Removal of pharmaceutical residues from wastewater effluent by Solar heterogeneous photocatalysis

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AIM AND SCOPE

The detection of chemicals of emerging concern (CECs) or Emerging Pollutants (EPs) in waste water treatment plants (WWTP) effluents is of great concern due to their potential risks to the environment and human health, even if they are present in low environmental concentrations (i.e. between ng L^{-1} and µg L^{-1}). Among EPs pharmaceuticals (PhMCs) are discharged into surface waters probably due to their incessant release from WWTPs, which is significantly faster than their removal rates. Therefore, there is a clear need to curb this problem through innovative and environmentally friendly technologies developed in WWTPs to remove these EPs effectively.

With this end, heterogeneous photocatalysis (HP) consists of the acceleration of a chemical reaction (photoreaction) by the action of a catalyst involving the combination of photochemistry and catalysis [1]. The main advantage of these technologies is that they achieve the removal or at least the reduction of PhMCs by mineralization, rather than transferring them from one place to another as is the case with conventional processes [2]. Therefore, we have assessed the effectivity of TiO_2 (photocatalyst) in combination with $Na_2S_2O_8$ (oxidant) under natural sunlight (Figure 1) for the treatment of a wastewater effluent (WWe) and deionized water (DW) polluted with six PhMCs (atenolol, carbamazepine, clarithromycin, erythromycin, irbesartan and ketoprofen) commonly used worldwide (Figure 2).

MATERIAL & METHODOLOGY

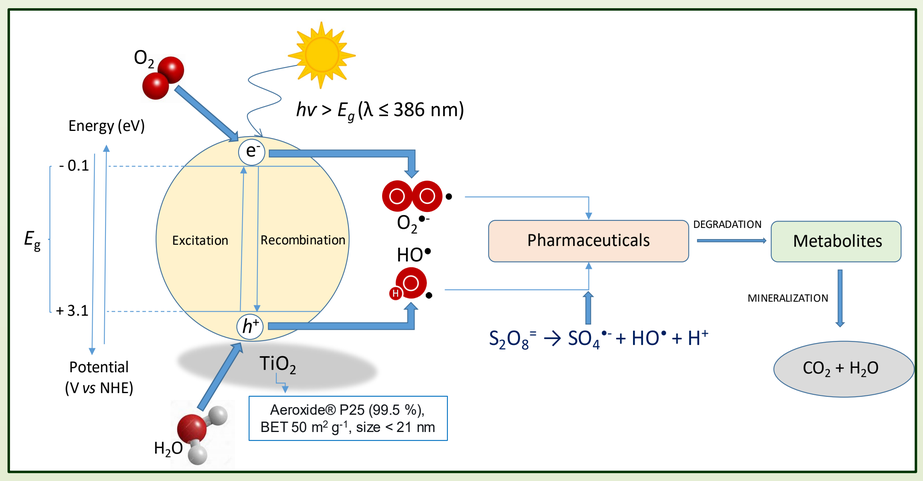


Figure 1: Photocatalytic process

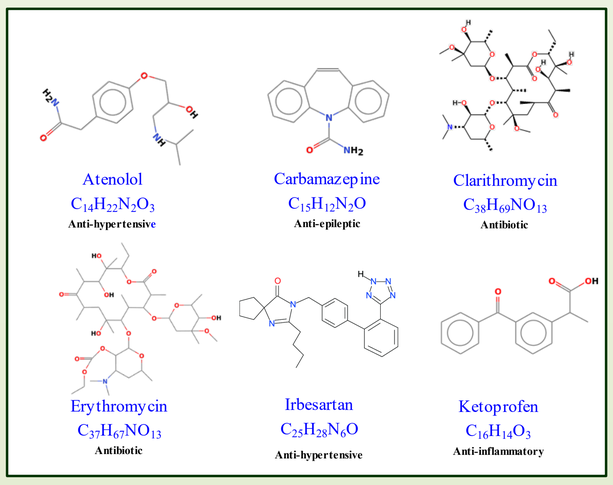


Figure 2: Structures of selected pharmaceuticals

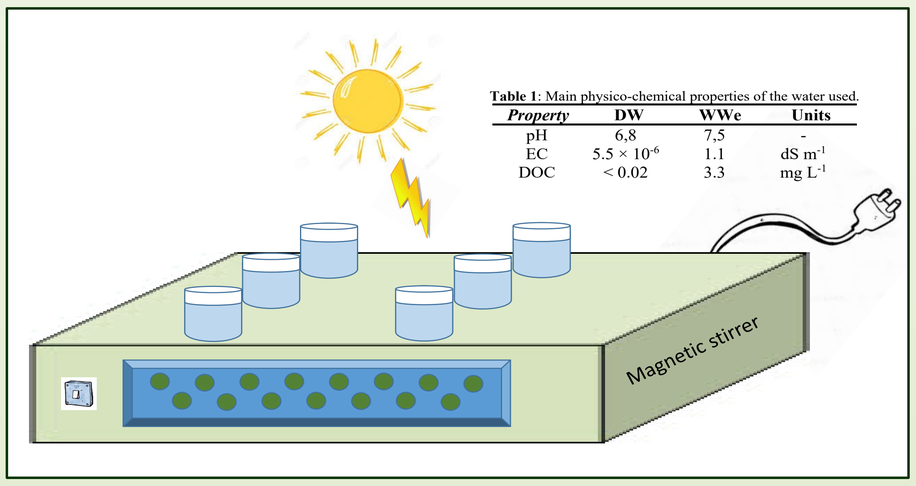


Table 1: Main physico-chemical properties of the water used.

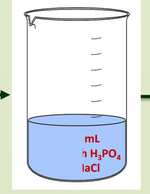
Property	DW	WWe	Units
pH	6,8	7,5	-
EC	5.5×10^{-6}	1.1	dS m^{-1}
DOC	< 0.02	3.3	mg L^{-1}

Figure 3: Scheme of the experimental setup

Photocatalytic trials were performed in Pyrex glass vessels exposed to sunlight (Figure 3). In all cases, 500 mL of water were spiked with PhMCs at 100 µg L^{-1} of each compound and 250 mg L^{-1} of TiO_2 and kept for 30 min in the dark before to illumination to achieve the maximum adsorption of the PhMCs onto the TiO_2 surface. Subsequently, $Na_2S_2O_8$ (250 mg L^{-1}) used as electron acceptor to avoid electron/hole (e^-/h^+) recombination was added. Samples were exposed to direct sunlight for 240 min (10 to 14 h). Several samples (50 mL) were taken during the illumination period (240 min). Three replications were made in each case.

ANALYTICAL DETERMINATIONS

1. PhMCs



1. Conditioned with 5 mL CH_3OH
2. Equilibrated with 5 mL Milli-Q water
3. Eluted with 5 mL CH_3CN

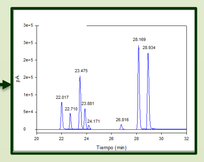
Vacuum, flow rate ≈ 2 mL min^{-1}

Supernatant filtration

0.45 µm

HPLC Agilent Series 1200 G6410A TQ MS

ESI^+ ion mode, (Zorbax Eclipse XDB-C8)



2. CATIONS → An Agilent 5110 ICP-OES (Santa Clara, CA, USA) was used.

3. ANIONS → They were measured using a Thermo Scientific Dionex ICS-2100 ion chromatograph (Waltham, MA, USA) with an AS19 column.

4. DOC → Dissolved organic carbon content was determined by means of an Analytik Jena Multi N/C 3100 TOC Analyzer (AG, Jena, Germany).

RESULTS & DISCUSSION

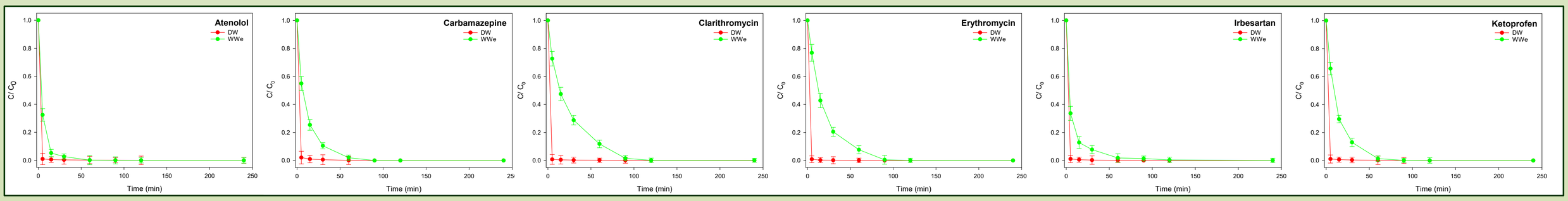


Figure 4: Comparison of photocatalytic degradation of PhMCs in WWe and DW by HF (TiO_2/$Na_2S_2O_8$) in presence of natural sunlight.

In all cases, as shown in Figure 4, the degradation rate of PhMCs is much faster in DW causing 100 % in few min (below 5) as compared to WWe due to the matrix effect. These findings indicate that the occurrence of dissolved salts (mainly anions) that can act as scavengers of $HO^{\bullet}$, and organic matter (dissolved organic carbon) that produces a strong filter effect, have a powerful influence on the efficiency of the process.

Obtained data were adjusted to a pseudo-first-order kinetics (SFO). Thus, apparent velocity rate (k) can be obtained in the following way, where t is the reaction time, C_0 is the initial concentration of PhMCs and C_t its residual concentration at t (Table 2-3). Hence the time required for x % of PhMCs to disappear (Disappearance Time) from the water can be calculated following equation:

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

PhMCs show enhanced photocatalytic degradation rate in WWe, ranging from 90 to 98%. Degradation experiments in WWe showed that the time required for 90 % of PhMCs to disappear (DT_{90}) ranged from 10-53 min for atenolol and clarithromycin, respectively (Table 3).

REFERENCES

[1] Augugliaro, V., Palmisano, G., Palmisano, L., Soria, J., 2019. Heterogeneous photocatalysis and catalysis: An overview of their distinctive features. In: *Heterogeneous photocatalysis*. Elsevier, Netherlands, pp. 1-24. https://doi.org/10.1016/B978-0-444-64015-4.00001-8

[2] 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 Research* **139**, 118-131. https://doi.org/10.1016/j.watres.2018.03.042

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Table 2: Kinetic parameters obtained following SFO model for the photocatalytic degradation of PhMCs in DW

COMPOUND	$C_t = C_0\ e^{-kt}$				
	R^2	C_t/C_0	k (min^{-1})	$S_{y/x}$	DT_{50}/DT_{90} (min)
Atenolol	1.0000***	1.00	0.9210	0.003	0.8/2.5
Carbamazepine	0.9998***	1.00	0.7725	0.005	0.9/3.0
Clarithromycin	1.0000***	1.00	0.9656	0.003	0.7/2.4
Erythromycin	1.0000***	1.00	0.9421	0.002	0.7/2.4
Irbesartan	0.9999***	1.00	0.9019	0.003	0.8/2.6
Ketoprofen	0.9999***	1.00	0.9019	0.003	0.8/2.6

***$p < 0.001$; $S_{y/x}$: Standard Error of Estimation

Table 3: Kinetic parameters obtained following SFO model for the photocatalytic degradation of PhMCs in WWe

COMPOUND	$C_t = C_0\ e^{-kt}$				
	R^2	C_t/C_0	k (min^{-1})	$S_{y/x}$	DT_{50}/DT_{90} (min)
Atenolol	0.9989***	1.00	0.2216	0.013	3.1/10.4
Carbamazepine	0.9925***	0.97	0.0958	0.034	7.2/24.0
Clarithromycin	0.9926***	0.96	0.0430	0.035	16.1/53.4
Erythromycin	0.9983***	1.00	0.0530	0.017	13.0/43.1
Irbesartan	0.9840***	0.99	0.1960	0.047	3.5/11.8
Ketoprofen	0.9989***	0.99	0.0779	0.017	8.9/29.6

***$p < 0.001$; $S_{y/x}$: Standard Error of Estimation

CONCLUSIONS

Solar-driven heterogeneous photocatalytic processes using photocatalyst materials as TiO_2 in tandem with $Na_2S_2O_8$ constitutes a valuable tool (efficient, eco-friendly and cost-effective) for wastewater remediation, particularly in those areas receiving a large number of sunshine hours per year like Mediterranean basin.