Photocatalytic abatement of triazine and phenylurea herbicides in wastewater effluents using $TiO_2/Na_2S_2O_8$ and LED lamps as UV-A light source

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BACKGROUND, AIM and SCOPE

Spain, like most European countries, faces serious problems of pollution of its water resources. Thus, the presence of emerging pollutant residues (among them pesticides) in wastewater has become a major environmental problem even at low concentrations, as many of them are catalogued endocrine disruptors.

Ultimately, many of them end up entering the wastewater treatment plants (WWTPs) as influent waters where conventional water treatments are not able to remove them completely and eventually these pollutant residues are detected in their effluents [1]. There is therefore an urgent need to effectively treat these polluted wastewater (WW) for reuse and, in addition to make it suitable for different uses, including crop irrigation. In this context, Directive 2013/39/EU promotes the development of innovative, low-cost and effective decontamination technologies that do not endanger either human health or the environment.

Thus, advanced oxidation processes (AOPs), mainly heterogeneous photocatalysis (HP), are of particular interest to remove pesticides and other pollutants from water [2]. In these processes, UV irradiation acts on a semiconducting oxide (TiO_2, Aeroxide® P25, BET 50 $m^2\ g^{-1}$, size < 21 nm) to generate strongly oxidising species (hydroxyl radicals, $HO^{\bullet}$) that are able to attack and mineralise pesticides. The addition of an oxidising agent, ($Na_2S_2O_8$), helps to generate more reactive species, ($SO_4^{\bullet -}$) improving the degradation efficiency (Figure 4). The artificial UV-A light source using light emitting diodes (LEDs) has revolutionised AOPs because of its cost and energy savings and environmental friendliness [3].

In this study, the photocatalytic degradation of six herbicides (three triazines and three substituted phenylurea compounds) (Figure 1) was evaluated in three different real WW effluents (WWe) (Figure 2). The experiments were performed at laboratory scale with $TiO_2/Na_2S_2O_8$ in water exposed to UV-A/LED irradiation through a photochemical reactor Photolab LED365-16/450-16c (APRIA Systems S.L., Cantabria, Spain) (Figure 3).

MATERIAL & METHODS

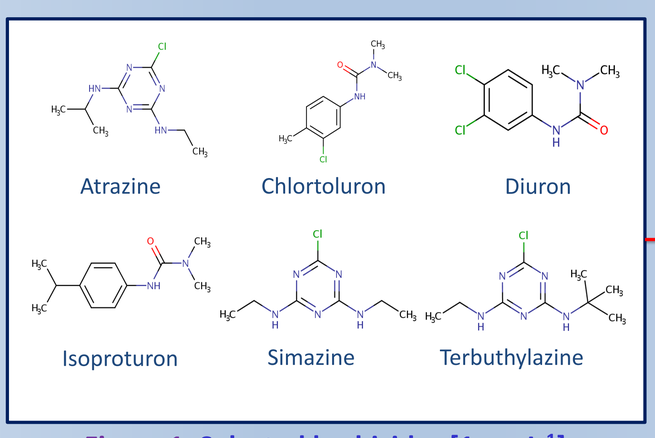


Figure 1. Selected herbicides [1 mg L^{-1}]

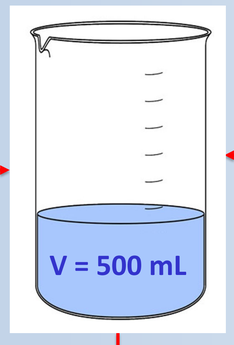
Table 2. Characteristics and main physico-chemical parameters of the three WWTPe used.

Physico-chemical parameters	WWTPe		
	Los Alcázares	Molina	Alcantarilla
Population supplied	21652	187356	62012
Design capacity, $m^3\ day^{-1}$	6308	18279	7469
pH	7.6	7.7	7.7
EC ($dS\ m^{-1}$)	6.1	4.5	2.6
TOC ($mg\ L^{-1}$)	13.0	14.8	14.8
BOD_5 ($mg\ L^{-1}$)	2.0	3.0	3.0
COD ($mg\ L^{-1}$)	22.0	34.0	27.0
SS ($mg\ L^{-1}$)	4.0	7.0	7.0
N_{Total} ($mg\ L^{-1}$)	1.7	6.5	11.8
P_{Total} ($mg\ L^{-1}$)	1.3	0.2	4.2

EC: electrical conductivity; TOC: total organic carbon; BOD_5: biological oxygen demand at 20 °C and 5 days; COD: chemical oxygen demand; SS: suspended solids.

Figure 2. Location of WWTPs

WWe samples



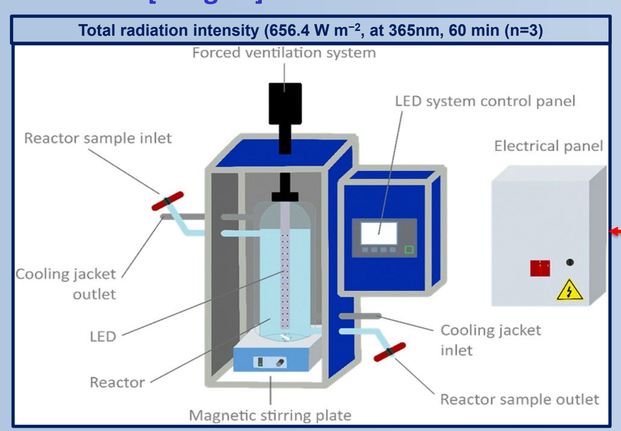


Figure 3. Schematic drawing photochemical reactor

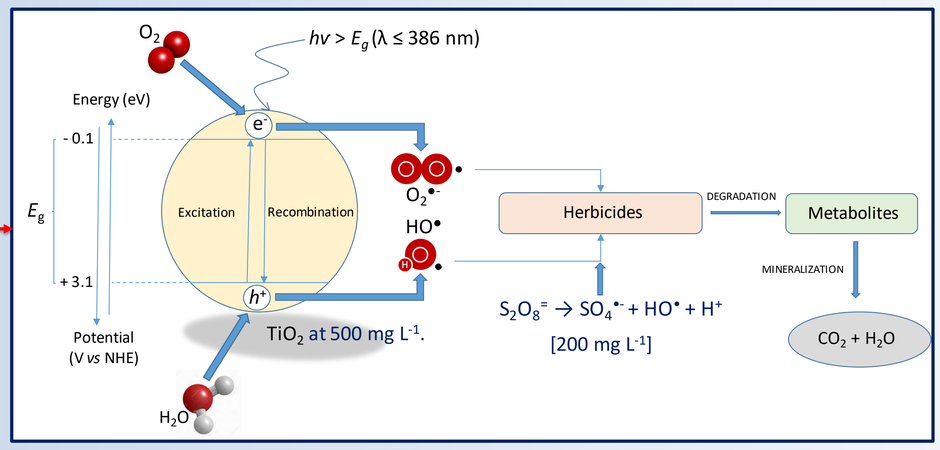


Figure 4. Photocatalytic process

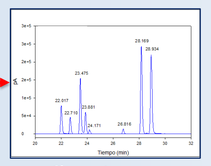
ANALYTICAL DETERMINATIONS

HERBICIDES

10 ± 0.1 mL sample + 10 mL CH_3CN (extractant) 2 ± 0.1 g NaCl by centrifugation (15 min at 4000 rpm at 4 °C)

Supernatant filtration (0.45 µm nylon)

HPLC Agilent Series 1200 + G6410A TQ MS ESI^+ ion mode, (Zorbax Eclipse XDB-C8)



Chromatogram

ANIONS

Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, NO_2^- and HCO_3^-

Thermo Dionex ICS-2100 IC

TOC

10 ± 0.1 mL of sample

Filtration (0.45 µm nylon)

AnalytiK Jena Multi N/C 3100 TOC Analyzer)

RESULTS & DISCUSSION

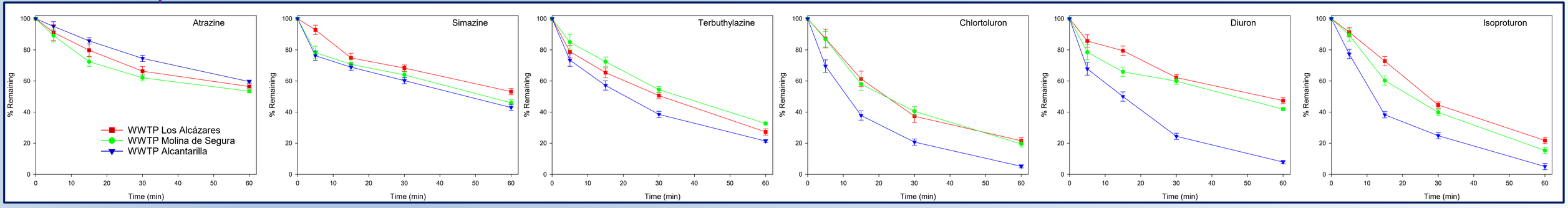


Figure 5: . Comparison of photocatalytic degradation of herbicides in three different WWe by HP ($TiO_2/Na_2S_2O_8$/UV-A) with LED lamps during 60 min of reaction time.

Triazine compounds had a similar behaviour in the three different WWe, whose final abatement (60 min) ranged from 44±3% for atrazine to 73±6% for terbuthylazine. On the other hand, phenylureas suffered a higher phocatalytic degradation efficiency (≥ 92%) in Alcantarilla WWe (Figure 5). The kinetic degradation of herbicides was studied as a function of exposure time to UV-A irradiation using single first-order (SFO) kinetics: $Ct = C_0 \cdot e^{-kt}$. Consistent with the data shown (Table 3), SFO model explains satisfactorily the photocatalytic degradation of the studied compounds. The lower value of EC found in Alcantarilla WWe seems to favour the degradation of phenylureas (Table 4).

Table 3. Kinetic parameters for the photocatalytic degradation of herbicides with $TiO_2/Na_2S_2O_8$/UV-A in three different WWTPe.

	Herbicides	Kinetic parameters	WWTPe Los Alcázares	WWTPe Molina	WWTPe Alcantarilla
Triazine	Atrazine	k	0.0102	0.0115	0.0088
		DT_{80}	157.8	140.0	182.9
	Simazine	k	0.011	0.0123	0.0137
		DT_{80}	146.3	130.8	117.5
	Terbuthylazine	k	0.0218	0.0189	0.0295
		DT_{80}	73.8	85.2	54.6
Phenylurea	Chlortoluron	k	0.0301	0.0303	0.0593
		DT_{80}	53.5	53.1	27.1
	Diuron	k	0.0127	0.0145	0.0463
		DT_{80}	126.7	111.0	34.8
	Isoproturon	k	0.0257	0.0318	0.0542
		DT_{80}	62.6	50.6	29.7

k: kinetic constant (min^{-1}), DT_{80}: degradation time calculated to achieve 80 % of abatement of herbicides (min).

Table 4. Anion concentration ($mg\ L^{-1}$) for the photocatalytic degradation of herbicides with $TiO_2/Na_2S_2O_8$/UV-A in three different WWTPe, at the beginning and end (60 min) of each experiment.

Anion ($mg\ L^{-1}$)	WWTPe Los Alcázares		WWTPe Molina		WWTPe Alcantarilla	
	0 min	*60 min*	*0 min*	*60 min*	*0 min*	*60 min*
Cl^-	434.7	1276.7	343.6	878.4	191.2	388.7
NO_3^-	< 5	< 5	< 5	< 5	8.9	< 5
SO_4^{2-}	255.7	869.9	382.0	1030.9	180.6	498.7
PO_4^{3-}	< 5	< 5	< 5	< 5	< 5	< 5
NO_2^-	< 0.5	< 0.5	< 0.5	3.4	< 0.5	< 0.5
HCO_3^-	116.4	327.4	178.0	475.5	191.2	371.4

CONCLUSIONS

HP has proven to be an effective, innovative and environmentally friendly process for the treatment of WWe polluted with herbicide residues. Phenylurea compounds suffered a faster degradation than triazine compounds in all tested WWe, especially in Alcantarilla. $TiO_2/Na_2S_2O_8$/UV-A, with LED lamps as light source, is a suitable alternative to remove herbicide residues from WW, although an important effect of the water matrix composition was observed.

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