



# Comparison between heterogeneous and homogeneous solar driven advanced oxidation processes for urban wastewater treatment: Pharmaceuticals removal and toxicity

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## ARTICLE INFO

### Keywords:

Contaminants of emerging concern  
Pharmaceuticals  
Photocatalysis  
Solar photo Fenton  
Wastewater reuse

## ABSTRACT

The release of toxic contaminant of emerging concern from urban wastewater treatment plants (UWTPs) into the environment calls for more effective (tertiary) treatment methods. In this manuscript, homogeneous solar-driven advanced oxidation processes (AOPs), namely  $\text{H}_2\text{O}_2/\text{sunlight}$ , solar photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{sunlight}$ ) and solar photo-Fenton with ethylenediamine-N,N'-disuccinic acid (EDDS) complex ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{EDDS}/\text{sunlight}$ ) were compared to a new heterogeneous process (supported nitrogen-doped  $\text{TiO}_2$  (N-TiO<sub>2</sub>)/sunlight), with the aim of contributing to fill the gap between lab scale tests and full scale applications as well as to provide a sustainable solution for tertiary treatment in small UWTPs. Process efficiency was evaluated in terms of effluent toxicity and degradation of a mixture of three pharmaceuticals (namely carbamazepine (CBZ), diclofenac and trimethoprim), at initial concentration of 200  $\mu\text{g}/\text{L}$  each, in deionized water (DW) and real wastewater (WW).  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{EDDS}/\text{sunlight}$  was found to be the most effective process (98% removal of CBZ from WW in 60 min, 5.6 kJ/L as cumulative solar energy per unit of volume). Conventional solar photo Fenton was drastically and negatively affected by water matrix, due to the spontaneous neutral pH and iron precipitation in real WW. Although N-TiO<sub>2</sub>/sunlight process was not so affected by water matrix, it was found to be less efficient (30% removal of CBZ in 180 min, 13.3 kJ/L) than  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{EDDS}/\text{sunlight}$  process. Toxicity values were found to be lower in WW compared to DW matrix. Class weight scores for WW samples showed a toxicity reduction up to the no acute toxicity level for N-TiO<sub>2</sub>/sunlight and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{EDDS}/\text{sunlight}$  treatments, while  $\text{H}_2\text{O}_2/\text{sunlight}$  and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{sunlight}$  increased the final effluent toxicity up to slightly acute levels.

## 1. Introduction

### 1.1. Contaminants of emerging concern into the environment and in urban wastewater treatment plants

In the last decades increasing attention has been paid to the occurrence of contaminants of emerging concern (CECs) into the environment as well as on their release from urban wastewater treatment plants (UWTPs) effluents (Teodosiu et al., 2018). CECs include

pharmaceuticals and personal care products, pesticides and herbicides among others. Although CECs are usually detected at low concentration (ng/L– $\mu\text{g}/\text{L}$ ) in urban wastewater and receiving water bodies, they can produce sub-chronic or chronic toxicity with potential collateral effect on aquatic ecosystems and human health through the food chain, in particular when treated wastewater are reused for crop irrigation [1,2]. Among pharmaceuticals, antibiotics occurrence in wastewater is of particular concern because they can promote the development of antibiotic resistance [3,4]. Conventional secondary (e.g., activated sludge

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<https://doi.org/10.1016/j.seppur.2019.116249>

Received 30 August 2019; Received in revised form 16 October 2019; Accepted 22 October 2019

Available online 23 October 2019

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process) and tertiary (such as filtration and disinfection) treatments in UWTs are unable to completely remove CECs [5,6].

### 1.2. Effect of consolidated and new tertiary treatment methods on CECs removal

Consolidated advanced/tertiary treatments such as chlorination (poorly effective in CECs removal, formation of toxic chlorination by products) [7,8], activated carbon (AC) adsorption (poorly effective in bacterial inactivation) [9], ozonation (possible formation of toxic oxidation by products) [10], membrane filtration (high energy demand), UV-C disinfection (poorly effective in CECs removal) either did not show to be effective or did result in some drawbacks [6]. In order to minimize the release of CECs in the effluents, advanced oxidation processes (AOPs) seem to be a particularly attractive option. AOPs are based on the generation of powerful reactive radicals (among which hydroxyl radicals,  $\cdot\text{OH}$ ) which have a significant role in the removal of CECs due to high oxidation potential [11,12].

### 1.3. Homogeneous Vs heterogeneous photo driven AOPs

AOPs can be categorized as photo- (among which UV/ $\text{H}_2\text{O}_2$ , photo-Fenton and  $\text{TiO}_2$  photocatalysis) and non-photo- (such as Fenton,  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$  etc.) driven AOPs. Depending on the process, a number of current drawbacks exist making them a not economically sustainable solution, mainly because of the pH operating conditions (e.g., Fenton and photo-Fenton) and high electricity demand (e.g., ozone and UV-based AOPs) [6]. As photo Fenton process is of concern, different solutions have been recently suggested and investigated to overcome the pH-related problem, like heterogeneous photo-Fenton [13] and the use of chelating agents such as ethylenediamine-N,N'-disuccinic acid (EDDS) [14] or new purposely synthesized complexing agents [15], which avoid metal precipitation and make the process effective even under neutral pH condition. To save energy cost and make the process more sustainable, photo-driven AOPs can be operated also with solar radiation [16,17]. Heterogeneous photo driven AOPs have been also investigated in the removal of CECs from water [18,19]. However, heterogeneous solar driven photocatalytic processes, in particular those implementing semiconductors (such as  $\text{TiO}_2$ ) as catalyst, have found to be less effective than solar photo-Fenton [20], because  $\text{TiO}_2$  is less efficient under solar light sources. In order to improve radiation absorption under solar light,  $\text{TiO}_2$  has been doped by nitrogen [21]. Moreover, the photocatalyst used in its powder form would request an additional treatment step to remove it before effluent disposal or reuse, further increasing treatment cost. However, this problem can be addressed by fixing the photocatalyst onto a support [22]. These limitations, under both a technological and process viewpoint, make the above described AOPs not ready for full scale applications in tertiary/advanced urban wastewater treatment [6]. Several gaps about the efficiency of supported photocatalysts solar driven AOPs in removing CECs at environmentally relevant concentrations from real wastewater are still present, discouraging the up-scale of this technology.

### 1.4. Objectives, experimental design and novelty

The aim of this study was to comparatively assess the performance of homogeneous and heterogeneous solar driven AOPs in a pilot-scale compound triangular collector (CTC) plant in removing a mixture of CECs (carbamazepine (CBZ), diclofenac (DCF) and trimethoprim (TMP)) in real wastewater (WW). More specifically heterogeneous solar driven AOP using a supported nitrogen-doped  $\text{TiO}_2$  (N- $\text{TiO}_2$ ) photocatalyst was compared with three different homogeneous solar driven AOPs at spontaneous aqueous solutions pH: (i)  $\text{H}_2\text{O}_2/\text{sunlight}$ ; (ii) solar photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{sunlight}$ ); and (iii) solar photo-Fenton with EDDS complex ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{EDDS}/\text{sunlight}$ ). The effect of water matrix (deionized water (DW) vs real WW) and toxicity were also evaluated.

Antiepileptic drug CBZ, non-steroidal anti-inflammatory agent DCF and antibiotic TMP were selected as model CECs because they are (i) typically detected in urban wastewater, (ii) included in the EU Watch List (DCF), (iii) relevant for crop uptake and (iii) antibiotic resistance (TMP) [5]. Even though, a number of studies on the effect of homogeneous and heterogeneous solar driven AOPs on CECs removal have been carried out, just poor information is available about comparative investigations, and no attempt has been made so far, to our knowledge, to compare solar driven photo Fenton (even with a chelating agent) to solar heterogeneous photocatalysis using new generation photocatalysts (such as N- $\text{TiO}_2$  in our case) in real wastewater.

## 2. Material and methods

### 2.1. Chemicals

CBZ, DCF and TMP, all high purity grade (> 99%) were purchased from Sigma-Aldrich (Germany). Hydrogen peroxide (30% w/v), catalase, titanium (IV) oxysulfate, hydroxylamine hydrochloride, ammonium acetate, o-phenanthroline, EDDS (35%) were supplied from Sigma-Aldrich (Germany). Sodium thiosulfate (99% w/w),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , hydrochloric acid (1 N), and glacial acetic acid were obtained from Carlo Erba (France). Hydrochloric acid (37%) was purchased from Titolchimica (Italy). All solvents used for ultrahigh performance liquid chromatography/mass spectrometry (UPLC/MS) were UPLC grade and purchased from Carlo Erba (Italy). Water used for liquid chromatography as well as for preparing all aqueous solutions (18.2 M $\Omega$  cm, organic carbon content  $\leq 4 \mu\text{g/L}$ ) was obtained from Milli-Q Gradient A-10 system (Millipore).

### 2.2. Wastewater samples

Wastewater samples were taken from a large UWT (300.000 equivalent inhabitants) located in the province of Salerno (Campania Region, Italy). Samples were taken from the effluent of the biological treatment step just upstream of the disinfection unit. Samples were collected in 25 L tanks. The samples were stored at about 4 °C during transport. The average values of the main parameters are given in Table S11 (in supplementary information file). The background concentrations in the wastewater samples of CBZ, DCF and TMP were also measured before each experiments (Table S12).

### 2.3. Pilot scale solar photoreactor

Experiments under direct sunlight were carried out at University of Salerno (southern Italy), in a CTC solar reactor [23]. The CTC reactor (10.24 L irradiated volume) consists of 8 acrylic glass tubes (150 cm length, 3.3 cm external diameter, 0.25 cm thickness). The platform was inclined to 40° during the experiments, according to the latitude of the Laboratory, to maximize sunlight absorption. In order to perform some tests in parallel, each process was operated in one tube of the reactor. A vessel was filled with 2.7 L of CECs WW/DW solution and the system was operated in a recirculation mode at a flow rate of 260 mL/min. The solar irradiation ( $\text{W/m}^2$ ) was measured by a radiometer (Black Comet, StellarNet Inc.). The average solar UVA irradiance for all tests was  $29.7 \pm 5.3 \text{ W/m}^2$ , with a maximum value of  $35.6 \text{ W/m}^2$ . In this study, CECs removal rates are plotted as function of both experimental time (t) and cumulative solar energy per unit of volume ( $Q_s$ ) received in the photoreactor, according to Eq. (1):

$$Q_{s,n} = Q_{s,n-1} + \Delta t_n \cdot \text{SR}_{G,n} \cdot A_r / (1000 \cdot V_t) \quad (1)$$

$Q_{s,n}$  and  $Q_{s,n-1}$  are the cumulative solar energy per unit of volume (kJ/L) at times n and n-1, respectively;  $\text{SR}_{G,n}$  is the average incident sunlight radiation on the irradiated area ( $\text{W/m}^2$ ),  $\Delta t_n$  (s) is the experimental time of the sample,  $A_r$  is the illuminated area of the reactor ( $\text{m}^2$ ) and  $V_t$  is the total volume of the treated water (L).

## 2.4. Solar driven AOPs experiments

The experiments were carried out for 300 min from the morning (typical start time 11.00 am) to the afternoon (4.00 pm), from July to November 2018. Water samples (10 mL) were collected for the analyses of CECs concentration from the reactor tank every 15 min for the first hour and every 30 min for the following hours during the photocatalytic tests. The initial concentration of the target CECs used (200 µg/L for each CEC) was selected as a compromise between environmentally relevant concentrations and experimental needs.

Solar experiment was performed as control test to discriminate the contribution of sunlight in the degradation of the target CECs. Before to start the experiments the tubes were covered by aluminum foil to allow the preliminary operations (tubes filling by the water solution, reagents addition where relevant). All experiments were performed at spontaneous pH. In homogeneous solar driven AOPs, taking into account matrix effect, an initial concentration of 20 mg/L of H<sub>2</sub>O<sub>2</sub> was used in DW experiments, while it was increased to 50 mg/L in WW experiments due to the higher oxidant demand of the real water matrix and according to the scientific literature [24,25]. Sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) was added to DW and WW samples to quench residual H<sub>2</sub>O<sub>2</sub> (200 mg/L of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> for 20 mg/L of H<sub>2</sub>O<sub>2</sub> and 500 mg/L of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> for 50 mg/L of H<sub>2</sub>O<sub>2</sub>) before CECs measurements [26]. Temperature, pH, residual iron concentration (where relevant) and residual H<sub>2</sub>O<sub>2</sub> concentration (where relevant) were monitored (Tables S13–S16). In H<sub>2</sub>O<sub>2</sub>/sunlight and solar photo-Fenton tests, H<sub>2</sub>O<sub>2</sub> was added during the treatment as necessary to keep the concentration close to the initial value. The operating conditions of the investigated AOPs are summarized in Table S17.

### 2.4.1. H<sub>2</sub>O<sub>2</sub>/sunlight

After filling the tube of the reactor with the solution and H<sub>2</sub>O<sub>2</sub>, the aqueous matrix was mixed for 6 min (time of one cycle), before to uncover the reactor to start H<sub>2</sub>O<sub>2</sub>/sunlight experiment.

### 2.4.2. Solar photo-Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/sunlight)

The reactor was filled in with the aqueous solution and H<sub>2</sub>O<sub>2</sub>; Fe(II) was added as FeSO<sub>4</sub>·7H<sub>2</sub>O after 6 min mixing. The reactor was uncovered after further 6 min. In wastewater experiments, 50 mg/L of H<sub>2</sub>O<sub>2</sub> and 0,1 mM (5.6 mg/L) of Fe(II) were used, according to the scientific literature [24,25]. In DW experiments, the concentrations of H<sub>2</sub>O<sub>2</sub> and Fe(II) were fixed at 20 mg/L and 5.6 mg/L, respectively.

### 2.4.3. Solar photo-Fenton with EDDS (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/EDDS/sunlight)

The stock solution was prepared under dark conditions by dissolving FeSO<sub>4</sub>·7H<sub>2</sub>O in Milli-Q grade water previously acidified at pH 3 with 1 N HCl solution [27]. Once the iron dissolved, the EDDS was added and the mixture was stirred for 6 min. The following concentrations of the reagents were used during the tests in WW: 50 mg/L of H<sub>2</sub>O<sub>2</sub>, 5.6 mg/L (0.1 mM) of Fe(II), 58 mg/L (0.2 mM) of EDDS, according to a previous work [27]. In DW tests a lower H<sub>2</sub>O<sub>2</sub> concentration was used (20 mg/L).

### 2.4.4. N-TiO<sub>2</sub>/sunlight

In heterogeneous solar driven AOP tests, one tube of the module was packed with N-TiO<sub>2</sub> structured photocatalyst (434 g), which preparation method and characteristics are explained elsewhere [23]. N-TiO<sub>2</sub> photocatalysts was first investigated in powder form [21,28] and subsequently the powder was immobilized on the support through the solvent-casting method, by mixing 0.5 g of N-TiO<sub>2</sub> to 25 mL of acetone, the amount of the photocatalyst being selected according to previous results [23,29].

## 2.5. Analytical measurements

Temperature (Table S13) and pH (Table S14) were measured by

Hanna instrument (Woonsocket, USA). Samples were filtered through 0.22 mm nylon filters (Aisimo, Millipore Millex® GN) before CECs measurement. CECs concentration was monitored at various reaction times by an Ultimate 3000 UPLC System (Thermo Fisher Scientific), according to the procedure explained in the supplementary information file. Iron concentration was measured spectrophotometrically by a Lambda 25 instrument (Perkin Elmer, Massachusetts, USA), at 510 nm according to the 1, 10 – phenanthroline method (ISO 6332) (Table S15), while hydrogen peroxide was determined at 410 nm using titanium (IV) oxysulfate solution (DIN 38 402 H15) (Table S16).

## 2.6. Toxicity tests

A battery of acute (A) and chronic (C) toxicity tests (*Vibrio fischeri* (A), *Raphidocelis subcapitata* (C), and *Daphnia magna* (A)) was carried out on treated (60 and 300 min), untreated (0 min) WW and DW (100 mL) samples [30,31]. These toxicity tests were selected according to their consolidated use for toxicity assessment of treated and untreated wastewater, particularly as indirect measurement of the formation of toxic oxidation intermediates during AOPs treatment of water and wastewater [32]. In order to quench residual H<sub>2</sub>O<sub>2</sub>, stock solution of catalase (100 mg/L) was added to the samples to reach the concentration of 2 mg/L and 5 mg/L of catalase in DW and WW, respectively. Toxicity tests with *V. fischeri* (NRRL-B-11177), *R. subcapitata*, and *D. magna* were carried out according to standardized methods ([33–35], respectively) and procedures explained in previous works [36,37]. Toxicity was expressed as percentage of the effect on the undiluted samples. Homoscedasticity (F test,  $p < 0.05$ ) and normality (Shapiro-Wilk test,  $p < 0.05$ ) of data were verified, the significance of differences between average values of different experimental treatments and controls was assessed by the analysis of variance (ANOVA,  $p < 0.05$ ). When ANOVA revealed significant differences among treatments, *post-hoc* tests were carried out with Tukey's test ( $p < 0.05$ ) according to SigmaPlot version 11.0. Toxicity data were integrated according to Personne et al. [38] approach for natural water. The hazard classification system based on the percentage of the effect (PE) includes Class I for PE < 20% (score 0), Class II for 20% ≤ PE < 50% (score 1), Class III for 50% ≤ PE < 100% (score 2), Class IV when PE = 100% in at least one test (score 3), and Class V when PE = 100% in all bioassays (score 4). Finally, the integrated class weight score was determined by averaging the values corresponding to each microbiotest class normalised to the most sensitive organism (highest score) [39].

## 3. Results and discussion

### 3.1. Control test

Control tests with DW were performed to evaluate the effect on CECs of sunlight and H<sub>2</sub>O<sub>2</sub> as standalone processes, respectively (Fig. 1).

DCF was effectively degraded by sunlight as standalone process (80% after 120 min treatment (15.3 kJ/L)), consistently with a previous work [40]. However, sunlight was poorly effective in the degradation of TMP (only 15% removal after 300 min and 35.0 kJ/L) and not effective in the degradation of CBZ, in agreement with the results available in scientific literature [41,42]. The effect of H<sub>2</sub>O<sub>2</sub> on the degradation of CBZ, DCF and TMP under dark conditions was investigated for 20 mg/L of H<sub>2</sub>O<sub>2</sub>. Degradation rate changed depending on the target CEC: from 18% after 300 min for TMP to 35% after 150 min for CBZ and 40% after 240 min for DCF. Sunlight and H<sub>2</sub>O<sub>2</sub> processes cannot effectively remove all the target CECs thus making AOPs necessary to further minimize the release of CECs into the environment.

### 3.2. Comparison among solar driven AOPs in DW

The combination sunlight and H<sub>2</sub>O<sub>2</sub> promoted the formation of ·OH

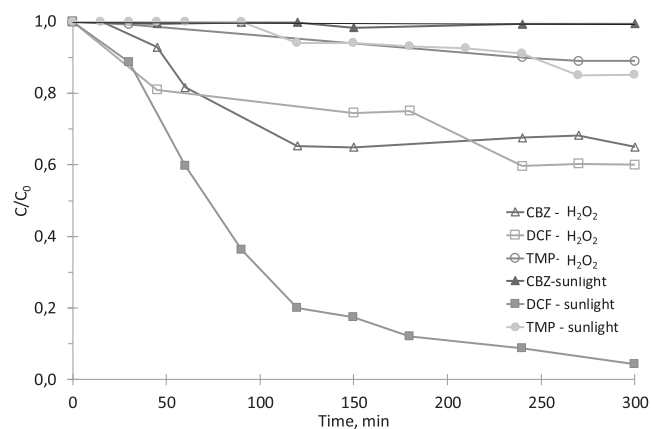


Fig. 1. Degradation of CECs: control test with  $\text{H}_2\text{O}_2$  (20 mg/L) and sunlight as standalone processes in DW.

and enhanced the degradation of the target CECs (Fig. 2) compared to sunlight and  $\text{H}_2\text{O}_2$  processes, respectively. CBZ was effectively oxidized after 150 min (80% removal) as well as TMP (85% removal after 150 min) and DCF (99% removal after 120 min,  $Q_S = 12.1$  kJ/L). While the removal of CECs by UV-C/ $\text{H}_2\text{O}_2$  process has been widely investigated [24,43,44], less information is available about  $\text{H}_2\text{O}_2$ /sunlight process [25].

As heterogeneous solar driven AOP is of concern, the effect on CECs in aqueous matrices has been mainly investigated by using  $\text{TiO}_2$  (typically P25 in powder form) as photocatalyst [45–47]. Unfortunately, such approach has some drawbacks including low photon efficiency due to the poor absorption of  $\text{TiO}_2$  under sunlight and need of a post-treatment to remove  $\text{TiO}_2$  particles before effluent disposal or reuse. These limitations can be overcome by fixing the photocatalyst on a support and by doping the photocatalyst with non-metals [23,48]. In our study N- $\text{TiO}_2$ /sunlight process resulted in 99% degradation of CBZ after 300 min ( $Q_S = 35.0$  kJ/L). A faster degradation kinetic was observed for DCF and even in this case a total removal was observed after 300 min of solar exposure. Total removal was also observed for TMP, at a lower irradiation time (240 min,  $Q_S = 30.0$  kJ/L). The removal efficiency observed for CBZ and DCF in our work is consistent with a previous work where solar photocatalytic efficiency of  $\text{TiO}_2$  immobilized on glass spheres (sol being prepared by titanium isopropoxide, commercial P25 and polyethylene glycol) was investigated in different aqueous matrices spiked with 15 CECs, in a compound parabolic collector (CPC) solar based reactor [48]. The formation of CBZ oxidation intermediates by photocatalysis was also investigated and carbamazepine epoxide, acridine, and acridone were detected [49]. The oxidation process results in the attack of the CBZ olefinic bond in a central heterocyclic ring and subsequently in an intramolecular cyclization mechanism.

When solar photo Fenton was investigated (spontaneous pH 3.43, Table S14), high CECs degradation was observed already under dark conditions (solar reactor uncovered). As matter of fact, 99% of all CECs were removed just after  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  addition (4 min contact time). Similar results were observed in the solar photo Fenton experiment with EDDS. Before uncovering the reactor, CBZ, DCF and TMP were removed at 67%, 70% and 81% respectively, already under dark conditions. In this case the initial spontaneous pH was higher (5.73) and increased during the treatment (Table S14). The results observed under dark conditions are in agreement with the scientific literature. As matter of fact, Miralles-Cuevas et al. [14] compared degradation of CECs by solar photo-Fenton mediated by EDDS at neutral pH and solar photo-Fenton at pH 3.5 and they also observed a high degradation of CECs in dark. The formation of oxidation intermediates of CECs was investigated even during solar-driven photo Fenton process and azepane ring contraction, azepane ring cleavage, and delamination

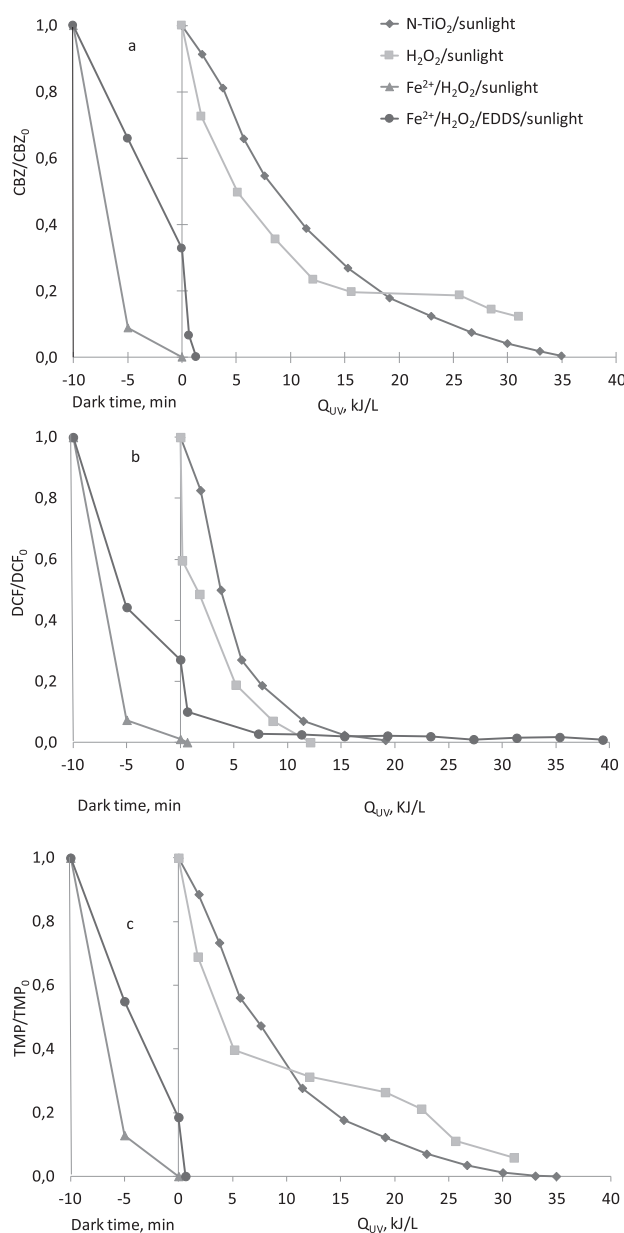
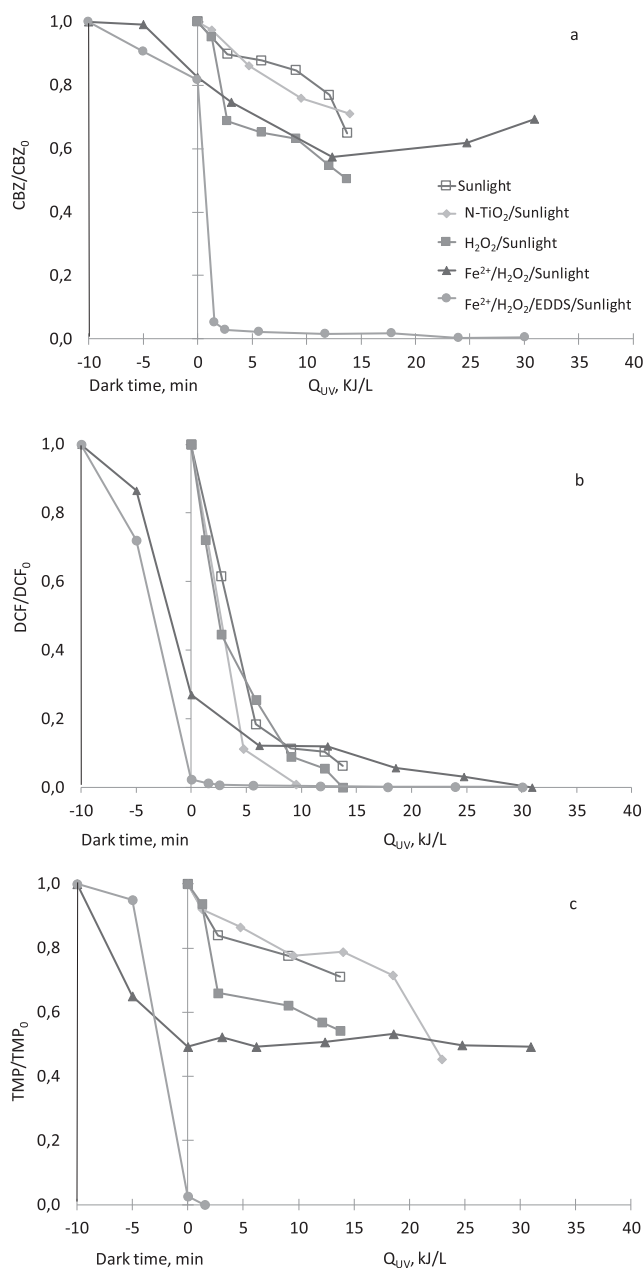


Fig. 2. Degradation of CBZ (a), DCF (b) and TMP (c) by N-  $\text{TiO}_2$ /sunlight,  $\text{H}_2\text{O}_2$ /sunlight (20 mg/L), photo Fenton ( $C_{\text{Fe}^{2+}} = 0,1$  mM (5.6 mg/L);  $C_{\text{H}_2\text{O}_2} = 20$  mg/L) and photo-Fenton with EDDS ( $C_{\text{Fe}^{2+}} = 0,1$  mM (5.6 mg/L);  $C_{\text{EDDS}} = 0,2$  mM (58 mg/L);  $C_{\text{H}_2\text{O}_2} = 20$  mg/L) processes in DW.

mechanisms were observed following CBZ degradation [50]. In the case of DCF, the degradation took place through a dechlorination mechanism, and carboxylic acids (maleic, acetic, formic and oxalic acids) were detected as degradation products [51]. The main pathway of the DCF degradation was attributed to the initial hydroxylation of the phenylacetic acid (moiety in the C-4 position) and to the formation of a quinone imine intermediate which was later hydroxylated, decarboxylated, and/or oxidate [52]. An alternative pathway was based on the oxidative process of C–N bond cleavage. The TMP transformation pathways in solar-driven photo Fenton process include hydroxylation, oxidation, demethylation, and decarboxylation mechanisms [53]. Trimethoxybenzoylpyrimidine has been found as the primary product of TMP degradation intermediate. In particular, the hydroxylation mechanism resulted in the formation of monohydroxylated, dihydroxylated and polyhydroxylated by-products. Some of TMP by-products are formed during hydroxylation–demethylation mechanism. The



**Fig. 3.** Degradation of CBZ (a), DCF (b) and TMP (c) by sunlight, N-TiO<sub>2</sub>/sunlight; H<sub>2</sub>O<sub>2</sub>/sunlight (50 mg/L); photo Fenton (C<sub>Fe<sup>2+</sup></sub> = 0,1 mM (5,6 mg/L); C<sub>H<sub>2</sub>O<sub>2</sub></sub> = 50 mg/L); photo-Fenton with EDDS (C<sub>Fe<sup>2+</sup></sub> = 0,1 mM (5,6 mg/L); C<sub>EDDS</sub> = 0,2 mM (58 mg/L); C<sub>H<sub>2</sub>O<sub>2</sub></sub> = 50 mg/L) processes in WW.

electrophilic addition of the hydroxyl radical to the aromatic ring, with subsequent addition of molecular oxygen and elimination of a hydroperoxyl radical results in the formation of phenolic product. Keto-derivatives have been found as products of further oxidation.

### 3.3. Comparison among solar driven AOPs in WW

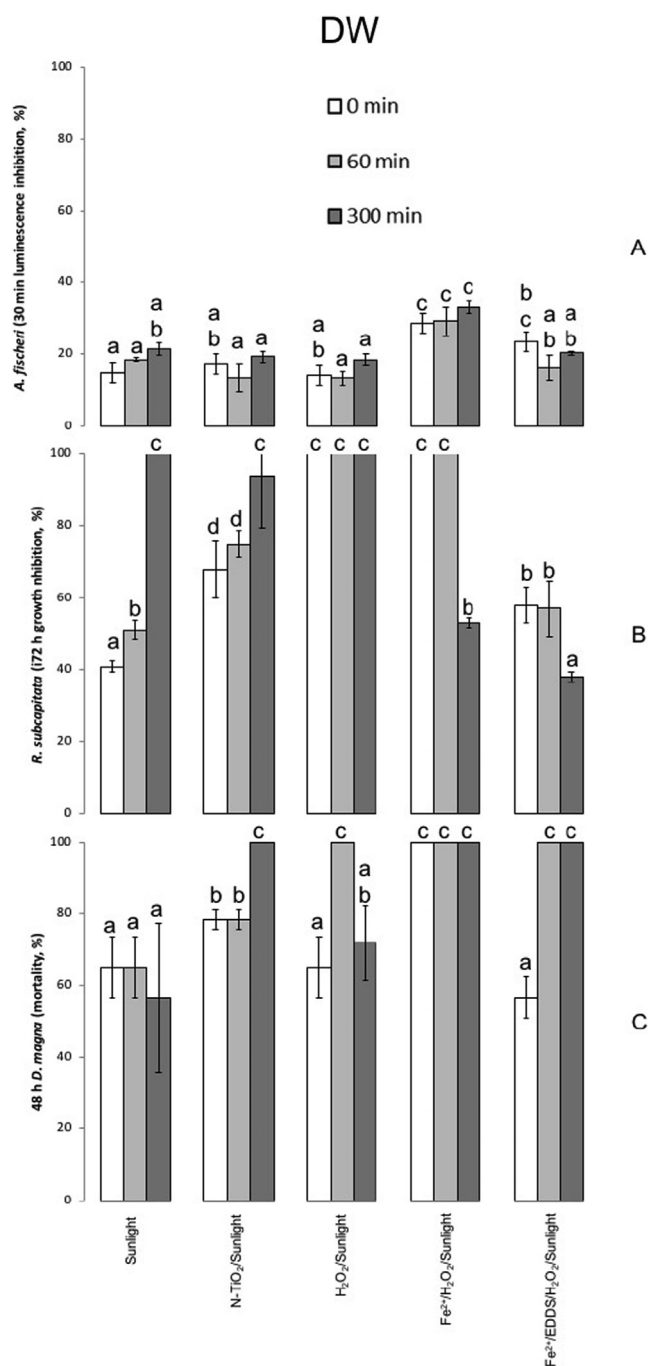
Control experiment by sunlight as standalone process in WW (Fig. 3) resulted in photodegradations of CBZ (23%) and TMP (29%) significantly lower than DCF (99%, after 300 min, Q<sub>S</sub> = 13.7 kJ/L).

Due to the oxidant demand of WW, the initial concentration of H<sub>2</sub>O<sub>2</sub> was increased to 50 mg/L. H<sub>2</sub>O<sub>2</sub>/sunlight process decreased CBZ, DCF and TMP concentration up to 45%, 99% and 44%, respectively, in the early 240 min (Q<sub>S</sub> = 12.1 kJ/L) (Fig. 3). In spite of the higher initial H<sub>2</sub>O<sub>2</sub> concentration, the process was less effective in WW matrix than

the same process in DW, possibly because of the competition with other contaminants and/or radical scavengers occurring in WW. Basically, a similar trend was observed in solar photo Fenton tests compared to DW experiments. Noteworthy, even dark Fenton resulted in a significant removal of the target CECs, being them removed in the following order DCF > TMP > CBZ (Fig. 3). The pH of the aqueous solution strongly affected process efficiency. As matter of fact, solar photo Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/sunlight) efficiency drastically decreased in WW (Fig. 3) compared to DW (Fig. 2). The spontaneous pH of DW was lower than WW, where iron precipitation took place. According to the results of dissolved iron concentration in the respective water matrices, it decreased faster in WW tests than DW (Table S15). The removal of CECs by photo-Fenton has been previously investigated [54,55]. Klammerth et al., [56] investigated the effect of solar photo Fenton in the degradation of 15 CECs under comparable experimental set-up (CPC reactor) and operating conditions. These ones included: (i) an initial concentration of 100 µg/L for each CEC, (ii) different water matrices (including WW), (iii) slight acidification (to decrease pH at 5–6 to remove radicals scavengers such as carbonates) and the same H<sub>2</sub>O<sub>2</sub> and Fe concentrations. The same behavior (removal of CBZ and DCF even under dark conditions (Fenton) and improved removal with solar photo Fenton) was observed.

Unlike of conventional solar photo Fenton, when EDDS was added, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/EDDS/sunlight process confirmed the higher efficiency compared to the other processes (Fig. 3) already observed in DW experiments. In such a case, the process was affected by the water matrix to a less extent compared to solar photo Fenton, because the addition of the chelating agent prevented the precipitation of iron at neutral pH. Even in this case the reaction started under dark (Fenton process) and the degradation of the target CECs significantly improved under solar radiation (99% removal of CBZ and TMP was achieved in the early 15 min, Q<sub>S</sub> = 1.2 kJ/L). These results are consistent with those observed in a previous work, under comparable set-up and operating conditions [57].

Water matrix effect was also observed for N-TiO<sub>2</sub>/sunlight process, with a decreased efficiency in WW compared to DW. As matter of fact, N-TiO<sub>2</sub>/sunlight process was less effective than the other investigated processes in the removal of CBZ and TMP (27% and 55% respectively after 300 min, Q<sub>S</sub> = 22.9 kJ/L) in WW. Only conventional solar photo Fenton resulted in a lower TMP removal, but just at the end of the exposure time. The scientific literature lacks comparative studies on homogeneous and heterogeneous solar driven AOPs in the removal of CECs from real wastewater, and only recently heterogeneous photocatalysis using three catalysts in powder form (200 mg/L each) (TiO<sub>2</sub>-P25, a composite consisting of TiO<sub>2</sub> and 4.0 wt% of graphene oxide (GO-TiO<sub>2</sub>), but without the addition of GO) was compared to photo-Fenton process (initial pH adjusted to 5.5, 20 mg/L of H<sub>2</sub>O<sub>2</sub> and 10 mg/L of Fe<sup>2+</sup>) in the degradation of three CECs, among which CBZ and DCF [58]. Heterogeneous photocatalysis with TiO<sub>2</sub>-P25 was more efficient (80% CBZ removal for Q<sub>S</sub> < 40 kJ/L) compared to solar photo-Fenton (20% CBZ removal), possibly because of iron precipitation. In addition to pH, initial iron concentration and organic matter, also temperature affects iron precipitation [59]. Therefore, the higher removal of CBZ observed in our work (40%, Q<sub>S</sub> = 12.4 kJ/L) can be explained by (i) the different wastewater characteristics, (ii) the lower temperature (max 27 °C in our work, Table S13, up to 43 °C in the above quoted work) and (iii) the lower initial iron concentration (Table S15). The lower efficiency of N-TiO<sub>2</sub> photocatalysis in the removal of CBZ (30%, Q<sub>S</sub> = 14.0 kJ/L) in our work compared to the TiO<sub>2</sub>-P25 tests in the quoted manuscript, can be explained by (i) the wastewater characteristics, (ii) the different photocatalyst (N-TiO<sub>2</sub> Vs TiO<sub>2</sub>-P25) and (iii) the different form of the photocatalysts (supported Vs suspended).

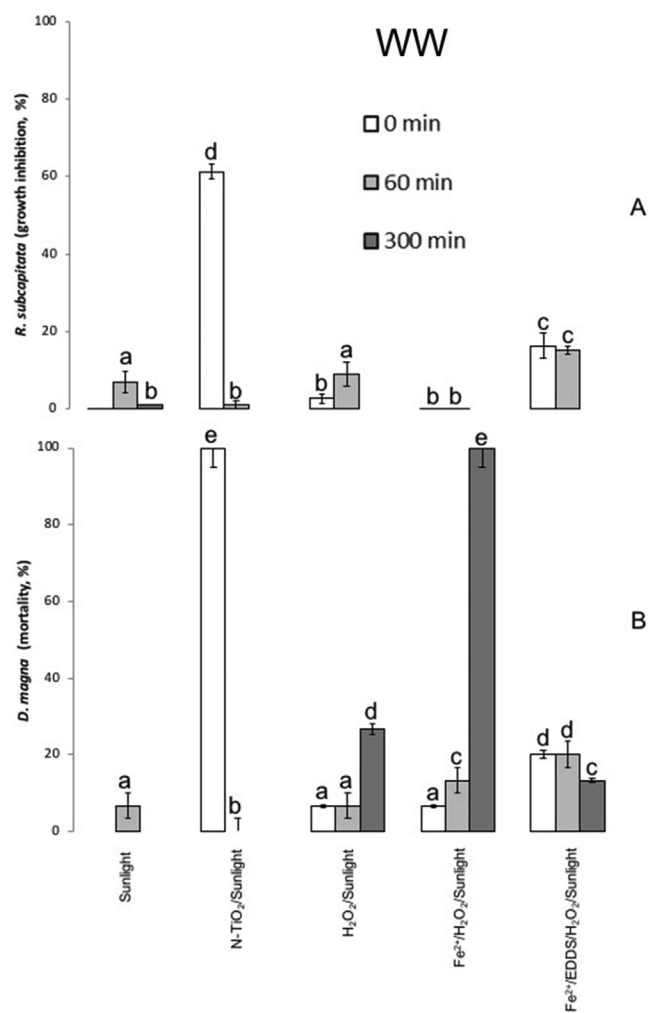


**Fig. 4.** . Toxicity of CECs solutions (CBZ, TMP and DCF at 200 µg/L initial concentration each one) treated with solar driven AOPs assessed considering *A. fischeri* (A), *R. subcapitata* (B) and *D. magna* (C) in DW; letters (a-e) indicate significant statistical difference ( $\alpha = 0.05$ ) according to Tuckey's test.

### 3.4. Effect of solar driven AOPs on effluent toxicity

Toxicity of treated DW and WW based samples are summarized in Figs. 4 and 5, respectively. Results of spiked DW treated with solar driven AOPs showed species-specific effects with increasing level of toxicity as follows: *A. fischeri* < *R. subcapitata* < *D. magna* (Fig. 4A–C).

In DW control samples with sunlight as standalone process less toxicity was observed compared to all others experiments, possibly because the process did not effectively remove CBZ and TMP, thus not forming toxic oxidation intermediates. After 300 min of illumination,



**Fig. 5.** . Toxicity of CECs solutions (CBZ, TMP and DCF at 200 µg/L initial concentration each one) treated with solar driven AOPs assessed considering *R. subcapitata* (A) and *D. magna* (B) in WW; letters (a–e) indicate significant statistical difference ( $\alpha = 0.05$ ) according to Tuckey's test.

toxicity values decreased from 100% up to 53% and from 57% to 38% in *R. subcapitata* in the solar photo Fenton and solar photo-Fenton with EDDS complex, respectively. The toxicity of samples tested with *D. magna* increased as the exposure time increased from day 1 to day 2 (24 h data were not reported here). *D. magna* test showed high toxicity levels (100%) for both experiments. None of the treatments was able to reduce up to 50% the toxicity, and frequently toxicity increased as treatment time increased from 0 to 300 min for all endpoints. Apparently, CECs toxicity cannot be effectively removed via the considered treatments in DW, suggesting that CECs oxidation intermediates are more toxic than their parental compounds [32].

Lower toxicity was observed in the WW treated samples compared to DW tests (Fig. 5A and B). This trend can be possibly explained by the matrix effect which resulted in a lower efficiency in the removal of the target CECs compared to DW matrix, which in turn possibly resulted in a lower formation of oxidation intermediates.

Data about the *A. fischeri* were not reported here because effects were all slightly negative and proxy to zero. Microalgae and daphnids evidenced that the whole toxicity in WW was lower than in DW. Treatments like N-TiO<sub>2</sub>/sunlight and Fe/H<sub>2</sub>O<sub>2</sub>/sunlight still increased the final toxicity of the effluent like in the case of DW based samples after 300 min, while H<sub>2</sub>O<sub>2</sub>/sunlight process only slightly increased it. To provide an integrated interpretation of toxicity results, further considerations according to [31] were summarized in Table 1 (details

**Table 1**  
Class weight score (%) after 0, 60 and 300 min of treatment for both DW and WW.

Min	DW			WW		
	0	60	300	0	60	300
Sunlight	50	50	83	0	0	0
N-TiO <sub>2</sub> /sunlight	67	67	67	56	0	0
H <sub>2</sub> O <sub>2</sub> /sunlight	56	67	67	0	0	33
Fe/H <sub>2</sub> O <sub>2</sub> /sunlight	78	78	67	0	0	33
Fe/H <sub>2</sub> O <sub>2</sub> /EDDS/sunlight	83	56	83	33	33	0

have been reported in Tables S18 and S19). The class weight scores evidenced that the toxicity of CECs' mixture in DW was never effectively reduced, neither after 300 min of treatment, resulting always at the end of the process as acutely toxic.

Conversely, the same mixture of CECs in WW highlighted lower toxicity levels after treatment than in DW scenario, suggesting, in addition to the lower formation of oxidation intermediates, even a positive "matrix" effect. Class weight scores for WW samples treated with solar radiation showed no acute hazard, and a toxicity reduction up to the "no acute toxicity" level was evidenced for N-TiO<sub>2</sub>/sunlight and Fe/EDDS/H<sub>2</sub>O<sub>2</sub>/sunlight treatments, while H<sub>2</sub>O<sub>2</sub>/sunlight and Fe/H<sub>2</sub>O<sub>2</sub>/sunlight increased the final effluent toxicity up to "slightly acute" levels. Similarly to our findings in DW based treatments, Donner et al. [60] highlighted that the toxicity of CBZ solution increased as degradation time increased, indicating that the mixture of degradation products formed was more toxic than the parent compound. The three endpoint used were still inhibited more than 60% (compared to negative controls) even after 90 min of UV-treated CBZ solution. Some authors suggested that the increased toxicity after photocatalytic treatment in TiO<sub>2</sub> water suspensions, even after 300 min of treatment, could be attributed to the formation of hardly oxidizable organic intermediates [61,62].

#### 4. Conclusions

Solar driven photo Fenton with chelating agent EDDS was found to be the most effective process in the removal of the target CECs from the investigated water matrices. Aqueous matrix drastically and negatively affected process efficiency of conventional solar photo Fenton, possibly due to the precipitation of iron in real WW at neutral pH. Noteworthy, N-TiO<sub>2</sub>/sunlight was less effective than the other investigated processes in the removal of CBZ and TMP in WW. Toxicity values were found to be lower in WW compared to DW matrix, possibly due to both a lower formation of oxidation intermediates (as consequence of a lower removal rate of the target CECs), and a positive "matrix" effect. These results also confirm that monitoring residual concentration of the target CECs in the effluent is not sufficient and toxicity should be also measured to avoid to dispose/reuse tertiary treated wastewater more toxic than secondary treated one. Although progresses to improve heterogeneous solar driven AOPs have been made by synthesizing new photocatalysts active under sunlight, this process (namely N-TiO<sub>2</sub>/sunlight) is not yet competitive with Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/EDDS/sunlight in the removal of CECs from secondary treated urban wastewater because higher irradiation times are necessary, which would result in larger surface area for solar reactors. According to the results achieved, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/EDDS/sunlight process is a promising sustainable solution for tertiary treatment in small UWTPs.

#### Declaration of Competing Interest

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

#### Acknowledgement

Gulnara Maniakova would like to thank University of Salerno, Italian Ministry for University and Research (MIUR) and European Union (European Social Fund) for supporting her PhD grant through "Programma Operativo Nazionale Ricerca e Innovazione 2014-2020 (CCI 2014IT16M2OP005), Fondo Sociale Europeo, Azione I.1 "Dottorati Innovativi con caratterizzazione Industriale". Katarzyna Kowalska would like to thank the Ministry of Science and Higher Education (Poland) for the financial support (Project 08/080/BKM18/0060 and 08/080/BK\_18/0054). Luigi Rizzo would like to thank the University of Salerno for the financial support through FARB2017 - Codice ORSA178411 (Trattamento terziario di acque reflue urbane mediante processi di ossidazione avanzata foto-attivati).

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.116249>.

#### References

- [1] M. Rand-Weaver, L. Margiotta-Casaluci, A. Patel, G.H. Panter, S.F. Owen, J.P. Sumpter, The read-across hypothesis and environmental risk assessment of pharmaceuticals, *Environ. Sci. Technol.* 47 (2013) 11384–11395.
- [2] T. Malchi, Y. Maor, G. Tadmor, M. Shenker, B. Chefetz, Irrigation of root vegetables with treated wastewater: evaluating uptake of pharmaceuticals and the associated human health risks, *Environ. Sci. Technol.* 48 (2014) 9325–9333.
- [3] C.M. Manaia, J. Rocha, N. Scaccia, R. Marano, E. Radu, F. Biancullo, F. Cerqueira, G. Fortunato, I.C. Iakovides, I. Zammit, I. Kampouris, I. Vaz-Moreira, O.C. Nunes, Antibiotic resistance in wastewater treatment plants: tackling the black box, *Environ. Int.* 115 (2018) 312–324, <https://doi.org/10.1016/j.envint.2018.03.044>.
- [4] L. Rizzo, C. Manaia, C. Merlin, T. Schwartz, C. Dagot, M.C. Ploy, I. Michael, D. Fatta-Kassinos, Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: a review, *Sci. Total Environ.* 447 (2013) 345–360, <https://doi.org/10.1016/j.scitotenv.2013.01.032>.
- [5] P. Krzeminski, M.C. Tomei, P. Karaolia, A. Langenhoff, C.M.R. Almeida, E. Felis, F. Gritten, H.R. Andersen, T. Fernandes, C.M. Manaia, L. Rizzo, D. Fatta-Kassinos, Performance of secondary wastewater treatment methods for the removal of contaminants of emerging concern implicated in crop uptake and antibiotic resistance spread: a review, *Sci. Total Environ.* 648 (2019) 1052–1081, <https://doi.org/10.1016/j.scitotenv.2018.08.130>.
- [6] L. Rizzo, S. Malato, D. Antakyali, V. Beretsou, M. Đolić, W. Gernjak, E. Heath, I. Ivancev-Tumbas, P. Karaolia, Ribeiro A. Lado, G. Mascolo, C. McArdell, H. Schaar, A. Silva, D. Fatta-Kassinos, Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater, *Sci. Total Environ.* 655 (2019) 986–1008.
- [7] W. Fu, et al., New insights into the chlorination of sulfonamide: smiles-type rearrangement, desulfation, and product toxicity, *Chem. Eng. J.* 331 (2018) 785–793, <https://doi.org/10.1016/j.cej.2017.09.024>.
- [8] G. Cerreta, M.A. Roccamante, I. Oller, S. Malato, L. Rizzo, Contaminants of emerging concern removal from real wastewater by UV/free chlorine process: a comparison with solar/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> at pilot scale, *Chemosphere* 236 (2019) 124354, <https://doi.org/10.1016/j.chemosphere.2019.124354>.
- [9] P. Biswas, R. Bandyopadhyaya, Water disinfection using silver nanoparticle impregnated activated carbon: escherichia coli cell-killing in batch and continuous packed column operation over a long duration, *Water Res.* 100 (2016) 105–115, <https://doi.org/10.1016/j.watres.2016.04.048>.
- [10] J. Hollender, S.G. Zimmermann, S. Koepke, M. Krauss, C.S. McArdell, C. Ort, H. Singer, U. von Gunten, S. Hansruedi, Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a fullscale post-ozonation followed by sand filtration, *Environ. Sci. Technol.* 43 (2009) 7862–7869, <https://doi.org/10.1021/es9014629>.
- [11] D. Fatta-Kassinos, M.I. Vasquez, K. Kümmerer, Transformation products of pharmaceuticals in surface waters and wastewater formed during photolysis and advanced oxidation processes – degradation, elucidation of byproducts and assessment of their biological potency, *Chemosphere* 85 (2011) 693–709, <https://doi.org/10.1016/j.chemosphere.2011.06.082>.
- [12] L. Rizzo, G. Lofrano, C. Gago, T. Bredneva, P. Iannece, M. Pazos, N. Krasnogorskaya, M. Carotenuto, Antibiotic contaminated water treated by photo driven advanced oxidation processes: ultraviolet/H<sub>2</sub>O<sub>2</sub> Vs ultraviolet/peracetic acid, *J. Cleaner Prod.* 205 (2018) 67–75, <https://doi.org/10.1016/j.jclepro.2018.09.101>.
- [13] A. Kumar, A. Rana, G. Sharma, M. Naushad, P. Dhiman, A. Kumari, F.J. Stadler, Recent advances in nano-Fenton catalytic degradation of emerging pharmaceutical contaminants, *J. Mol. Liq.* 290 (2019) 111177, <https://doi.org/10.1016/j.molliq.2019.111177>.
- [14] S. Miralles-Cuevas, I. Oller, A. Ruiz-Delgado, A. Cabrera-Reina, L. Cornejo-Ponce, S. Malato, EDDS as complexing agent for enhancing solar advanced oxidation processes in natural water: effect of iron species and different oxidants, *J. Hazard.*

- Mater. 372 (2019) 129–136, <https://doi.org/10.1016/j.jhazmat.2018.03.018>.
- [15] A. Fiorentino, R. Cucciniello, A. Di Cesare, D. Fontaneto, P. Prete, L. Rizzo, G. Corno, A. Proto, Disinfection of urban wastewater by a new photo-Fenton like process using Cu-iminodisuccinic acid complex as catalyst at neutral pH, *Water Res.* 146 (2018) 206–215, <https://doi.org/10.1016/j.watres.2018.08.024>.
- [16] S. Malato, P. Fernández, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catal. Today* 147 (2009) 1–59.
- [17] A. Fiorentino, B. Esteban, J.A. Garrido Cardenas, K. Kowalska, L. Rizzo, A. Agüera, J.A. Sánchez Pérez, Effect of solar photo-Fenton process in raceway pond reactors at neutral pH on antibiotic resistance determinants in secondary treated urban wastewater, *J. Hazard. Mater.* (2019), <https://doi.org/10.1016/j.jhazmat.2019.06.014>.
- [18] G. Sharma, V.C. Gupta, S. Agarwal, S. Bhogal, M. Naushad, A. Kumar, F.J. Stadler, Fabrication and characterization of trimethylammonium nano-photocatalyst for remediation of ampicillin antibiotic, *J. Mol. Liq.* 260 (1) (2018) 342–350, <https://doi.org/10.1016/j.molliq.2018.03.059>.
- [19] Y. Zhang, J. Zhou, X. Chen, L. Wang, W. Cai, Coupling of heterogeneous advanced oxidation processes and photocatalysis in efficient degradation of tetracycline hydrochloride by Fe-based MOFs: Synergistic effect and degradation pathway, *Chem. Eng. J.* 369 (2019) 745–757, <https://doi.org/10.1016/j.cej.2019.03.108>.
- [20] G. Ferro, A. Fiorentino, M.C. Alferez, M.I. Polo-López, L. Rizzo, P. Fernández-Ibáñez, Urban wastewater disinfection for agricultural reuse: effect of solar driven AOPs in the inactivation of a multidrug resistant *E. coli* strain, *Appl. Catal. B* 178 (2015) 65–73, <https://doi.org/10.1016/j.apcatb.2014.10.043>.
- [21] L. Rizzo, D. Sannino, V. Vaiano, O. Sacco, A. Scarpa, D. Pietrogiamici, Effect of solar simulated N-doped TiO<sub>2</sub> photocatalysis on the inactivation and antibiotic resistance of an *E. coli* strain in biologically treated urban wastewater, *Appl. Catal. B* 144 (2014) 369–378, <https://doi.org/10.1016/j.apcatb.2013.07.033>.
- [22] L. Paredes, S. Murgolo, H. Dzinun, M.H. Dzarfan Othman, A.F. Ismail, M. Carballa, G. Mascolo, Application of immobilized TiO<sub>2</sub> on PVDF dual layer hollow fibre membrane to improve the photocatalytic removal of pharmaceuticals in different water matrices, *Appl. Catal. B* 240 (2019) 9–18, <https://doi.org/10.1016/j.apcatb.2018.08.067>.
- [23] O. Sacco, V. Vaiano, L. Rizzo, D. Sannino, Photocatalytic activity of a visible light active structured photocatalyst developed for municipal wastewater treatment, *J. Cleaner Prod.* 175 (2018) 38–49, <https://doi.org/10.1016/j.jclepro.2017.11.088>.
- [24] N. De la Cruz, L. Esquius, D. Grandjean, A. Magnet, A. Tungler, L.F. de Alencastro, C. Pulgarín, Degradation of emergent contaminants by UV, UV/H<sub>2</sub>O<sub>2</sub> and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant, *Water Res.* 47 (2013) 5836–5845, <https://doi.org/10.1016/j.watres.2013.07.005>.
- [25] G. Ferro, M.I. Polo-López, A. Martínez-Piernas, P. Fernández-Ibáñez, A. Agüera, L. Rizzo, Cross-contamination of residual emerging contaminants and antibiotic resistant bacteria in lettuce crops and soil irrigated with wastewater treated by sunlight/H<sub>2</sub>O<sub>2</sub>, *Environ. Sci. Technol.* 49 (2015) 11096–11104, <https://doi.org/10.1021/acs.est.5b02613>.
- [26] W. Liu, S.A. Andrews, M.I. Stefan, J.R. Bolton, Optimal methods for quenching H<sub>2</sub>O<sub>2</sub> residuals prior to UFC testing, *Water Res.* 37 (2003) 3697–3703, [https://doi.org/10.1016/S0043-1354\(03\)00264-1](https://doi.org/10.1016/S0043-1354(03)00264-1).
- [27] P. Soriano-Molina, J.L. García Sánchez, S. Malato, L.A. Pérez-Estrada, J.A. Sánchez Pérez, Effect of volumetric rate of photon absorption on the kinetics of micropollutant removal by solar photo-Fenton with Fe<sup>3+</sup>-EDDS at neutral pH, *Chem. Eng. J.* 331 (2018) 84–92, <https://doi.org/10.1016/j.cej.2017.08.096>.
- [28] O. Sacco, M. Stoller, V. Vaiano, P. Ciambelli, A. Chianese, D. Sannino, Photocatalytic degradation of organic dyes under visible light on n-doped TiO<sub>2</sub> photocatalysts, *Int. J. Photoenergy* (2012), <https://doi.org/10.1155/2012/626759> Article ID 626759.
- [29] R. Ata, O. Sacco, V. Vaiano, L. Rizzo, G.Y. Tore, D. Sannino, Visible light active N-doped TiO<sub>2</sub> immobilized on polystyrene as efficient system for wastewater treatment, *J. Photochem. Photobiol. A* 348 (2017) 255–262, <https://doi.org/10.1016/j.jphotochem.2017.08.054>.
- [30] G. Lofrano, G. Libralato, M. Carotenuto, M. Guida, M. Inglesse, A. Siciliano, S. Meriç, Emerging concern from short-term textile leaching: a preliminary ecotoxicological survey, *Bull. Environ. Contam. Toxicol.* 97 (2016) 646–652, <https://doi.org/10.1007/s00128-016-1937-x>.
- [31] G. Lofrano, G. Libralato, A. Casaburi, A. Siciliano, P. Iannece, M. Guida, L. Pucci, E.F. Dentice, M. Carotenuto, Municipal wastewater spiramycin removal by conventional treatments and heterogeneous photocatalysis, *Sci. Total Environ.* 624 (2018) 461–469, <https://doi.org/10.1016/j.scitotenv.2017.12.145>.
- [32] L. Rizzo, Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment, *Water Res.* 45 (2011) 4311–4340, <https://doi.org/10.1016/j.watres.2011.05.035>.
- [33] ISO, Water quality – Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test), ISO 11348-3:2007, 2007.
- [34] ISO, Water quality – Fresh water algal growth inhibition test with unicellular green algae, ISO 8692:2012, 2012b.
- [35] ISO, Water quality — Determination of the inhibition of the mobility of *Daphnia magna* Straus (Cladocera, Crustacea) — Acute toxicity test ISO 6341:2012, 2012a.
- [36] G. Libralato, A.V. Ghirardini, F. Avezzù, Evaporation and air-stripping to assess and reduce ethanalamines toxicity in oily wastewater, *J. Hazard. Mater.* 153 (2008) 928–936.
- [37] M. Carotenuto, G. Libralato, H. Gürses, A. Siciliano, L. Rizzo, M. Guida, G. Lofrano, Nonylphenol deca-ethoxylate removal from wastewater by UV/H<sub>2</sub>O<sub>2</sub>: degradation kinetics and toxicity effects, *Process Saf. Environ. Prot.* 124 (2019) 1–7, <https://doi.org/10.1016/j.psep.2019.01.030>.
- [38] G. Personne, B. Marsalek, I. Blinova, A. Torokne, D. Zarine, L. Manusadzianas, et al., A practical and user-friendly toxicity classification system with microbioesters for natural waters and wastewaters, *Environ. Toxicol.* 18 (2003) 395–402.
- [39] G. Libralato, V.G. Annamaria, A. Francesco, How toxic is toxic? a proposal for wastewater toxicity hazard assessment, *Ecotoxicol. Environ. Saf.* 73 (2010) 1602–1611.
- [40] L. Rizzo, T. Agovino, S. Nahim-Granados, M. Castro-Alferez, P. Fernández-Ibáñez, M.I. Polo-López, Tertiary treatment of urban wastewater by solar and UV-C driven advanced oxidation with peracetic acid: Effect on contaminants of emerging concern and antibiotic resistance, *Water Res.* 149 (2019) 272–281, <https://doi.org/10.1016/j.watres.2018.11.031>.
- [41] I.N. Dias, B.S. Souza, J.H.O.S. Pereira, F.C. Moreira, M. Dezotti, R.A.R. Boaventura, V.J.P. Vilar, Enhancement of the photo-Fenton reaction at near neutral pH through the use of ferrioxalate complexes: a case study on trimethoprim and sulfamethoxazole antibiotics removal from aqueous solutions, *Chem. Eng. J.* 247 (2014) 302–313, <https://doi.org/10.1016/j.cej.2014.03.020>.
- [42] B. Yang, R.S. Kookana, M. Williams, J. Du, H. Doan, A. Kumar, Removal of carbamazepine in aqueous solutions through solar photolysis of free available chlorine, *Water Res.* 100 (2016) 413–420, <https://doi.org/10.1016/j.watres.2016.05.048>.
- [43] Z. Shu, J.R. Bolton, M. Belosevic, M. Gamal El Din, Photodegradation of emerging micropollutants using the medium-pressure UV/H<sub>2</sub>O<sub>2</sub> Advanced Oxidation Process, *Water Res.* 47 (2013) 2881–2889, <https://doi.org/10.1016/j.watres.2013.02.045>.
- [44] M.C.V.M. Starling, P.P. Souza, A. Le Person, C.C. Amorim, J. Criquet, Intensification of UV-C treatment to remove emerging contaminants by UV-C/H<sub>2</sub>O<sub>2</sub> and UV-C/S2O8<sup>2-</sup>: Susceptibility to photolysis and investigation of acute toxicity, *Chem. Eng. J.* (2019), <https://doi.org/10.1016/j.cej.2019.01.135>.
- [45] O. Gimeno, J.F. García-Araya, F.J. Beltrán, F.J. Rivas, A. Espejo, Removal of emerging contaminants from a primary effluent of municipal wastewater by means of sequential biological degradation-solar photocatalytic oxidation processes, *Chem. Eng. J.* 290 (2016) 12–20, <https://doi.org/10.1016/j.cej.2016.01.022>.
- [46] N. Klammerth, N. Miranda, S. Malato, A. Agüera, A.R. Fernández-Alba, M.I. Maldonado, J.M. Coronado, Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO<sub>2</sub>, *Catal. Today* 144 (2009) 124–130, <https://doi.org/10.1016/j.cattod.2009.01.024>.
- [47] L. Prieto-Rodríguez, I. Oller, N. Klammerth, A. Agüera, E.M. Rodríguez, S. Malato, Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents, *Water Res.* 47 (2013) 1521–1528, <https://doi.org/10.1016/j.watres.2012.11.002>.
- [48] N. Miranda-García, S. Suárez, B. Sánchez, J.M. Coronado, S. Malato, M.I. Maldonado, Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO<sub>2</sub> in a solar pilot plant, *Appl. Catal. B* 103 (2011) 294–301, <https://doi.org/10.1016/j.apcatb.2011.01.030>.
- [49] N. Ortiz, Green water treatment for pharmaceutical pollution, green chemistry applications, *IntechOpen* (2019), <https://doi.org/10.5772/intechopen.85116>.
- [50] A. Bernabeu, S. Palacios, R. Vicente, R.F. Vercher, S. Malato, A. Arques, A.M. Amat, Solar photo-Fenton at mild conditions to treat a mixture of six emerging pollutants, *Chem. Eng. J.* 198–199 (2012) 65–72, <https://doi.org/10.1016/j.cej.2012.05.056>.
- [51] L.A. Pérez-Estrada, M.I. Maldonado, W. Gernjak, A. Agüera, A.R. Fernández-Alba, M.M. Ballesteros, S. Malato, Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale, *Catal. Today* 101 (2005) 219–226, <https://doi.org/10.1016/j.cattod.2005.03.013>.
- [52] L.A. Pérez-Estrada, S. Malato, W. Gernjak, A. Agüera, E.M. Thurman, I. Ferrer, A.R. Fernández-Alba, Photo-fenton degradation of diclofenac: identification of main intermediates and degradation pathway, *Environ. Sci. Technol.* 39 (2005) 8300–8306, <https://doi.org/10.1021/es050794n>.
- [53] I. Michael, E. Hapeshi, V. Osorio, S. Perez, M. Petrovic, A. Zapata, S. Malato, D. Barceló, D. Fatta-Kassinos, Solar photocatalytic treatment of trimethoprim in four environmental matrices at a pilot scale: transformation products and ecotoxicity evaluation, *Sci. Total Environ.* 430 (2012) 167–173, <https://doi.org/10.1016/j.scitotenv.2012.05.003>.
- [54] I. De la Obra, L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, S. Malato, J.A. Sánchez Pérez, Microcontaminant removal in secondary effluents by solar photo-Fenton at circumneutral pH in raceway pond reactors, *Catal. Today* 287 (2017) 10–14, <https://doi.org/10.1016/j.cattod.2016.12.028>.
- [55] W. Huang, M. Brigante, F. Wu, K. Hanna, G. Mailhot, Development of a new homogenous photo-Fenton process using Fe(III)-EDDS complexes, *J. Photochem. Photobiol. A* 239 (2012) 17–23, <https://doi.org/10.1016/j.jphotochem.2012.04.018>.
- [56] N. Klammerth, L. Rizzo, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba, Degradation of fifteen emerging contaminants at µg/L – 1 initial concentrations by mild solar photo-Fenton in MWTP effluents, *Water Res.* 44 (2010) 545–554, <https://doi.org/10.1016/j.watres.2009.09.059>.
- [57] N. Klammerth, S. Malato, A. Agüera, A. Fernández-Alba, Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison, *Water Res.* 47 (2013) 833–840, <https://doi.org/10.1016/j.watres.2012.11.008>.
- [58] N.F.F. Moreira, C. Narciso-da-Rocha, M.I. Polo-López, L.M. Pastrana-Martínez, J.L. Faria, C.M. Manaia, P. Fernández-Ibáñez, O.C. Nunes, A.M.T. Silva, Solar treatment (H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>-P25 and GO-TiO<sub>2</sub> photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related genes in urban wastewater, *Water Res.* 135 (2018) 195–206, <https://doi.org/10.1016/j.watres.2018.01.064>.
- [59] A. Zapata, I. Oller, L. Rizzo, S. Hilgert, M.I. Maldonado, J.A. Sánchez-Pérez, S. Malato, Evaluation of operating parameters involved in solar photo-Fenton treatment of wastewater: interdependence of initial pollutant concentration, temperature and iron concentration, *Appl. Catal. B* 97 (2010) 292–298, <https://doi.org/10.1016/j.apcatb.2010.01.018>.



- [org/10.1016/j.apcatb.2010.04.020](https://doi.org/10.1016/j.apcatb.2010.04.020).
- [60] E. Donner, T. Kosjek, S. Qualmann, Kusk K. Ole, E. Heath, D.M. Revitt, A. Ledin, Andersen H. Rasmus, Ecotoxicity of carbamazepine and its UV photolysis transformation products, *Sci. Total Environ.* 443 (2013) 870–876, <https://doi.org/10.1016/j.scitotenv.2012.11.059>.
- [61] P. Calza, V.A. Sakkas, C. Medana, C. Baiocchi, A. Dimou, E. Pelizzetti, T. Albanis, Photocatalytic degradation study of diclofenac over aqueous TiO<sub>2</sub> suspensions, *Appl. Catal. B* 67 (2006) 197–205, <https://doi.org/10.1016/j.apcatb.2006.04.021>.
- [62] L. Rizzo, S. Meric, M. Guida, D. Kassinos, V. Belgiorno, Heterogenous photocatalytic degradation kinetics and detoxification of an urban wastewater treatment plant effluent contaminated with pharmaceuticals, *Water Res.* 43 (2009) 4070–4078, <https://doi.org/10.1016/j.watres.2009.06.046>.