Nowelties
European Joint Doctorate

NOWELTIES – Joint PhD Laboratory for New Materials and Inventive Water Treatment Technologies. Harnessing resources effectively through innovation

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D3.1 Degradation of targeted OMPs and first evaluation of their transformation products with photochemical processes

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1. Introduction

This document provides an overview of the progress of the research activities carried out for the realisation of the Task 3 within WP3 of the project NOWELTIES. The Individual Research Project related to the Task 3 of WP3 is *Application of UV-LEDs AOPs for the efficient removal of OMPs from wastewater* (ESR6).

The WP3 aims at developing more efficient technological concepts for physico-chemical wastewater treatment putting an emphasis on the evaluation of reactor geometries and designing treatment applications. The goal of Task 3 (within WP3) is the development and optimization of innovative technology based on UV-LED AOP for the economically viable treatment of wastewaters containing OMPs. Accordingly, research goals for the ESR6 project were defined.

This document presents a description of the research goals and results of the ESR6 project obtained within the reporting period, including (1) degradation of targeted OMPs with photochemical processes (chapter 3), (2) preliminary evaluation of toxicity (chapter 4), and (3) preliminary evaluation of targeted OMPs transformation products (chapter 5).

2. Research goals

The objective of the ESR6 project is to contribute to the development and evaluation of new technologies for water treatment involving photolytic and photocatalytic degradation of organic micropollutants (OMPs) using TiO_2 as catalyst and UV-LEDs as light sources. New reactor designs which are able to explore exclusive LED features in comparison to UV Hg lamps will be studied. The influence of multiple parameters such as UV light intensity and wavelength, controlled periodic illumination, wavelength coupling, addition of H_2O_2, and matrix composition of real and synthetic wastewaters will be evaluated. The impact of the novel technology on degradation rates, energy consumption and toxicity will be assessed. Finally, transformation products of the pharmaceuticals will be identified and monitored by LC-MS. Further, the influence of each matrix and treatment process on degradation routes and toxicity will be evaluated.

3. Degradation of targeted OMPs with photochemical processes

Prior to the experiments, a comprehensive literature research was carried on to familiarize with the topic and its main current trends, research hurdles and bottlenecks. The main conclusions

were that most research is performed: 1) without concern regarding photoreactor design; 2) in ultra-pure water matrices; 3) with pollutants at initial concentrations considerably higher than the ones typically found in the environment.

The electric efficiency of LED-based processes has been increasing since technologic advancements on the field allowed higher wall-plug efficiencies. Exclusive features of LEDs such as their point-source character, flexibility, wavelength tailoring and controlled period illumination should be better explored for process optimization, but few studies are available in the literature since UV-LEDs became widely commercially available only recently.

3.1. Photoreactor design and light modelling software

The proposed reactor was a lab-scale cylinder made of quartz (d_o = 4 cm and L = 15 cm). UVA LED strips (365 nm) were positioned in radically symmetric vertical columns, illuminating the reactor laterally (**Figure 1**).

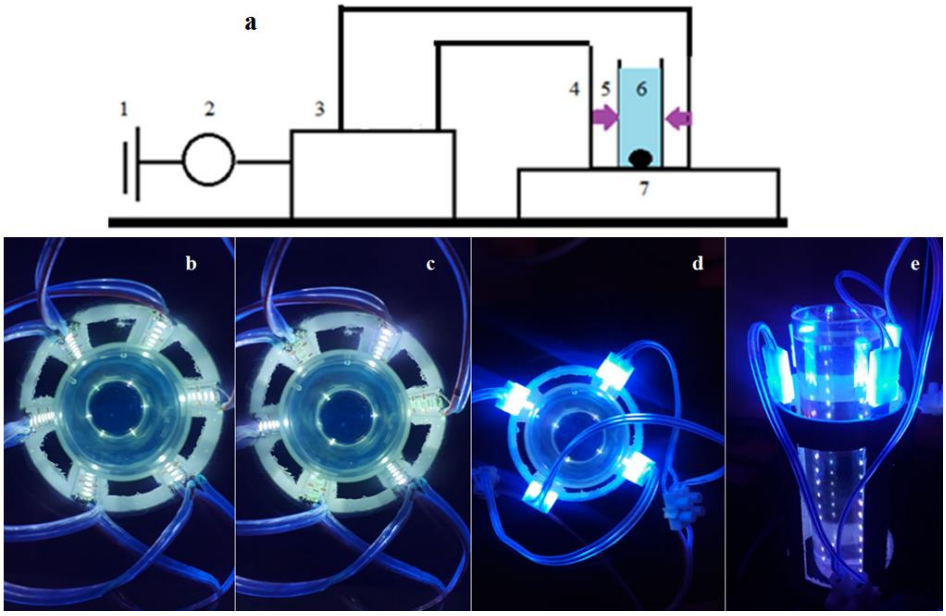

Figure 1. Experimental setup. (a) 1 - energy source, 2 - power meter, 3 - LED control board, 4 - LED columns, 5 - UV rays reaching the reactor, 6 – reactor, and 7 - magnetic stirrer. Below, upview of (b) arrays #LED = 6, D_W = 15 mm; (c) #LED = 3, D_W = 15 mm; and (d), #LED = 4, D_W = 10 mm. Side view of #LED = 4, D_W = 10 mm (e).

A total of 8 LEDs array with different number of LED columns (#LED) and different distance between the photoreactor's wall and LEDs (D_W) were tested. The simulation of the light in the reactor's middle cross section and lateral surface was made with the professional version of the

Zemax OpticStudio software for different LED arrays around the reactor (**Figure 2)**. The addition of extra light sources reduced the presence of "dark zones" but did not result in a more homogenous light distribution, since all light rays converge to the centre of the cylinder.

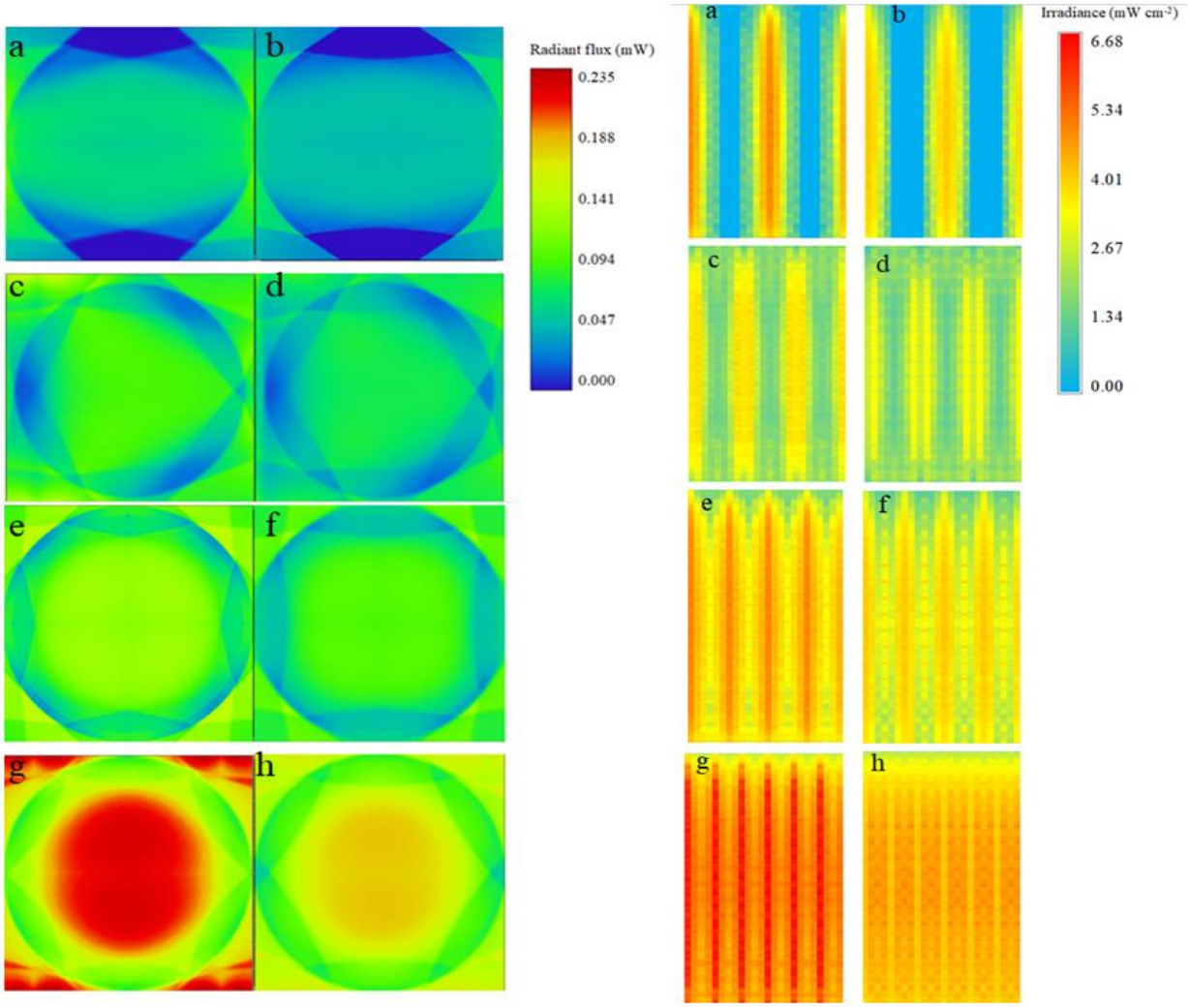

Figure 2. Light profiles obtained withZemas OpticStudio software: a) 2 LED columns, 10 mm away; b) 2 LED columns, 15 mm away; c) 3 LED columns, 10 mm away; d) 3 LED columns, 15 mm away, e) 4 LED columns, 10 mm away; f) 4 LED columns, 15 mm away; g) 6 LED columns, 10 mm away; h) 6 LED columns, 15 mm away

The results of photoreactor optimization using optical software were presented as a poster presentation titled *Photoreactor design for UV-LED photocatalytic degradation of micropollutants,* authors: D. Bertagna Silva, S. Babić, G. Buttiglieri, at the XIII Meeting of Young Chemical Engineers held in Zagreb, 20-21 February 2020.

3.2. Degradation of ciprofloxacin

Figure 3 shows the apparent kinetic degradation rate (k_{app}) of the antibiotic ciprofloxacin in ultrapure water and the electrical energy per order consumption (E_{EO}) for several photolytic and photocatalytic processes. Each array from **figure 2** was evaluated. Additionally, for photocatalytic experiments, an identical reactor had its inner walls impregnated with TiO_2 nanofilm. The LEDs were connected to a control board which allowed the adoption of controlled periodic illumination, with duty cycles (DCy) of 0.50, 0.75 and 1.00.

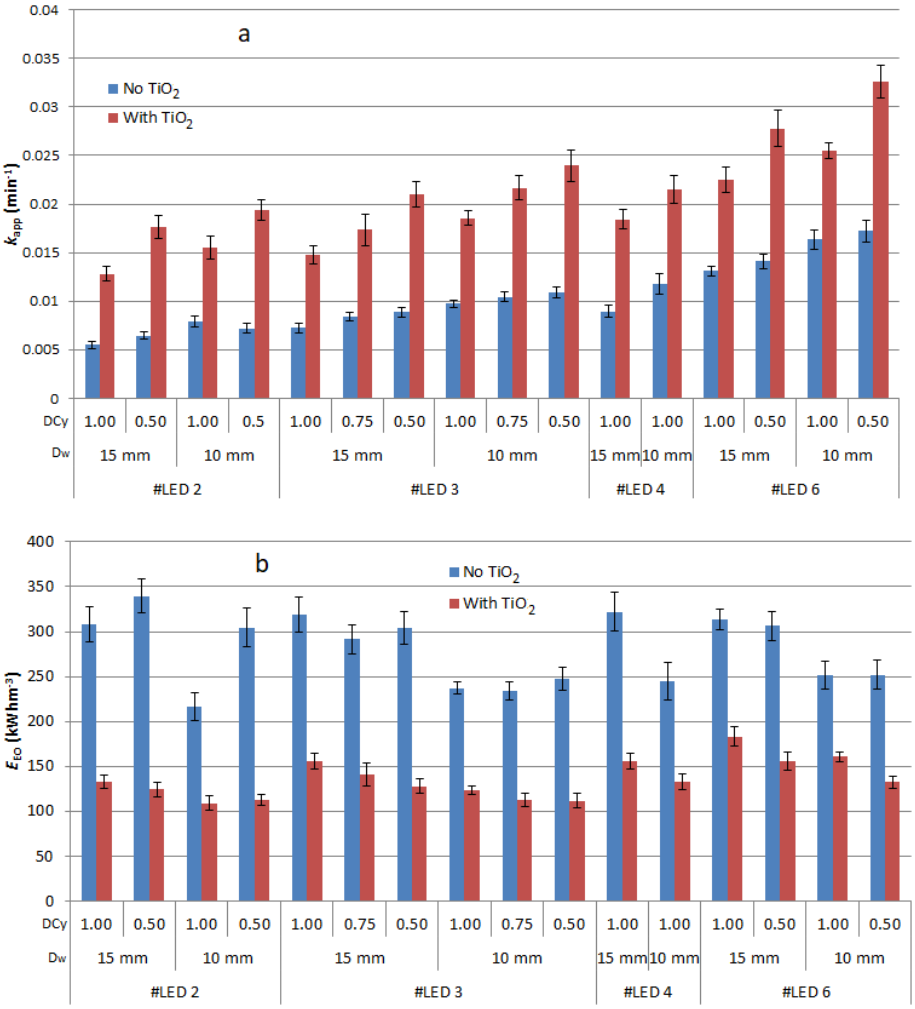

Figure 3. k_{app} (a) and E_{EO} (b) values for all experiments of ciprofloxacin degradation as a function of different variables (DCy, Ti, D_w and #LED)

Figure 4 shows the predicted and experimental values of k_{app} and E_{EO} for all experiments. The predicted values were calculated adopting an equation obtained from a full-factorial experimental design of experiments.

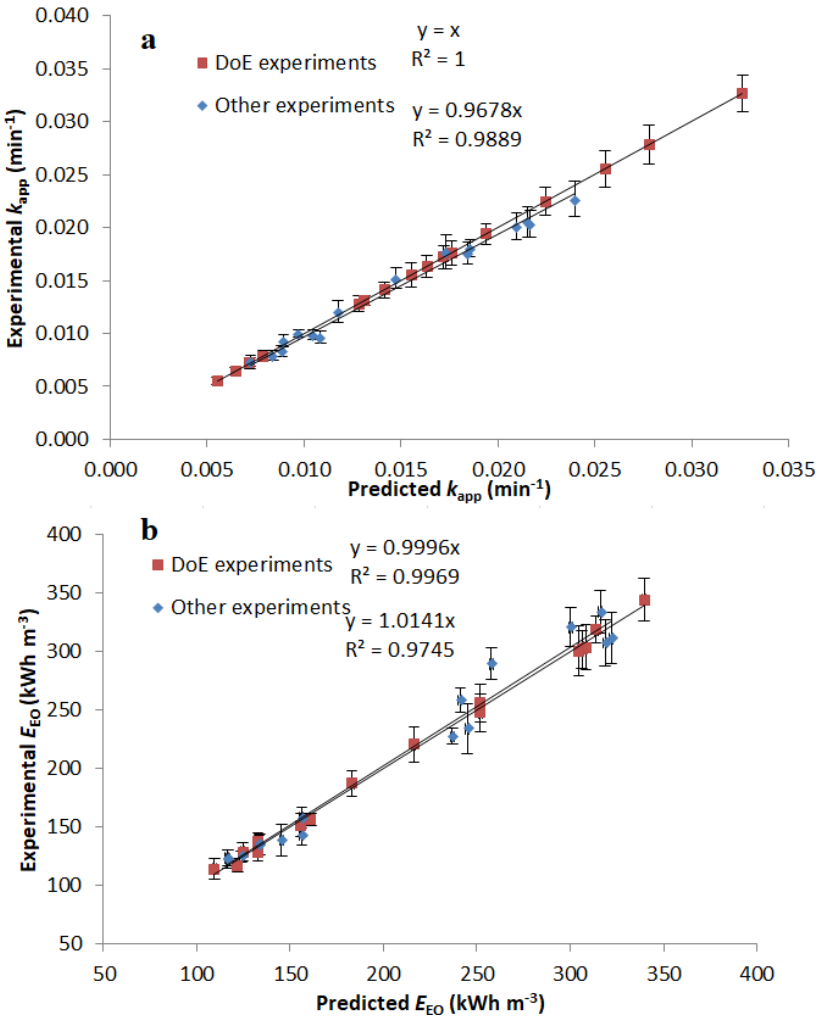

Figure 4. Predicted and experimental values of k_{app} (a) and E_{EO} (b) for all experiments

In **figure 5,** Lenth's analysis shows the parameters which are most relevant for degradation rates and energy consumption values for ciprofloxacin's degradation. Although all individual variables tested (duty cycle, TiO_2 presence, number of LED columns around the reactor and their distance to the reactor's walls) are beyond the significance's threshold (margin of error, ME) for degradation rate, only the presence of TiO_2 and wall distance had a significant impact on electrical energy per order consumption. This happens because the energetic trade-off was not sufficient to turn the kinetic gain into lower electricity demands. The array c (3 LED columns, D_W=10 mm, TiO_2 and DCy = 0.50) was considered the best one evaluated, since it combined low energy consumption with high degradation rates and homogenous light distribution.

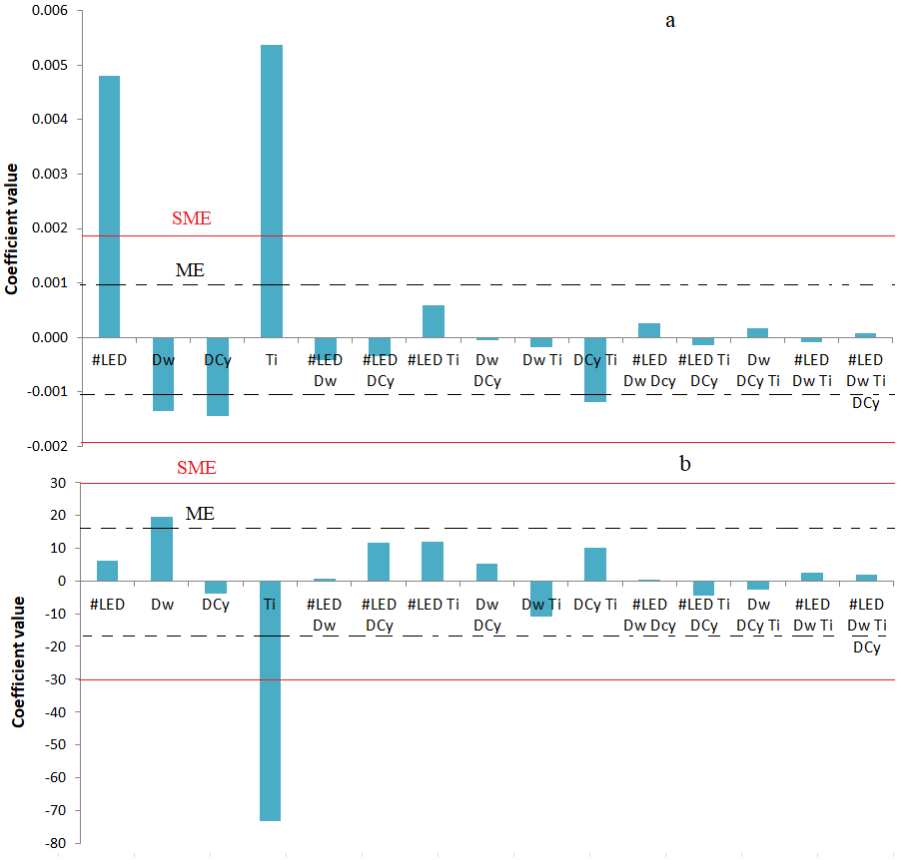

Figure 5. Lenth's analysis for (a) k_{app} and (b) E_{EO}

3.3. Degradation of mixture of targeted OMPs

In the next research phase, simultaneous degradation of multiple organic micropollutants was studied. Targeted OMPs are: ciprofloxacin (CIP), sulfamethoxazole (SMX), trimethoprim (TMP), venlafaxine (VX) and O-desmethylvenlafaxine (DVX). They (CIP, SMX and TMP) were selected from the list of pharmaceuticals established under the D1.1 report of the NOWELTIES project (Table 4. Indicator substances for Systems Using Ozone or other AOPs). Additionally, VX and its metabolite DVX were included in targeted OMPs based on their frequent detection in environmental waters and usually low to moderate removal rates in conventional wastewater treatment plants. Moreover, to be noted that all the targeted OMPs are included in the recent Watch list 2020/1161.

The degradation of targeted OMPs was monitored using the developed high-performance liquid chromatography method with a diode array detector (HPLC-DAD).

Figure 6 shows the apparent constant rate of degradation of all 5 OMPs after different photolytic and photocatalytic processes using UV-LED sources of different wavelengths (UVA = 365 nm, UVC = 257 nm). Although each compound reacts differently, it is possible to state that hydrogen

peroxide's presence (0.12 mM) increased degradation rates in all cases. Only CIP was susceptible to degradation by UVA alone.

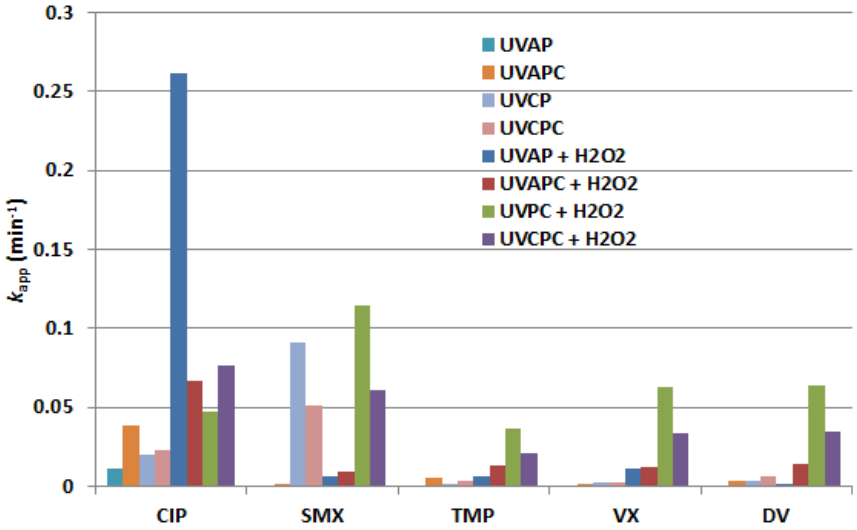

Figure 6. k_{app} values for multiple processes. UVAP: UVA photolysis; UVAPC: UVA photocatalysis; UVCP: UVC photolysis; UVCPC: UVC photocatalysis

The impact on degradation rates of UVA and UVC adopted simultaneously was also evaluated and results are shown in **figure 7**. In comparison to **figure 6**, no synergistic improvement was observed.

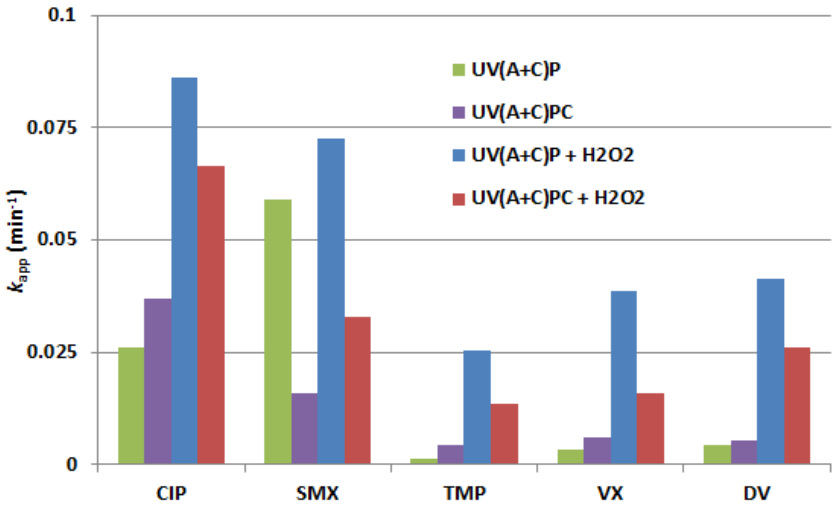

Figure 7. k_{app} values for multiple processes using combined wavelengths (UVA and UVC). UV(A+C)P: combined photolysis; UV(A+C)PC: combined photocatalysis

4. Preliminary evaluation of toxicity

Figure 8 shows luminescence variation on *Vibrio fischeri* after the degradation tests described in the section 3.3. The results show that photolysis and photocatalysis performed with UVA light (UVAP and UVAPC) generated more toxic substances. Other treatments showed a decrease in toxicity.

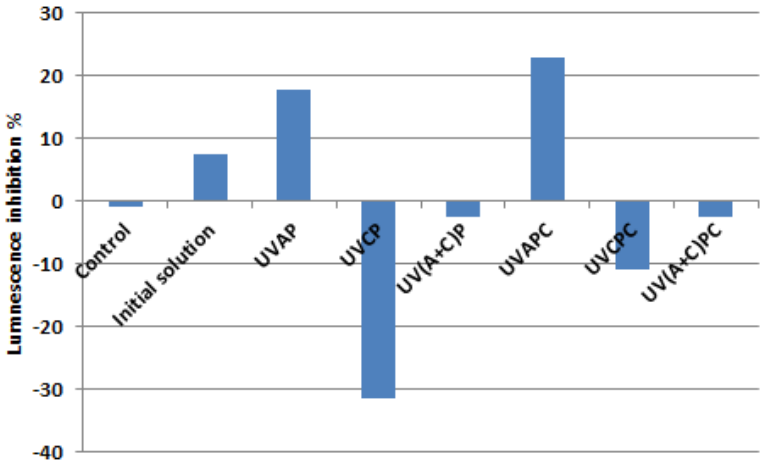

Figure 8. Luminescence inhibition on *Vibrio fischeri* after treatments after 1 h.

5. Preliminary evaluation of targeted OMPs transformation products

For preliminary evaluation of transformation products, OMPs degradation was monitored using high performance liquid chromatography coupled to triple quadrupole mass spectrometer (HPLC-MS/MS) with electrospray ionisation (ESI).

Figure 9 shows Total Ion Chromatogram (TIC) of SMX reaction solution (c_0=10 ppm, in ultrapure water) obtained after certain times of degradation by UVC photolysis. Extracted ion chromatograms (EIC) are shown in **figures 10 and 11** for *m/z* values of 254 and 174, respectively. The formation of a SMX's isomer can be observed in **figure 10a.** Complete degradation of SMX and its isomer were observed after 1 and 2 hours of reaction, respectively. Their mass spectrum is shown in **figure 12**. The second TP can be a combination of sulfanilic acid and its hydroxyl derivative, 4-(hydroxyamino)benzenesulfonic acid. The proposed TPs and their structures were based on studies by Trovó [1] and Periša [2].

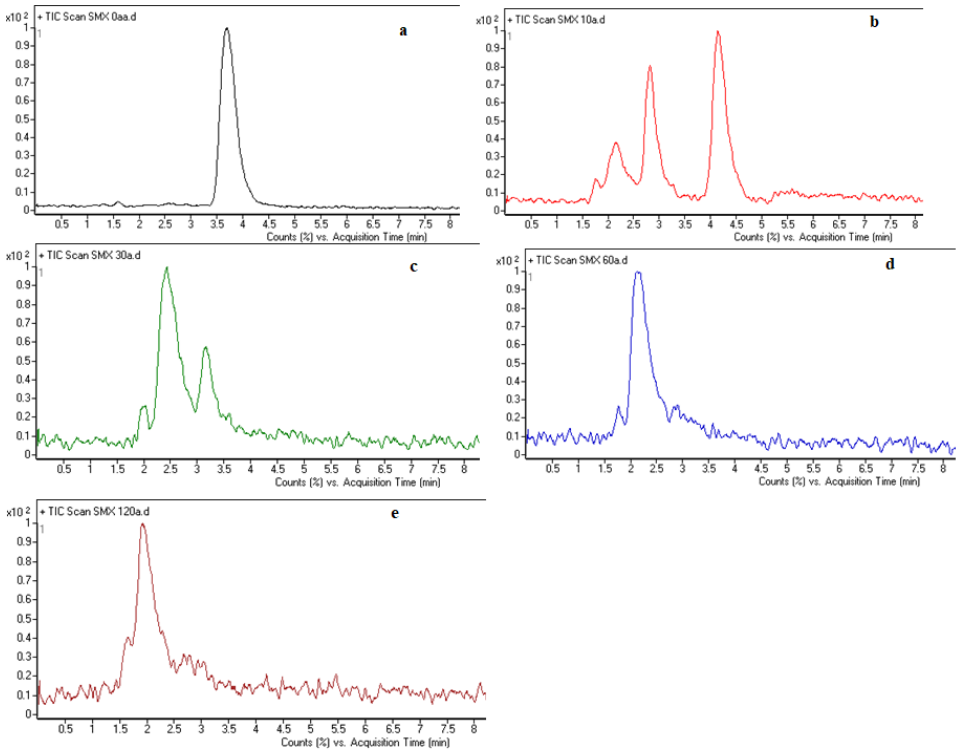

Figure 9. LC-MS TIC chromatograms for SMX degradation by UVC photolysis at times a) 0 min, b) 10 min, c) 30 min, d) 60 min, and e) 120 minutes

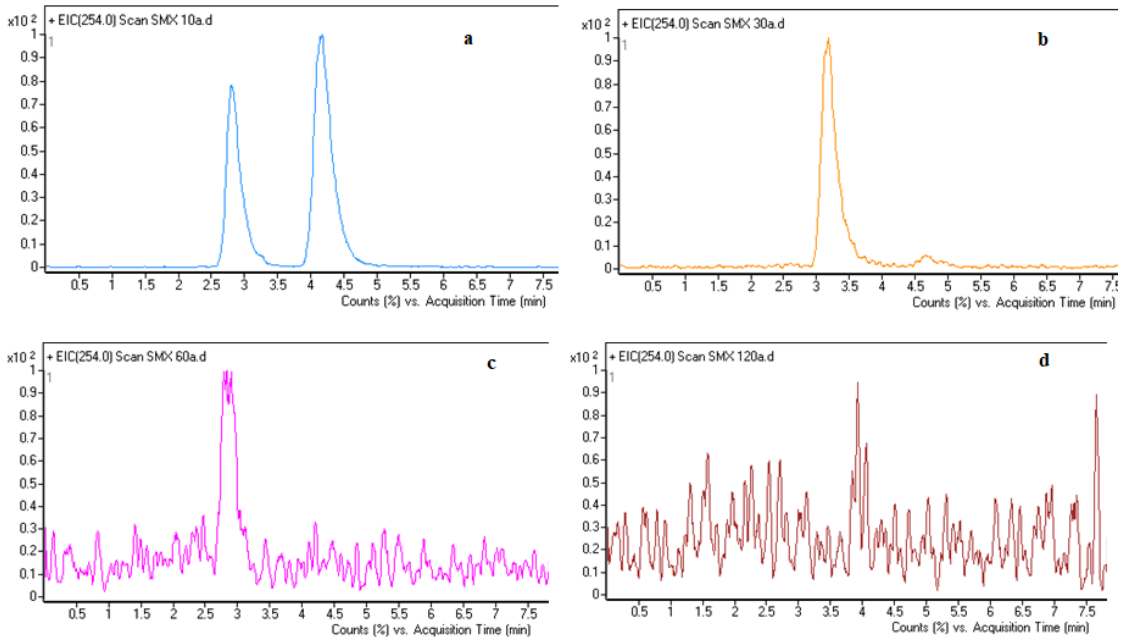

Figure 10. LC-MS EIC (*m/z* = 254) chromatograms for SMX degradation by UVC photolysis at times a) 10 min, b) 30 min, c) 60 min, and d) 120 minutes

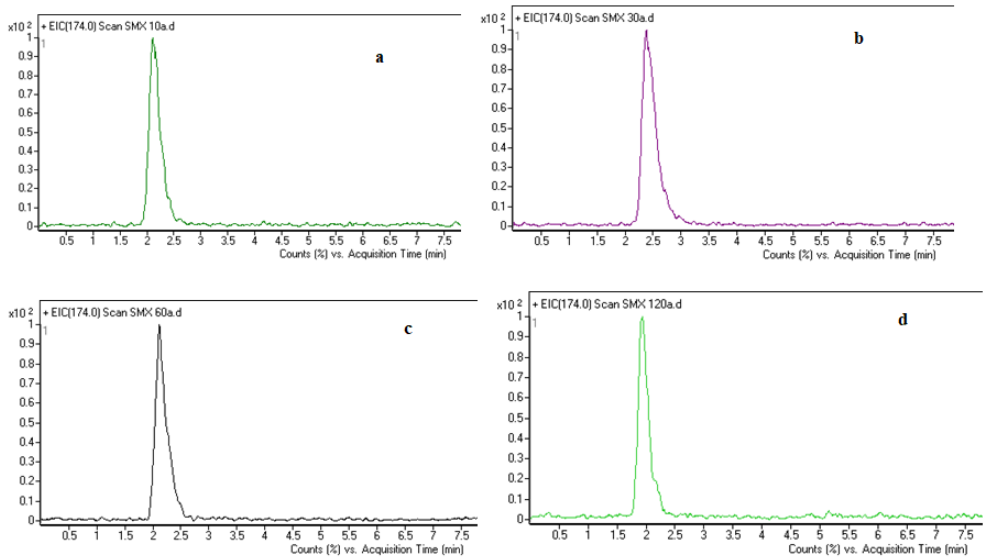

Figure 11. LC-MS EIC (*m/z* = 174) chromatograms for SMX degradation by UVC photolysis at times a) 10 min, b) 30 min, c) 60 min, and d) 120 minutes

Figure 12 shows TIC of CIP reaction solution (c_0=10 ppm, in ultrapure water) obtained after certain times of degradation by UVA photocatalysis. Extracted ion chromatograms (EIC) are shown in **figure 13** for *m/z* values of 332, 291, and 346 respectively after 1 hour of degradation. CIP did not get completely degraded. According to Babić [3], the formation of the TP with *m/z* 346 is related to oxidation of the piperazine ring by photolysis. While, according to Li and Hu [4], TP with *m/z* 291 is the result of oxidation followed by dealkylation of the piperazine ring caused by reaction with hydroxyl radicals.

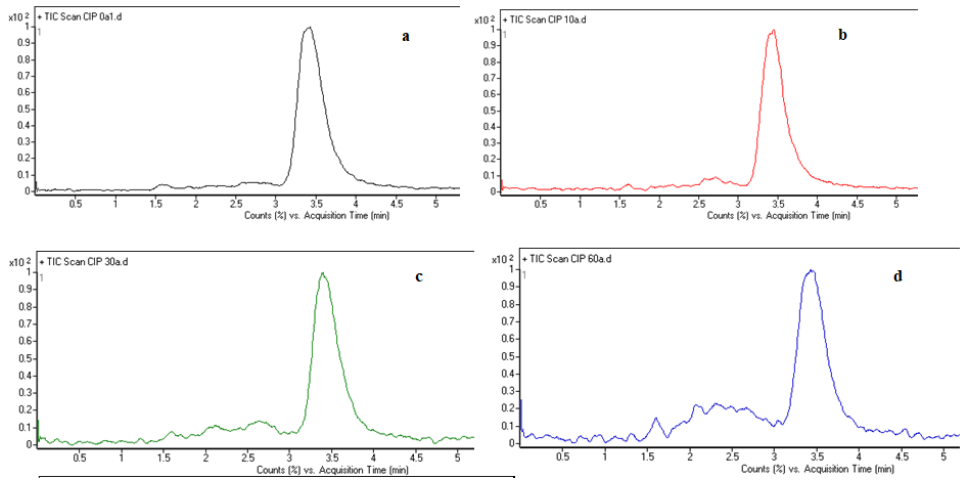

Figure 12. LC-MS TIC chromatograms for CIP degradation by UVA photocatalysis at times a) 0 min, b) 10 min, c) 30 min, d) 60 min

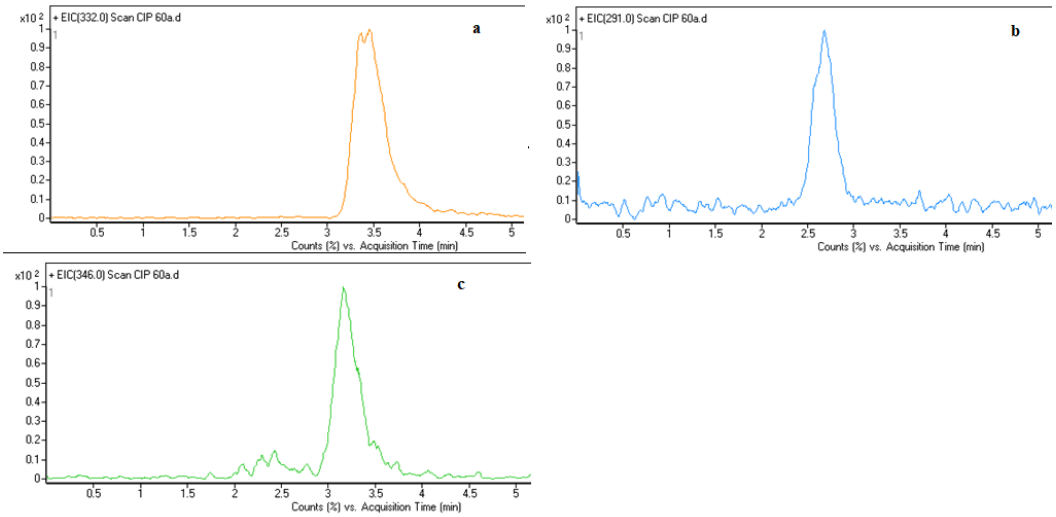

Figure 13. LC-MS EIC for CIP degradation by UVA photocatalysis at *t* = 60 minutes for *m/z* values 332 (a), 291 (b), and 346 (c)

6. References

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