *Off. J. Eur. Union*, L78, 40-42. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32015D0495.
10. EC. 2018. Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495. *Off. J. Eur. Union*, L141, 9-12. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018D0840.
11. EC. 2020. Commission Implementing Decision (EU) 2020/1161 of 4 August 2020 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. *Off. J. Eur. Union*, L257, 32-35. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020D1161.
12. EC. 2022. Commission Implementing Decision (EU) 2022/1307 of 22 July 2022 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council *Off. J. Eur. Union*, L197, 117-120. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32022D1307.
13. EU. 2020. EU Parliament Council Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast). *Off. J. Eur. Union*, L435, 1-62. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020L2184.
14. EU. 1991. Council Directive of 21 May 1991 concerning urban wastewater treatment (91/271/EEC). *Off. J. Eur. Union*, L135, 40-91. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31991L0271.
15. EEA, 2018, *European waters- assessment of status and pressures 2018*, EEA Report No 7/2018, European Environment Agency. https://www.eea.europa.eu/publications/state-of-water/.
16. Mohaupt, V., Völker, J., Altenburger, R., Birk, S., Kirst, I., Kühnel, D., Küster, E., Semeradova, S., Šubelj, G., Whalley, C. 2020. Pesticides in European rivers, lakes and groundwaters - Data assessment. European Topic Centre on Inland, Coastal and Marine Waters (European Environment Agency). Magdeburg, Germany. Technical Report 1/2020. Magdeburg, Germany. doi:10.13140/RG.2.2.21719.60325.
17. Serrano-Valera, M., Vela, N., Piuvezam, G., Mateo-Ramírez, F., Santiago-Fernandes, I.D., Martínez-Alcalá, I. 2024. Prevalence and concentration of pesticides in European waters: A protocol for systematic review and meta-analysis. *PLoS ONE*, 19, e0282386. doi:10.1371/journal.pone.0282386.

18. EC. 2022. Proposal for a Directive of the European Parliament and of the Council concerning urban wastewater treatment (recast). SWD/2022/541. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52022SC0541.
19. Parida, V.K., Saidulu, D., Majumder, A., Srivastava, A., Gupta, B., Gupta, A.K. 2021. Emerging contaminants in wastewater: A critical review on occurrence, existing legislations, risk assessment, and sustainable treatment alternatives. *J. Environ. Chem. Eng*., 9, e105966. doi:10.1016/j.jece.2021.105966.
20. EU. 2020. Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse. *Off. J. Eur. Union*, L177, 32-55. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020R0741.
21. Alvarino, T., Suarez, S., Lema, J., Omil, F. 2018. Understanding the sorption and biotransformation of organic micropollutants in innovative biological wastewater treatment technologies. *Sci. Total Environ*., 615, 297-306. doi:10.1016/j.scitotenv.2017.09.278.
22. Zhang, W., Liang, W., Zhang, Z., Hao, T. 2021. Aerobic granular sludge (AGS) scouring to mitigate membrane fouling: Performance, hydrodynamic mechanism and contribution quantification model. *Water Res*. 188, e116518. doi:10.1016/j.watres.2020.116518.
23. Vasilachi, I.C., Asiminicesei, D.M., Fertu, D.I., Gavrilescu, M. 2021. Occurrence and fate of emerging pollutants in water environment and options for their removal. *Water*, 13, e181. doi:10.3390/w13020181.
24. Rout, P.R., Zhang, T.C., Bhunia, P., Surampalli, R.Y. 2021. Treatment technologies for emerging contaminants in wastewater treatment plants: A review. *Sci. Total Environ*., 753, e141990. doi:10.1016/j.scitotenv.2020.141990
25. Saha, M.P. 2021. Advanced oxidation processes for effluent treatment plants. Elsevier, Amsterdam.
26. Soto-Verjel, J., Maturana, A.Y., Villamizar, S.E. 2022. Advanced catalytic oxidation coupled to biological systems to treat pesticide contaminated water: A review on technological trends and future challenges. *Water Sci. Technol*., 85, 1263-1294. doi:10.2166/wst.2021.642.
27. Miklos, D.B., Remy, C., Jekel, M., Linden, K.G., Drewes, J.E., Hübner, U. 2018. Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review. *Water Res.*, 139, 118-131. doi:/10.1016/j.watres.2018.03.042.
28. Yang, Q., Ma, Y., Chen, F., Yao, F., Sun, J., Wang, S., Yi, K., Hou, L., Li, X., Wang, D. 2019. Recent advances in photo-activated sulfate radical-advanced oxidation process (SR-AOP) for refractory organic pollutants removal in water. *Chem. Eng. J., 378*, e122149. doi: 10. 1016/j. cej. 2019. 122149.
29. Lee, J., Von Gunten, U., Kim, J.H. 2020. Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks. *Environ. Sci. Technol*., *54*, 3064-3081. doi:10.1021/acs.est.9b07082.
30. Brillas, E. 2023. Activation of persulfate and peroxymonosulfate for the removal of herbicides from synthetic and real waters and wastewaters. *J. Environ. Chem. Eng*., 110380. doi:10.1016/j.jece.2023.110380.
31. Olmez-Hanci, T., Arslan-Alaton, I., 2013. Comparison of sulfate and hydroxyl radical based advanced oxidation of phenol. *Chem. Eng. J*,. 224, 10-16. doi:10.1016/j.cej.2012.11.007.
32. Oh, W.D., Dong, Z., Lim, T.T., 2016. Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects. *App. Catal. B Environ*., 194, 169-201. doi:10.1016/j.apcatb.2016.04.003.
33. Wang, J., Wang, S. 2018. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.*, 334, 1502-1517. doi:10.1016/j.cej.2017.11.059.
34. Wacławek, S., Lutze, H.V., Grübel, K., Padil, V.V.T., Černík, M., Dionysiou, D.D., 2017. Chemistry of persulfates in water and wastewater treatment: A review. *Chem. Eng. J.,* 330, 44-62. doi:10.1016/j.cej.2017.07.132.
35. Matzek, L.W., Carter, K.E., 2016. Activated persulfate for organic chemical degradation: a review. *Chemosphere*, 151, 178-188. doi10.1016/j.chemosphere.2016.02.055.
36. Ren, W., Huang, X., Wang, L., Liu, X., Zhou, Z., Wang, Y., Lin, C., He, M., Ouyang, W. 2021. Degradation of simazine by heat-activated peroxydisulfate process: A coherent study on kinetics, radicals and models. *Chem. Eng. J*., 426, e131876. doi:10.1016/j.cej.2021.131876.
37. Serrano, K.G. 2018. Indirect Electrochemical Oxidation Using Hydroxyl Radical, Active Chlorine, and Peroxodisulfate. In: Electrochemical Water and Wastewater Treatment. (Martínez-Huitle, C.A., Rodrigo, M.A., Scialdone, O. (Eds.), Elsevier, Amsterdam. doi:10.1016/B978-0-12-813160-2.00006-7.
38. Ribeiro, A.R.L., Moreira, N.F.F., Li Puma, G., Silva, A.M.T. 2019. Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chem. Eng. J*., 363, 155-173. doi: 10. 1016/j. cej. 2019. 01. 080.
39. Vela, N., Fenoll, J., Garrido, I., Navarro, G., Gambín, M., Navarro, S. 2015. Photocatalytic mitigation of triazinone herbicide residues using titanium dioxide in slurry photoreactor. *Catal. Today*, 252, 70-77. doi:10.1016/j.cattod.2014.12.011.
40. Orellana-Garcia, F., Alvarez, M. A., Lopez-Ramon, V., Rivera-Utrilla, J., Sanchez-Polo, M., Mota, A.J. 2014. Photodegradation of herbicides with different chemical natures in aqueous solution by ultraviolet

radiation. Effects of operational variables and solution chemistry. *Chem. Eng. J.*, 255, 307-315. doi:10.1016/j.cej.2014.06.047.

41. ECHA. 2014. Proposal for Harmonised Classification and Labelling. CLH-227-637-9 Report for terbuthylazine. European Chemicals Agency. Merseyside, UK. https://echa.europa.eu/substance-information/-/substanceinfo/100.025.125.
42. Lin, C.C., Wu, M.S., 2014. UV/$S_2O_8^{2-}$ process for degrading polyvinyl alcohol in aqueous solutions. *Chem. Eng. Process.*, 85, 209-215. doi:10.1016/j.cep.2014.08.012.
43. Liu, B., Zhao, X., Terashima, C., Fujishima, A., Nakata, K., 2014. Thermodynamic and kinetics analysis of heterogeneous photocatalysis for semiconductor systems. *Phys. Chem. Chem. Phys.*, 16, 8751-8760. doi:10.1039/c3cp55317e.
44. Nafradi, M., Alapi, T., Bencsik, G., Janaky, C. 2022. Impact of reaction parameters and water matrices on the removal of organic pollutants by TiO_2/LED and ZnO/LED heterogeneous photocatalysis using 365 and 398 nm radiation. *Nanomaterials*, 12, e5. doi: 10. 3390/ nano120100 05.
45. Mack, J., Bolton, J.R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: a review. *J. Photochem. Photobiol. A. Chem.* 128, 1-13. doi10.1016/S1010-6030(99)00155-0
46. Ghauch, A., Baalbaki, A., Amasha, M., El Asmar, R., Tantawi, O. 2017. Contribution of persulfate in UV-254 nm activated systems for complete degradation of chloramphenicol antibiotic in water. *Chem. Eng. J.*, 317, 1012–1025. doi:10. 1016/j. cej. 2017. 02. 133.
47. Lin, C.C., Wu, M.S., 2014. Degradation of ciprofloxacin by UV/$S_2O_8^{2-}$ process in a large photoreactor. *J. Photochem. Photobiol. A: Chem.*, 285, 1-6. doi:10.1016/j.jphotochem.2014.04.002.
48. Cabrera-Reina, A., Aliste, M., Polo-López, M. I., Malato, S., Oller, I. 2023. Individual and combined effect of ions species and organic matter on the removal of microcontaminants by Fe3+-EDDS/solar-light activated persulfate. *Water Res.*, 230, e119566. doi:10.1016/j.watres.2023.119566.
49. Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. *J. Phys. Chem. Ref. Data*, 17, 513-886. doi:10.1063/1.555805.
50. Armstrong, D.A., Huie, R.E., Koppenol, W.H., Lymar, S.V., Merényi, G., Neta, P., Ruscic, B., Stanbury, D.M., Steenken, S., Wardman, P. 2015. Standard electrode potentials involving radicals in aqueous solution: inorganic radicals (IUPAC Technical Report). *Pure Appl. Chem.*, 87, 1139-1150. doi:10.1515/pac-2014-0502.
51. Bennedsen, L.R., Muff, J., Søgaard, E.G., 2012. Influence of chloride and carbonates on the reactivity of activated persulfate. *Chemosphere*, 86, 1092–1097. doi:10.1016/j.chemosphere.2011.12.011.
52. Canonica, S., Kohn, T., Mac, M., Real, F.J., Wirz, J., von Gunten, U. 2005. Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ. Sci. Tech.*, 39, 9182-9188. doi:10.1021/es051236b.
53. Acero, J.L., Benítez, F.J., Real, F.J., Rodríguez, E., 2018. Degradation of selected emerging contaminants by UV-activated persulfate: kinetics and influence of matrix constituents. *Sep. Purif. Technol.*, 201, 41-50. doi:10.1016/j. seppur.2018.02.055.
54. Lebik-Elhadi, H., Frontistis, Z., Ait-Amar, H., Madjene, F., Mantzavinos, D., 2020. Degradation of pesticide thiamethoxam by heat–activated and ultrasound–activated persulfate: effect of key operating parameters and the water matrix. *Process Saf. Environ. Prot.*, 134, 197–207. doi:10.1016/j.psep.2019.11.041.
55. Sbardella, L., Gala, I.V., Comas, J., Layret, R.R., Gernjak, W. 2019. The impact of wastewater matrix on the degradation of pharmaceutically active compounds by oxidation processes including ultraviolet radiation and sulfate radicals, *J. Hazard. Mat.*, 380, e120869. doi:10.1016/j.jhazmat.2019.120869.
56. Lin, C.C., Lee, L.T., Hsu, L.J. 2013. Performance of UV/$S_2O_8^{2-}$ process in degrading polyvinyl alcohol in aqueous solutions. *J. Photochem. Photobiol. A-Chem.* 252, 1-7. doi:10.1016/j.jphotochem.2012.10.017.
57. Manaham, S.E. 2010. Environmental chemistry, 9th Edition, CRC Press.
58. Zuo, Z.; Cai, Z.; Katsumura, Y.; Chitose, N.; Muroya, Y. Reinvestigation of the acid−base equilibrium of the (bi) carbonate radical and pH dependence of its reactivity with inorganic reactants. *Radiat. Phys. Chem.*, 1999, 55, 15-23. doi:10.1016/S0969-806X(98)00308-9.
59. Ma, J., Yang, Y., Jiang, X., Xie, Z., Li, X., Chen, C., Chen, H. 2018. Impacts of inorganic anions and natural organic matter on thermally activated persulfate oxidation of BTEX in water, *Chemosphere*, 190, 296-306. doi:10.1016/j. chemosphere.2017.09.148.
60. Xiao, R., Meng, Y., Fu, Y., Wacławek, S., Wei, Z., Spinney, R., Dionysiou, D., Hu, W.P. 2023. The overlooked carbonate radical in micropollutant degradation: An insight into hydration interaction. *Chem. Eng. J.*, 474, e145245. doi:10.1016/j.cej.2023.145245.
61. Mikhaylin, S., Bazinet, L. 2016. Fouling on ion-exchange membranes: Classification, characterization and strategies of prevention and control. *Adv. Colloid Interface Sci.*, 229, 34-56. doi:10.1016/j.cis.2015.12.006.
62. Haghsheno, R., Mohebbi, A., Hashemipour, H., Sarraf, A., 2009. Study of kinetic and fixed bed operation of removal of sulfate anions from an industrial wastewater by an anion exchange resin. *J. Hazard. Mat.*, 166, 961-966. doi:10.1016/j.jhazmat.2008.12.009.

63. Haque, M.M., Muneer, M. 2003. Heterogeneous photocatalysed degradation of an herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. *J. Environ. Manag.*, 69, 169-176. doi:10.1016/S0301-4797(03)00143-9
64. Fenoll, J., Sabater, P., Navarro, G., Pérez-Lucas, G., Navarro, S. 2013. Photocatalytic transformation of sixteen substituted phenylurea herbicides in aqueous semiconductor suspensions: Intermediates and degradation pathways. *J. Hazard. Mat.*, 244, 370-379. doi:10.1016/j.jhazmat.2012.11.055.
65. Fenoll, J., Hellin, P., Martinez, C. M., Flores, P., Navarro, S. 2012. Semiconductor-sensitized photodegradation of s-triazine and chloroacetanilide herbicides in leaching water using TiO_2 and ZnO as catalyst under natural sunlight. *J. Photochem. Photobiol. A: Chem.*, 238, 81-87. doi:10.1016/j.jphotochem.2012.04.017.
66. Roberts, T., Hutson, D. 1998. Metabolic Pathways of Agrochemicals. Part one: Herbicides and Plant Growth Regulators. The Royal Society of Chemistry. Cambridge, UK.