Simultaneous disinfection and microcontaminants elimination of urban wastewater secondary effluent by solar advanced oxidation sequential treatment at pilot scale

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Pre-review version of the manuscript published in Journal of Hazardous Materials (436 (2022) 129134, https://doi.org/10.1016/j.jhazmat.2022.129134).

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ABSTRACT

Simultaneous contaminants of emerging concern (CECs) removal and bacteria inactivation by sequential treatment sunlight/H_2O_2 and solar photo-Fenton (SPF) with EDDS at near neutral pH was investigated. Process efficiency was evaluated in terms of (i) degradation of five CECs (namely caffeine, carbamazepine, diclofenac, sulfamethoxazole and trimethoprim) at the initial concentration of 100 μgL^{-1} each and (ii) bacteria inactivation (*Escherichia coli (E. coli)* and *Salmonella spp*). The effect of H_2O_2, Fe and EDDS concentration and Fe:EDDS dosing time was evaluated. 60 % removal of the sum of total CECs and pathogens inactivation below the detection limit (DL) were observed by the sequential treatment with Fe:EDDS additions at 60 min and 45 min in simulated urban wastewater effluent. CECs degradation and bacteria inactivation rate were higher with Fe:EDDS 0.1:0.1 mM than with Fe:EDDS 0.05:0.05 mM. Sequential treatment was validated in actual urban wastewater effluent, being able to remove 60% of the target CECs and inactivate bacteria below the DL. Increasing EDDS concentration negatively affected *Salmonella spp* inactivation. Sequential treatment based on 120 minutes of sunlight/H_2O_2 (50 mg L^{-1}) and subsequent SPF with Fe:EDDS (0.1:0.1 mM) was chosen as best operation conditions for full scale treatment in urban wastewater treatment plants.

Keywords: Advanced Oxidation Processes, contaminants of emerging concern, *Escherichia coli*, *Salmonella spp*, , wastewater reuse

1 Introduction

Modern society is concerned about water scarcity and pollution of water resources. World population growth, economic development and climate change entail a growing demand for water resources that can only be met through the use of unconventional water sources. Treated urban wastewater are considered a necessary alternative to freshwater resources (Scheierling et al., 2011) and several studies have outlined the importance of urban wastewater treatment plant effluent (UWWE) reuse in agriculture, industry, urban development, domestic, potable water supply and other applications (Lahlou et al., 2021; Leonel and Tonetti, 2021; Liao et al., 2021). Urban wastewater treatment by conventional methods cannot effectively remove some challenging pollutants including contaminants of emerging concern (CECs) (pesticides, pharmaceuticals, personal care products, etc.) and pathogens (bacteria, viruses, protozoa and parasites) that can be easily taken up by plants irrigated with UWWE (Wu et al., 2014) and lead to toxic effects in humans (Delli Compagni et al., 2020; Fent et al., 2006).

One suitable option to improve the efficiency of conventional urban wastewater treatment plants (UWWTPs) is their upgrading with advanced/tertiary treatment methods such as Advanced Oxidation Processes (AOPs), which are based on the formation of highly reactive and non-selective hydroxyl radicals ($HO^{\bullet}$) that can effectively remove CECs as well as inactivate microorganisms. AOPs operated with solar radiation make the process more sustainable by saving energy cost (Malato et al., 2009). Solar photo-Fenton (SPF) has been successfully investigated for CECs removal and bacteria inactivation (Giannakis et al., 2017). Nevertheless, in spite of the high efficiency of such process, a main disadvantage is the necessity of adjusting pH to 2.8 to avoid iron precipitation and subsequent effluent neutralization before discharge or reuse (Pignatello et al., 2006). Using mono-, poly-, or amino-carboxylic acids such as Ethylenediamine-N, N′-disuccinic acid (EDDS) allows to solve these problems and speed up their full scale application. Fe:EDDS complex formation avoids iron precipitation and makes the process effective even at neutral pH (Zhang and Zhou, 2019). However, the efficiency of SPF

with EDDS for the inactivation of bacteria seems to be contradictory, with regard to the higher bacteria resistance in the presence of organic matter due to the EDDS dosing(García-Fernández et al., 2019). The results observed in scientific literature conclude that, though sunlight/H_2O_2 can easily and efficiently inactivate different microorganisms usually found in UWWE mainly due to internal photo-Fenton mechanism (Giannakis, 2018), it cannot produce sufficient radicals to effectively degrade CECs . Simultaneous removal of CECs and bacteria inactivation has received only poor attention so far (Soriano-Molina et al., 2019a).

In a recent work, Maniakova et al., (2021b) compared the efficiency of SPF with EDDS and sunlight/H_2O_2 processes separately for the simultaneous CECs removal and bacteria inactivation. They confirmed that sunlight/H_2O_2 is more effective than SPF with EDDS for bacteria inactivation and is not able to remove CECs. On the other side, they observed high efficiency of SPF with EDDS for CECs removal. Therefore, aiming to achieve a complete bacteria inactivation and, at least, 60% removal of CECs only in the tertiary step, sequential treatment by sunlight/H_2O_2 process and SPF with EDDS could be considered a suitable option. The aim to achieve 60 % removal of the sum of total CECs only in the tertiary treatment is based on the Switzerland law in which 80% removal of microcontaminants is requested along the whole train in the UWWTP (from primary to tertiary treatment).

Effluents from municipal wastewater treatment plants disinfection and CECs removal by solar driven AOPs (namely sunlight/H_2O_2 and SPF, separately) have been successfully investigated in low cost Raceway Pond Reactors (RPRs). RPR allows to reduce the treatment cost in this type of mild effluent in comparison with a tubular photo-reactor equipped with compound parabolic collectors (CPCs), commonly used in photocatalytic processes (Cabrera-Reina et al., 2021).

Treatment time plays a major role in full-scale UWWTPs. The minimization of treatment time for a specific treatment goal allows keeping the reactor solar collecting surface as small as possible, decreasing treatment costs. Therefore, the main goal of this work was to investigate the capability of a sequential treatment using sunlight/H_2O_2 followed by SPF, for guarantying both

disinfection and elimination of CECs, with EDDS in solar RPRs for tertiary treatment of UWWE at near neutral pH to minimize treatment time. The removal of a mixture of CECs as caffeine (CAF), carbamazepine (CBZ), diclofenac (DCF), sulfamethoxazole (SMX) and trimethoprim (TMP) and bacteria (*E. coli* and *Salmonella)* inactivation were monitored in both simulated and actual UWWE. To authors' knowledge, the effect of different times of Fe:EDDS dosing and H_2O_2 as well as different Fe:EDDS concentrations in the sequential treatment sunlight/H_2O_2 followed by sunlight/H_2O_2/Fe:EDDS at circumneutral pH was investigated for the first time focusing both CECs and bacteria.

2 Materials and methods

2.1 Chemicals and reagents

Selected model CECs were all of high-purity grade (>99%): CAF was provided by Fluka and CBZ, DCF, SMX and TMP were purchased from Sigma Aldrich. $Fe_2(SO_4)_3 \cdot H_2O$ 75% solution (Panreac) was used as Fe(III) source. EDDS water solution (35%w/v), H_2O_2 (35%, w/v), bovine liver catalase, acetonitrile (ACN) (UHPLC-grade) and formic acid (UHPLC-grade) were provided by Sigma Aldrich. Titanium(IV) oxysulfate (Sigma-Aldrich) was used for H_2O_2 measurements. Reagents for dissolved iron determination (namely,1,10-phenanthroline, ammonium acetate, ascorbic acid) were obtained from Sigma-Aldrich.

2.2 Water matrices

Two water matrices, simulated urban wastewater effluent (SUWWE) and UWWE, were used in the experiments. The main physicochemical properties measured for both water matrices are shown in Table 1. SUWWE was prepared using the following chemicals and concentrations (Sánchez-Montes et al., 2020): *i)* organic matter: sodium lignin sulfonate (2.4 mg L^{-1}), humic acid (4.2 mg L^{-1}), sodium lauryl sulphate (0.9 mg L^{-1}) (Sigma-Aldrich); peptone (2.7 mg L^{-1}) and beef extract (1.8 mg L^{-1}) (Biolife); acacia gum powder (4.7 mg L^{-1}) and tannic acid (4.2 mg L^{-1}) (Panreac); *ii)* inorganic salts: 23.6 mg L^{-1} $(NH_4)_2SO_4$ and 60 mg $L^{-1}CaSO_4 \cdot 2H_2O$

(from Panreac); 4 mg L^{-1} KCl (from J.T. Baker); 7.0 mg L^{-1} K_2HPO_4, 96 mg L^{-1} $NaHCO_3$, 580 mg L^{-1} NaCl and 60 mg L^{-1} $MgSO_4$ (Sigma-Aldrich).

Several samples of UWWE were freshly collected after secondary treatment and sand filtration of the urban UWWTP of Almería, El Bobar (Spain). The water samples were stored at 4 °C not more than 3 days and characterized before each use (Table 1). The samples showed a significant high carbonates concentration (446.0±82.5 mg L^{-1}: mainly as HCO_3^-), a known scavengers of $HO^{\bullet}$, therefore the water was previously adjusted to <75±6 mg L^{-1} through the addition of sulfuric acid. During the carbonates stripping, pH did not change significantly (it was in the range of neutrality, 6.9–7.9) and did not affect the naturally occurring microbial population.

Table 1 –SUWWE and UWWE characterization.

Parameter	SUWWE	UWWE
pH	7.6±0.3	7.9±0.1
Conductivity (mS/cm)	1.4±0.1	2.6±0.1
Turbidity (NTU)	3.4±0.2	8.3±2.6
*DOC (mg L^{-1})	15.5±0.6	20.0±2.6
HCO_3^- (mg L^{-1})	67.5.±6.0	446.0±83**
Cl^- (mg L^{-1})	355±9	547±10
NO_3^- (mg L^{-1})	5.4±0.2	17.5±1.0
PO_4^{3-} (mg L^{-1})	6.1±0.3	38.9±1
SO_4^{2-} (mg L^{-1})	119±5	138.0±2
NH_4^+ (mg L^{-1})	6.4±0.1	35.6±1.2
Na^+ (mg L^{-1})	256±10	275±9
K^+ (mg L^{-1})	14.8±1.1	28.0±2.5
Ca^+ (mg L^{-1})	27.8±1.7	100±2

*DOC – dissolved organic carbon; **adjusted to around 75±6mg L^{-1} before the treatment.

CECs mixed stock solution was prepared in methanol at 2.5 g L^{-1} of each CEC. Organic contribution of methanol was DOC = 12 mg L^{-1}. Further increase of DOC (12 mg L^{-1}) was also observed after the addition of 0.1 mM of EDDS.

2.3 Analytical measurements

The concentrations of Fe and H_2O_2 were measured spectrophotometrically by an UV-Vis Evolution 220 spectrophotometer (Thermo scientific). H_2O_2 concentration was monitored according to DIN 38402H15 method at 410 nm. Fe concentration was analyzed by 1,10-phentranoline following ISO 6332 method at 510 nm. All samples were filtrated by 0.45 μm nylon filter before the analysis. Temperature (Thermometer, HANNA), pH (GLP 22 pH meter,

CRISON), turbidity (2100N Turbidimeter, HACH) and conductivity (GLP 31 Conductimeter, CRISON) were also monitored. DOC and carbonates were measured using a TOC-VCSN analyzer (Shimadzu) in filtered samples (0.45 μm nylon filter).

CECs concentrations were analyzed by ultra-performance liquid chromatography (UPLC Agilent Technologies, Series 1200) through UV-DAD detector, Poroshell 120 EC-C18 column (Agilent Technologies: 50 mm × 3.0 mm, 2.7 μm particle). The simultaneous analysis of the 5 CECs was done according to previous reported working conditions (Maniakova et al., 2022). Briefly, the initial 100% aqueous (formic acid 25 mmolL^{-1}) solution was varied in 10 min up to achieve 50% of ACN, and 100% of ACN in the subsequent 2 min. 9 mL of collected sample was filtered using a 0.22 μm PTFE filter (Millipore), and mixed with 1 mL of ACN used for washing the filter to remove any adsorbed CEC.

2.4 Bacterial quantification analysis

E. coli O157:H7 (CECT 4972) and *S. enteritidis* (CECT 4155) (provided by the Spanish Culture Collection (CECT) as freeze-dried cultures) were used for SUWWE tests. *E.coli* and *S. enteritidis* strains were inoculated in 14 mL of Nutrient Broth (a mixture of NaCl, Beef extract, and Peptone), and Tryptone Soya Broth (OXOID), respectively, and grown aerobically in a rotary shaker (90 rpm) at 37°C for 20 h. Cells were harvested by centrifugation at 3000 rpm for 15 min (J.P. Selecta) and the pellet was re-suspended in 14 mL phosphate-buffer saline solution (PBS, Oxoid), yielding a final concentration of 10^9 CFU mL^{-1}.An aliquot of each bacterial suspension was added in SUWWE to obtain an initial concentration of 10^3 CFU mL^{-1}.

Indigenous *E.coli* and *Salmonella spp* were analysed in tests with freshly collected UWWE. Enumeration of bacteria was performed by standard plate counting method using selective agar media: Chromocult® (Merck) for *E.coli* and Salmonella Shigella agar (Scharlau) for *Salmonella spp*. Water samples (50-500 μL) were spread onto each corresponding selective agar Petri dish. Subsequently, plates were incubated for 24 h (*E.coli*) and 48 h (*Salmonella spp*) at 37 ºC and counted. The detection limit (DL) in SUWWE was 200 CFU 100 mL^{-1}. In UWWE, when

bacterial concentration was expected to be lower than 200 CFU 100 mL^{-1}, samples were processed by the membrane filtration method. For each bacteria species, 100 mL of sample were filtered using a 0.45 μm-pore-size cellulose nitrate membrane (Sartorius) and a Microfil Filtration System (Millipore) (Sánchez-Montes et al., 2020). Then, the obtained membranes were plated in the corresponding medium. DL of this technique is 1 CFU 100 mL^{-1}, to take into account the limit for class A treated wastewater (10 CFU of *E. coli*100 mL^{-1}) set by the new European Regulation on minimum requirements for water reuse ((EU) 2020/741).

To avoid any potential effect of residual H_2O_2 over bacterial viability, the residual H_2O_2 was quenched in the sample using bovine liver catalase (Sigma-Aldrich) (1 mL sample was mixed with 20 μL of catalase stock solutions at 0.1 g L^{-1}) (Sánchez-Montes et al., 2020).

2.5 Experimental set-up

Treatment tests were carried out in a RPR at pilot plant scale under natural solar irradiation at Plataforma Solar of Almeria, Spain, in clear sunny days. The five target CECs were added at an initial concentration of 100 μgL^{-1} each one from a mix stock solution. *E. coli* and *S. enteritidis* were spiked with SUWWE at an initial concentration of 10^3 CFU mL^{-1} each one. In UWWE, CECs were spiked and naturally occurring *E. coli* and *Salmonella spp* were analyzed.

The RPR photoreactor used has been described in detail elsewhere (Costa et al., 2020) and briefly it consists of an open reactor with dimensions of 97 x 45 cm, 15 cm liquid depth and a working total volume of 90 L. Prior to start with solar exposure, the aqueous solution was homogenized in the dark, according to the following additions sequence: CECs and bacteria mixture (if necessary) for 10 min and then H_2O_2 for 5 min. After, the reactor was uncovered and experiment started. The desired Fe:EDDS concentration (prepared according to the protocol described in Maniakova et al., (2021b)) was added after different times of sunlight/H_2O_2 process. The solar UV-A radiation (data in W/m^2) was measured by a pyranometer (280-400 nm, Model CUV-5, Kipp&Zonen) mounted on a horizontal platform and located close to the RPR at PSA facilities. To compare results from different experiments, the accumulated UV energy per unit

of treated volume (Q_{UV}, kJ L $^{-1}$) was calculated according to the following equation (Eq.2) (Malato et al., 2003):

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot \overline{UV}_{G,n} \cdot \frac{A_r}{V_t} \quad \text{(Eq. 2)}$$

where, Q_{UV} is the accumulated UV energy per treated volume between samples *n* and *n-1*. $\overline{UV}_{G,n}$ (W m^{-2}) is the average UV radiation measured and Δt_n is the experimental time between samples. A_r is the illuminated area (m^2) and V_t is the total volume of water (L).

The sequential treatment was always performed with sunlight/H_2O_2 process as initial step followed by the addition of Fe:EDDS to promote SPF. The performance of the sequential treatment was evaluated by varying the reagents concentration (H_2O_2 and Fe:EDDS) as well as the addition-time of Fe:EDDS (named dosing strategy, Table 2). In all performed experiments H_2O_2 concentration was measured during the treatment and kept close to the initial concentration (when the concentration of H_2O_2 decreased to around 10 mg L^{-1}, H_2O_2 was added to the solution).

Table 2 – Sequential treatment operating conditions and Fe:EDDS dosing strategy.

	SUWWE		**UWWE**		
$[H_2O_2]_0$	$[Fe:EDDS]_0$ 0.1:0.1 mM	$[Fe:EDDS]_0$ 0.05:0.05 mM	$[Fe:EDDS]_0$ 0.1:0.1 mM	$[Fe:EDDS]_0$ 0.1:0.2 mM	$[Fe:EDDS]_0$ 0.1:0.1 mM - twice
	Fe:EDDS dosing strategy				
30 mgL^{-1}	60 min	-	-	-	-
50 mgL^{-1}	30, 45 or 60 min	60 min	120 min	150 min	120 & 150 min
100 mgL^{-1}	45 min	-	-	-	-

3 Results and discussion

3.1 CECs degradation and bacteria inactivation in SUWWE

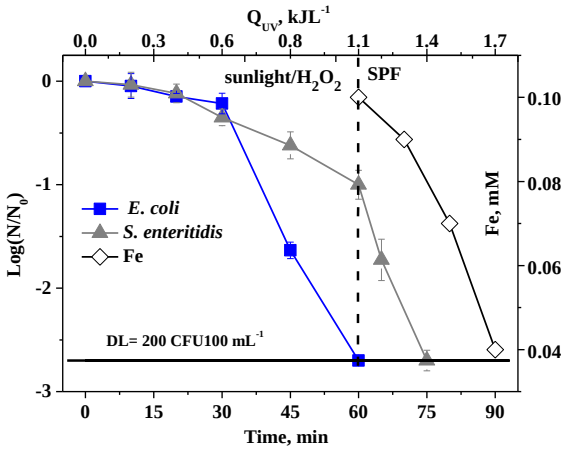
3.1.1 Effect of Fe:EDDS dosing strategy

To assess the best treatment time for simultaneous CECs removal and bacteria inactivation, the effect of different Fe:EDDS (0.1:0.1 mM) dosing times (60, 45 and 30 min after H_2O_2) were initially investigated with sunlight/H_2O_2 at 50 mg L^{-1}in SUWWE (Fig. 1).

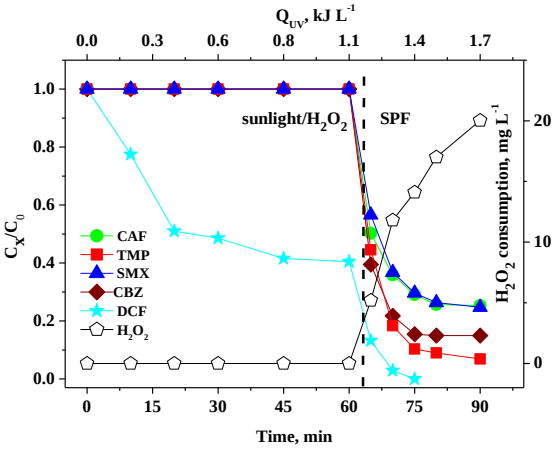
211 Sunlight/H_2O_2 disinfection efficiency was reduced as dosing time was decreased from 60 to 30

212 min (Fig. 1a, c, e). The effect of sunlight/H_2O_2 process on CECs degradation was poor for all

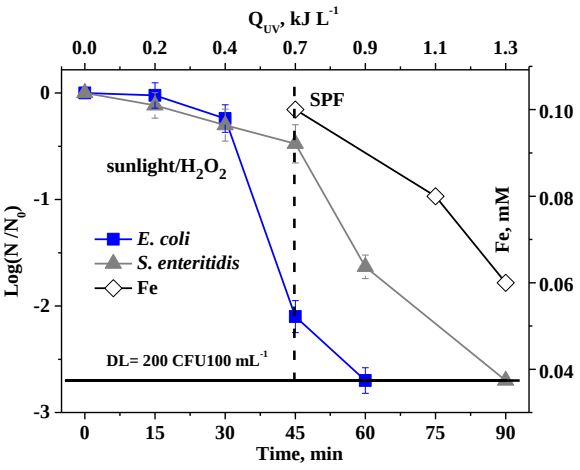
213 the investigated Fe:EDDS dosing times (Fig. 1b, d, f).



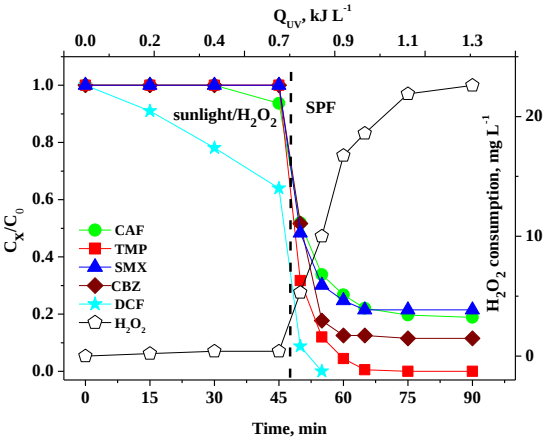
214 a)



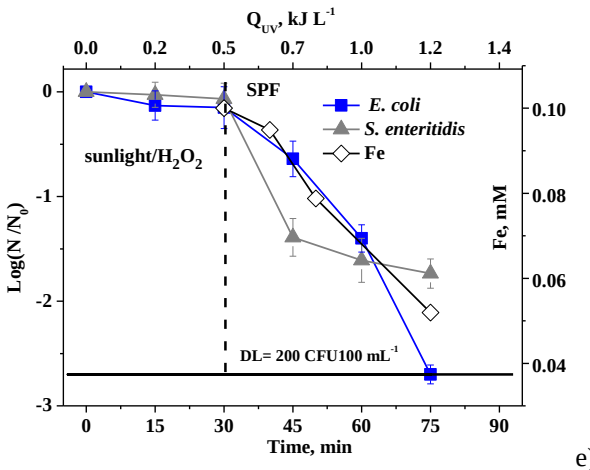
b)



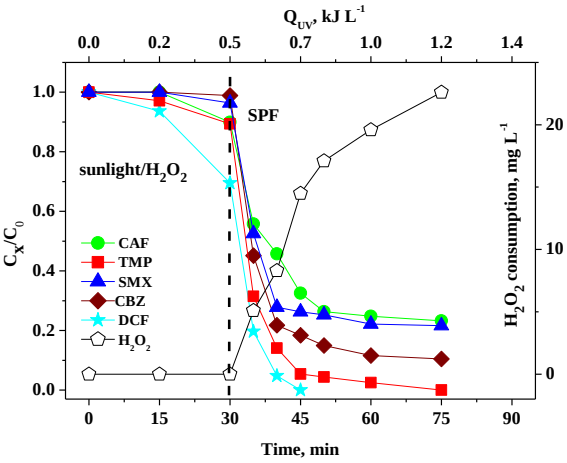
215 c)



d)



216 e)



f)

Figure 1–Bacteria inactivation and CECs degradation in SUWWE by sequential treatment with sunlight/H_2O_2 (H_2O_2=50 mg L^{-1}) with subsequent addition of Fe:EDDS (0.1 mM Fe:EDDS) at several dosing times: 60 min (a, b), 45 min (c, d) and 30 min (e, f) in RPR.

The inactivation of bacteria observed is attributed to the accumulated internal cell damages due to sunlight/H_2O_2 process. The internal cell damages are attributed to: *i)* the formation of reactive oxygen species (ROS) (direct action) by UV solar photons; *ii)* intracellular photo-Fenton-like reactions between H_2O_2, which penetrates through the bacterial cell wall, and naturally occurring intracellular-iron (indirect action), generating $HO^{\bullet}$. Other ROS directly attack susceptible moieties (oxidative stress) or are involved into the reduction of iron. Added H_2O_2 also initiate bacterial membrane auto-oxidation (outer damage). Light reduced ferric iron to ferrous initiating a photo-catalytic cycle. These processes affect different intracellular vital components leading to bacterial death or lack of viability (Giannakis et al., 2016).

Nevertheless, in our experimental conditions, the variation of the treatment time showed different inactivation behavior, and the susceptibility of both bacteria to this treatment was also different. *E. coli* showed a faster abatement than *S. enteritidis* in all cases, which is in agreement with previous findings (Maniakova et al., 2021b; Nahim-Granados et al., 2018). Higher resistance of *S. enteritidis* can be explained by its capability to adapt to sunlight stress. Some investigations suggest that the gene *RpoS*, which controls the expression of genes involved in prevention of oxidative damage, could be relevant in the photodynamic action of the radiation in *S. typhimurium* (Gómez-López et al., 2014). In spite of the differences between both bacteria, the solar irradiance time in combination with H_2O_2 plays a major role, indicating that 60 min of solar exposure is required to guarantee a complete inactivation of *E. coli* (DL= 200 CFU 100 mL^{-1}); while the DL was not reached for *S. enteritidis* during the sunlight/H_2O_2 process. The kinetics profiles obtained during sunlight/H_2O_2 process in all cases showed a first stage where the cell damages are being accumulating (shoulder phase) with a log-decay occurring

after that. The shoulder phase required 30 min of solar treatment for *E. coli*, while it was less evident for *S. enteritidis*. The oxidative damages accumulation over time was necessary to overcome the capability of self-defense of the cells to finally induce the cell death. During the subsequent SPF phase, the residual bacterial cells further decreased till the DL, except for *S. enteritidis* with Fe:EDDS and dosing time at 30 min. The bacterial inactivation behavior showed that the higher exposure time during the first phase (sunlight/H_2O_2), the faster inactivation in the second phase (SPF) in terms of treatment time. This effect could be explained by the sub-lethal damage state on the remaining viable cells occurring during the first phase, making them more vulnerable for the potential external damages generated by early minutes of SPF. Nevertheless, the particular case of *S. enteritidis* where the DL was not reached with Fe:EDDS dosing time at 30 min, indicated that the production of $HO^{\bullet}$ by SPF was not sufficient and that others boundary and protecting effects over bacteria occurred. In fact, this limited effect of SPF with EDDS for bacterial inactivation has been previously described, and can be possibly attributed to: *i)* the iron precipitation formed particles that may act as screen protecting bacteria from the action of solar UVA photons, and *ii)* the organic matter concentration from a biodegradable substance (EDDS) that made possible a more favorable ambient for bacteria survival.

The H_2O_2 concentration measured during sunlight/H_2O_2 did not show any significant change, which is expected due to the no O-O bond breaking (required for $HO^{\bullet}$ generation) under natural solar radiation (Giannakis et al., 2016). The absence of $HO^{\bullet}$ generation is the main reason of the low CECs degradation rate observed during this phase, except in the case of DCF which suffered photolysis, reaching 59, 36 and 30% removals, before Fe:EDDS was added after 60, 45 and 30 min of sunlight/H_2O_2, respectively. These results are in agreement with a previous work in which a poor removal of CBZ and SMX (only 20 % and 17 %, respectively) was observed by sunlight/H_2O_2, while DCF was efficiently photolysed (Moreira et al., 2018). Under SPF, similar CECs degradation kinetics were observed in all experiments (Fig. 1 b, d,

f) independently of the Fe:EDDS adding time. The aim of 60 % removal of the sum of total CECs was achieved after 5 min of Fe:EDDS addition. The highest elimination rate was observed in the first 15 minutes after Fe:EDDS addition, then the reaction rates slowed down and the residual concentration of the CECs did not significantly change till the end of the experiment. When Fe:EDDS was added, regardless of dosing time, a rapid consumption of almost 50% of H_2O_2 was observed. Such H_2O_2 consumption after Fe:EDDS addition can be explained by the degradation of the complex and Fe^{2+} release after the solar irradiation of Fe^{3+}:EDDS. Fe^{2+} reacts with H_2O_2 engendering to $HO^{\bullet}$ and Fe^{3+}, which precipitates as $Fe(OH)_3$ at circumneutral pH. Iron precipitation also explains the incomplete degradation of CECs.

The initial dissolved Fe concentration decreased during the treatment. Final Fe concentration was 0.04, 0.06 and 0.05 mM in the end of the sequential treatment with Fe:EDDS at 60, 45 and 30 min dosing times, respectively. Such high Fe precipitation means that Fe:EDDS was no longer stable and/or the Fe:EDDS was degraded by radicals in the treatment of SUWWE at circumneutral pH (Soriano-Molina et al., 2019). The Fe:EDDS complex yields the Fe:EDDS radical (reaction 1), promoting the generation of $HO^{\bullet}$ and $O_2^{\bullet-}$ under natural solar radiation (reactions 2, 3). As Fe:EDDS degradation starts, a major part of Fe precipitates, but a small amount could promote other photo-Fenton cycle reactions, or Fe:EDDS could be regenerated when more EDDS is available in the solution (Miralles-Cuevas et al., 2019).

$$Fe^{3+}\text{-EDDS} + h\nu\ (290\text{-}500\ nm) \rightarrow [Fe^{3+}\text{-EDDS}]^* \rightarrow Fe^{2+} + EDDS^{\bullet 3-} \quad (1)$$

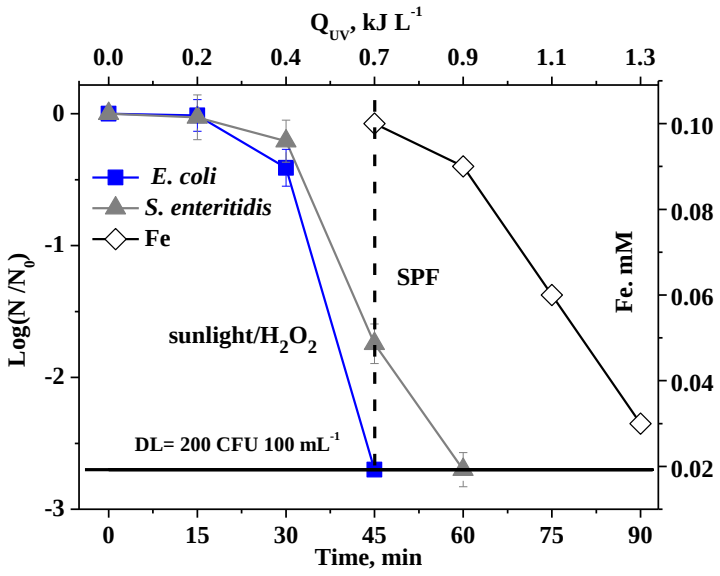
$$EDDS^{\bullet} + O_2 \rightarrow O_2^{\bullet-} + EDDS^{2-} \quad (2)$$

$$EDDS^{\bullet} + OH^- \rightarrow EDDS^{2-} + HO^{\bullet} \quad (3)$$

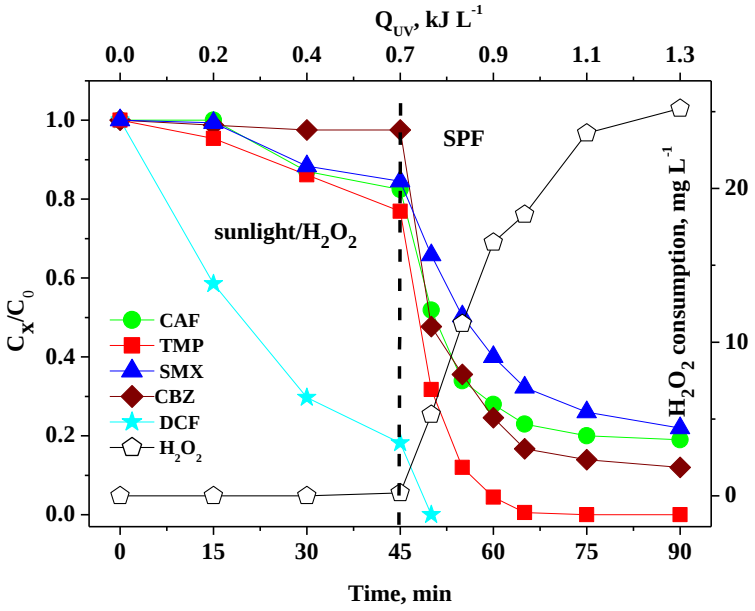
Summarizing, the best operating conditions for the removal goal of CECs and bacteria (DL = 200 CFU 100 mL^{-1}), were obtained after 75 min of sequential treatment time considering 60 min sunlight/H_2O_2 followed by 15 min of SPF.

295 *3.1.2 Effect of H_2O_2 concentration*

296 With the aim to evaluate the effect of initial H_2O_2 concentration on the efficiency of the
297 sequential treatment, different H_2O_2 doses were investigated. The results of the sequential
298 treatment with sunlight/H_2O_2 at 100 mgL^{-1} and Fe:EDDS (0.1:0.1 mM) dosing after 45 min are
299 presented in Fig. 2. H_2O_2 concentration improved slightly the efficiency of *E. coli* inactivation
300 showing 15 min faster inactivation with H_2O_2 100 mg L^{-1} in comparison with 50 mg L^{-1}. These
301 results are in agreement with scientific literature. Rodríguez-Chueca et al., (2014) investigated
302 *E.coli* inactivation by sunlight/H_2O_2 process with different H_2O_2 concentrations (5-50 mg L^{-1})
303 in a CPC reactor. These results can be explained through the mechanism of bacteria inactivation
304 discussed above. The frequency of oxidative attacks and the concentration of oxidative
305 species are responsible for bacterial inhibition and final destruction, limited by the iron
306 available inside the cells. Therefore, increasing H_2O_2 dose has a threshold (Rodríguez-Chueca
307 et al., 2012). However, the increase of H_2O_2 concentration till 100 mg L^{-1} improved *S.*
308 *enteritidis* inactivation, achieving DL 30 min faster, compared to 50 mg L^{-1} H_2O_2.
309 On the other hand, lower H_2O_2 initial concentration (30 mg L^{-1}) was less effective for both
310 bacteria inactivation, showing longer time to get the DL: 90 min (Q_{UV}=1.6 kJ L^{-1}) and 105 min
311 (Q_{UV}=1.7 kJ L^{-1}) for *E.coli* and *S. enteritidis*, respectively (Fig. 3).

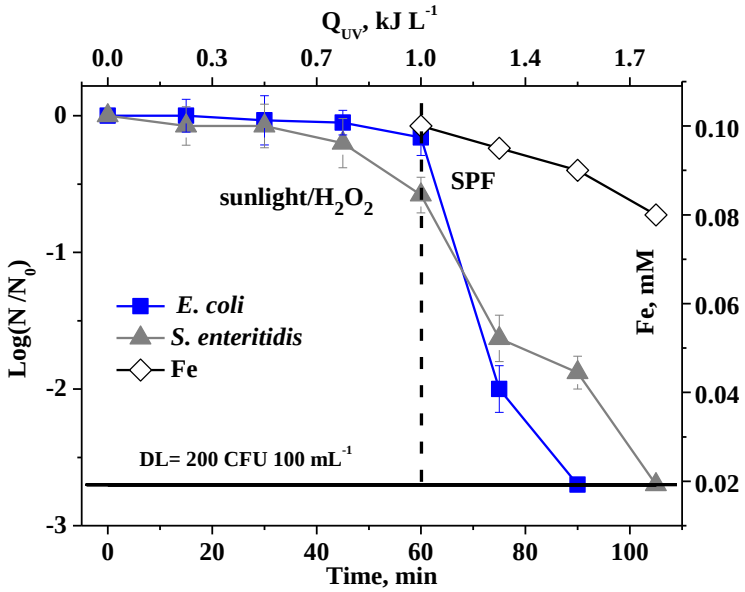


312 a)

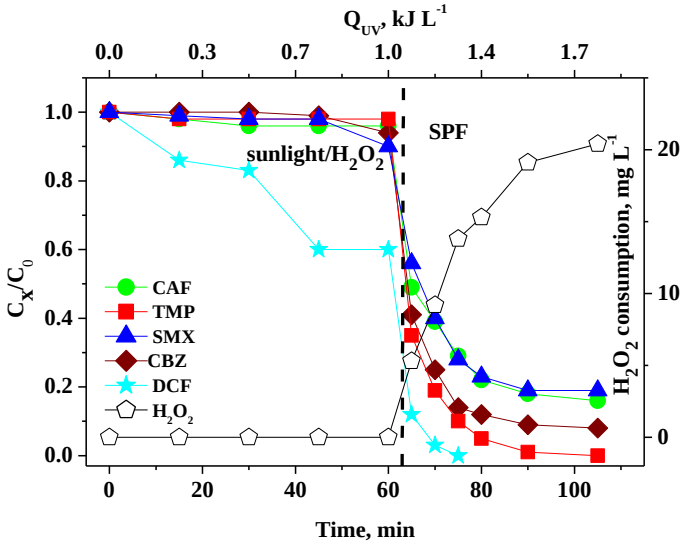


b)

Figure 2–Bacteria inactivation (a) and CECs degradation (b) in SUWWE by sequential treatment with sunlight/H_2O_2 (H_2O_2 =100 mg L^{-1}) and SPF (45 min Fe:EDDS dosing; Fe= 0.1 mM, EDDS=0.1 mM) in RPR.



a)



b)

Figure 3–Bacteria inactivation (a) and CECs degradation (b) in SUWWE by sequential treatment with sunlight/H_2O_2 (H_2O_2 =30 mg L^{-1}) and SPF (60 min Fe:EDDS dosing; Fe= 0.1 mM, EDDS=0.1 mM) in RPR.

H_2O_2 concentration did not affect the efficiency of CECs removal showing a similar behavior. The aim to remove 60 % of sum of total CECs was reached 5 minutes after the addition of Fe:EDDS even in the experiment with low H_2O_2 concentration (30 mg L^{-1}). These results are in agreement with a previous work (Dong et al., 2019). They investigated different Fe:EDDS and H_2O_2 concentrations and observed that the removal efficiencies of the target CECs by UVA/Fe/EDDS/H_2O_2 process strongly depended on the Fe:EDDS dose and less on the H_2O_2 dose. H_2O_2 consumptions were 25 mgL^{-1} and 20 mgL^{-1} at the end of the treatment for 100 mg L^{-1} and 30 mg L^{-1} of H_2O_2, respectively. The final Fe concentration with 100 mg L^{-1} and 30 mgL^{-1} of H_2O_2 was 0.03 mM and 0.08 mM, respectively.

3.1.3 Effect of decreasing Fe and EDDS concentration

In order to evaluate the effect of Fe and EDDS concentration on the CECs removal, sequential treatment with sunlight/H_2O_2 (50 mg L^{-1}) and SPF with Fe:EDDS 0.05:0.05 mM (60 min dosing time) was investigated (Fig. 4) and compared with the results presented in Fig. 1a,b

(Fe:EDDS 0.1:0.1mM). No attempt was done to increase EDDS or Fe concentration up 0.1 mM as Fe > 0.1 mM would not be consistent with reuse of treated water for irrigation or disposal and > 0.1 mM EDDS would increase organic content of treated effluent. The changing in Fe:EDDS concentration mainly affected CECs degradation. *E.coli* and *S. enteritidis* showed similar behavior (data not shown) compared to the results presented on the Fig 1 but 15 min and 30 min more were needed to reach the DL for *E.coli* and *S. enteritidis*, respectively. The differences could be attributed to the lower concentration of Fe:EDDS in reactions 1, 2 and 3.

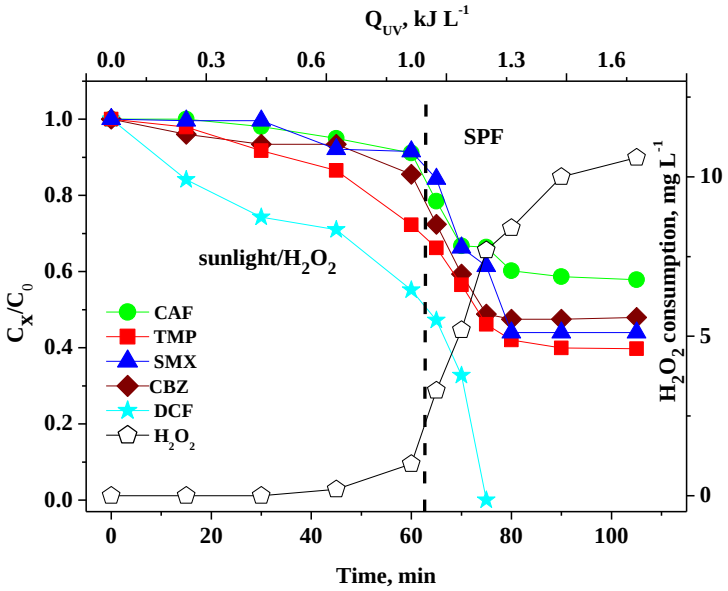


Figure 4– CECs degradation in SUWWE by sequential treatment with sunlight/H_2O_2 (H_2O_2 =50 mg L^{-1}) and SPF (60 min Fe:EDDS dosing; Fe= 0.05 mM, EDDS=0.05mM) in RPR.

The aim of getting 60% removal of total CECs was achieved within 5 min by SPF with Fe:EDDS 0.1:0.1 mM (Fig.1b), but longer solar irradiation time (20 min) was needed in sequential treatment with Fe:EDDS 0.05:0.05 mM. To the best of our knowledge simultaneous water decontamination by SPF with such low Fe and EDDS concentration (0.05 mM) has not been previously investigated. Results showed that low Fe:EDDS provoked not enough elimination of CECs to reach the goal. Therefore, no attempt was done to decrease further the concentration of the complex.

357

358 *3.2 CECs degradation and bacteria inactivation in UWWE*

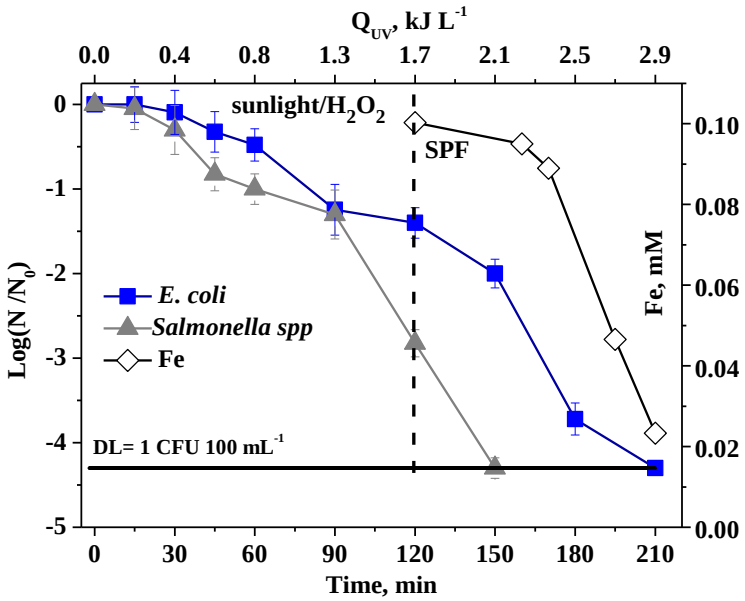
359 The capability of the sequential treatment was validated in UWWE in order to evaluate the
360 water matrix effect limitations on the entire processes performance.

361 Preliminary performed tests following best strategy obtained in SUWWE demonstrated that
362 running sunlight/H_2O_2 for 60 min was not efficient for naturally occurring bacteria inactivation
363 in UWWE (Maniakova et al., 2021a). It is well-known that bacteria inactivation in actual
364 UWWE usually requests more time compared to model one due to its inherent physical-
365 chemical and microbial complexity containing a variable concentration of different organic and
366 inorganic compounds which can act not only as $HO^{\bullet}$ scavenger but also protecting bacteria
367 from sunlight photons, resulting in an overall lower inactivation efficiency (Rincón and
368 Pulgarin, 2004). Therefore, in the experiment in UWWE the time of the first phase
369 (sunlight/H_2O_2) of the sequential treatment was increased twice (Fe:EDDS dose 0.1 mM was
370 added after 120 min). The results for simultaneous CECs removal and bacteria inactivation by
371 sequential treatment (sunlight/H_2O_2 and SPF with Fe:EDDS addition after 120 min) are shown
372 in Fig. 5. The treatment was effective for water disinfection as DL (1 CFU 100 mL^{-1}) was
373 reached for both investigated bacteria after 150 min (Q_{UV}= 2.1 kJ L^{-1}) and 210 min (Q_{UV}= 2.9
374 kJ L^{-1}) for *Salmonella spp* and *E. coli*, respectively.

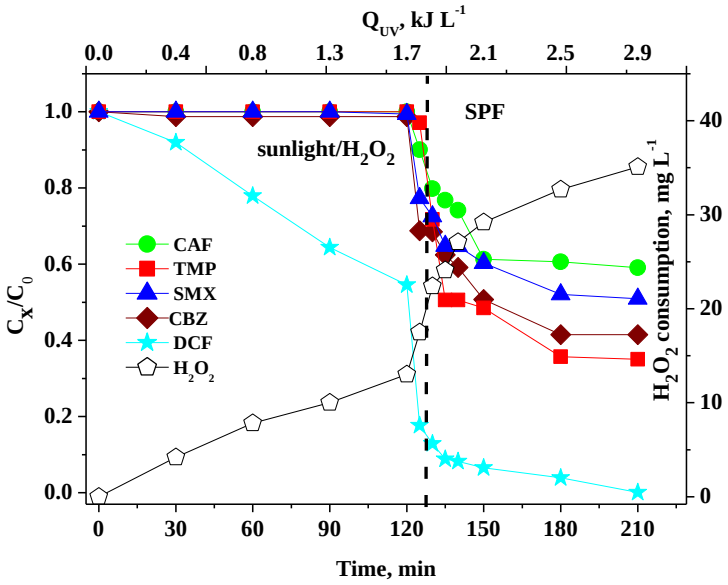
375 In SUWWE, *S. enteritidis* showed higher resistance compared to *E. coli.* Opposite, in
376 UWWE, *Salmonella spp* was inactivated faster than *E.coli*. These results are in agreement with
377 scientific literature. Aguas et al., (2019) investigated inactivation of *E. coli* and *Salmonella spp.*
378 naturally occurred in UWWE by sunlight/H_2O_2 and by SPF at neutral pH in CPC reactor. They
379 also observed *Salmonella spp* was inactivated faster than *E.coli*. Therefore, the different
380 resistance of both bacteria in different water matrices reinforces the currently approach
381 suggested in literature about the need to test different water matrices to determine the true
382 efficiency of a water disinfection treatment. Indeed, H_2O_2 consumption during

sunlight/H_2O_2 process was relevant (no consumption in SUWWE was detected). H_2O_2 consumption in UWWE after the first phase of the sequential treatment (sunlight/H_2O_2) was 18 mg L^{-1} and after Fe:EDDS addition it increased till 35 mg L^{-1} at the end of the treatment. Fe precipitated during the treatment and its concentration decreased till 0.02 mM.

The aim to achieve 60% removal of the sum of total CECs was reached 60 min after the addition of Fe:EDDS (180 min of sequential treatment, Q_{UV} = 2.5 kJ L^{-1}). The lower efficiency of the treatment in UWWE compared to the SUWWE can be explained by the fact that UWWE usually presents higher variety of organic compounds, which can compete for the oxidative radicals generated.



a)

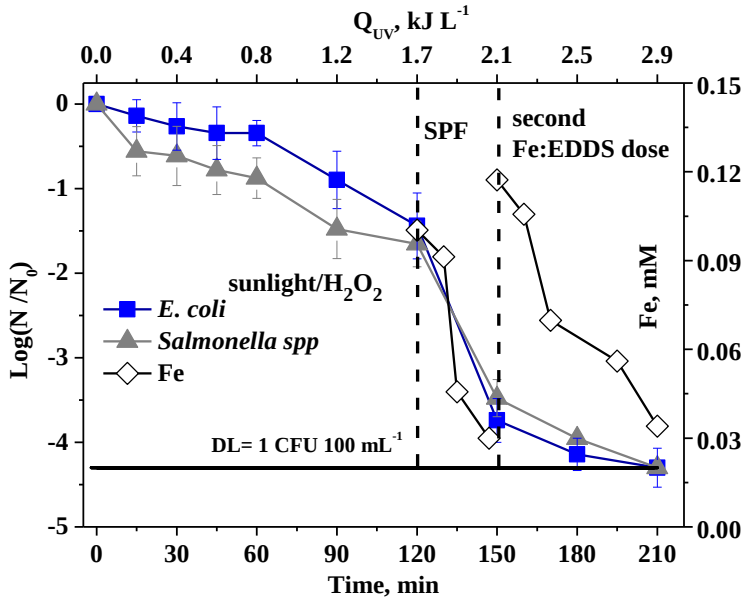


b)

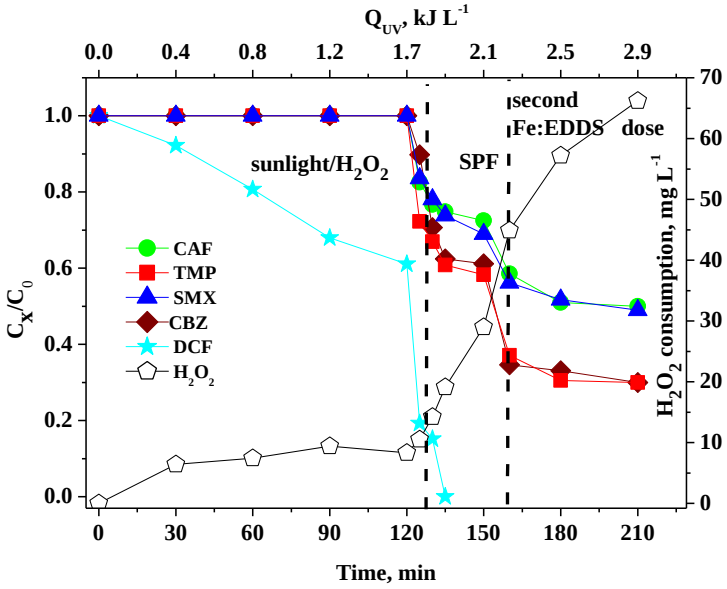
Figure 5–Bacteria inactivation (a) and CECs degradation (b) in UWWE by sequential treatment with sunlight/H_2O_2 (H_2O_2 =50 mg L^{-1}) and SPF (120 min Fe:EDDS dosing; Fe= 0.1mM, EDDS=0.1mM) in RPR

In order to evaluate Fe:EDDS concentration effect in UWWE for water disinfection and decontamination, sequential treatment was performed also using Fe:EDDS at molar ratio 1:2 (0.1:0.2 mM, data not shown) The main intention was to reinforce the photo-Fenton process adding more EDDS for enhancing Fe:EDDS persistence during the process (it was degraded during the whole preocess). *E. coli* showed similar behavior in both investigated Fe:EDDS molar ratio achieving the DL (1 CFU 100 mL^{-1}) in 210 min. *Salmonella spp* inactivation was lower in the case of Fe:EDDS 0.1:0.2 mM compared to Fe:EDDS 0.1:0.1mM. At the end of the treatment, *Salmonella spp* concentration was 2 CFU 100 mL^{-1} and so the DL (1 CFU 100 mL^{-1}) was not reached. The higher organic matter concentration due to the increased EDDS dosing acted as $HO^{\bullet}$ scavenger, resulting in a lower inactivation efficiency (Giannakis et al., 2016; Rincón and Pulgarin, 2004).CECs also showed similar behavior in both investigated Fe:EDDS molar ratio.

In order to improve the efficiency of the sequential treatment specifically for CECs removal in UWWE, sequential treatment with two dosages of Fe:EDDS (0.1:0.1 mM) was investigated. First, sunlight/H_2O_2 was operated for 120 min, then, a first addition of Fe:EDDS was performed and the SPF was run for 30 min and a second addition of Fe:EDDS (0.1:0.1 mM) was done. DL for disinfection was achieved at the end of the treatment. Regarding to the *Salmonella spp*, the sequential treatment with two Fe:EDDS (0.1:0.1 mM) additions was less effective, which can be explained by the higher DOC concentration (56.8 mg L^{-1}) due to the extra amount of EDDS. Second addition of Fe:EDDS resulted also in a higher iron precipitation and higher turbidity (from 3.4 to 30.3NTU). It possibly resulted in higher scattering of solar radiation and protection of bacteria against photons (García-Fernández et al., 2019).



a)



b)

Figure 6–Bacteria inactivation (a) and CECs degradation (b) in UWWE by sequential treatment in RPR by sunlight/H_2O_2– 120 min (H_2O_2 =50 mg/L) and SPF with double dosage of Fe:EDDS (120 min Fe:EDDS dosing, Fe= 0.1mM, EDDS=0.1mM and150 min second) Fe:EDDS dosing).

The target of 60 % of CECs removal by sequential treatment with double Fe:EDDS dosage was achieved after 160 min (Q_{UV} = 2.2 kJ/L), 10 min after adding the second Fe:EDDS dose (Fig. 6 b). CECs degradation rate was fast within 20 min after adding the first Fe:EDDS dose. Then the reaction stopped, due to the complex destruction under natural light (Soriano-Molina et al., 2019). After adding the second Fe:EDDS dose (150 min of sequential treatment) the degradation of the target CECs continued but stopped again after the same contact time. This behaviour further supports the statement that the process stops as complex degradation takes place. To our knowledge, sequential treatment with sunlight/H_2O_2 and SPF with double addition of Fe:EDDS complex dose was not previously investigated, and it was found to be more effective for CECs removal compared to the other sequential treatments options discussed above. However, although this approach is more effective, using two Fe:EDDS doses can result in some operating problems related to the high EDDS cost and increase of DOC. In

particular, increased DOC concentration could limit discharge (and reuse) due to the local legislation in force. The use of this sequential treatment option would be counterproductive for the overall performance.

Conclusions

An efficient solar sequential treatment by sunlight/H_2O_2 (50 mg L^{-1}) and SPF using EDDS (Fe and EDDS at 0.1 mM) at circumneutral pH should be considered when inactivation of the microbial targets did not reach DL by applying only SPF in UWWE. Increase in H_2O_2 concentration could improve inactivation but did not significantly affect CECs removal. Although double dosing of Fe:EDDS complex during SPF process could result in a higher CECs removal, it cannot be considered a sustainable option. The best operation conditions for disinfection and elimination of CECs in UWWE were sequential treatment with sunlight/H_2O_2 (50 mg L^{-1}) during 120 min and SPF with the addition of Fe:EDDS(0.1:0.1 mM) until reaching 60% elimination of the sum of total CECs. Sequential treatment is a promising sustainable solution for tertiary treatment which allows an effective simultaneous disinfection and CECs removal for possible disposal or reuse for crop irrigation. However, future studies should be performed to evaluate the best operation conditions for scaling-up the treatment, through the support of life cycle assessment (LCA) to comprehensively assess the potential environmental impacts of the investigated treatment method compared to consolidated technologies.

Acknowledgments

Dr. Gulnara Maniakova and prof. Luigi Rizzo would like to thank PRIMA consortium of the European Union for the support through post-doc grant within the project “Decision support-based approach for Sustainable Water reuse application in Agricultural Production – DSWAP”. The authors wish to thanks also the Spanish Ministry of Science and Innovation,

State Investigation Agency (AEI) and the European Regional Development Fund (FEDER) for funding NAVIA Project (PID2019–110441RB-C32).

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References

Aguas, Y., Hincapie, M., Martínez-Piernas, A.B., Agüera, A., Fernández-Ibáñez, P., Nahim-Granados, S., Polo-López, M.I., 2019. Reclamation of Real Urban Wastewater Using Solar Advanced Oxidation Processes: An Assessment of Microbial Pathogens and 74 Organic Microcontaminants Uptake in Lettuce and Radish. Environ. Sci. Technol. 53, 9705–9714. https://doi.org/10.1021/acs.est.9b00748

Cabrera-Reina, A., Miralles-Cuevas, S., Sánchez Pérez, J.A., Salazar, R., 2021. Application of solar photo-Fenton in raceway pond reactors: A review. Science of The Total Environment 800, 149653. https://doi.org/10.1016/j.scitotenv.2021.149653

Costa, E.P., Roccamante, M., Amorim, C.C., Oller, I., Sánchez Pérez, J.A., Malato, S., 2020. New trend on open solar photoreactors to treat micropollutants by photo-Fenton at circumneutral pH: Increasing optical pathway. Chemical Engineering Journal 385, 123982. https://doi.org/10.1016/j.cej.2019.123982

Delli Compagni, R., Gabrielli, M., Polesel, F., Turolla, A., Trapp, S., Vezzaro, L., Antonelli, M., 2020. Risk assessment of contaminants of emerging concern in the context of wastewater reuse for irrigation: An integrated modelling approach. Chemosphere 242, 125185. https://doi.org/10.1016/j.chemosphere.2019.125185

Dong, W., Sun, S.-P., Yang, X., Zhou, K., Li, Y., Wang, X., Wu, Z., Wu, W.D., Chen, X.D., 2019. Enhanced emerging pharmaceuticals removal in wastewater after biotreatment

493 by a low-pressure UVA/FeIII-EDDS/H2O2 process under neutral pH conditions.
494 Chemical Engineering Journal 366, 539–549.
495 https://doi.org/10.1016/j.cej.2019.02.109
496 Fent, K., Weston, A.A., Caminada, D., 2006. Ecotoxicology of human pharmaceuticals.
497 Aquatic Toxicology 76, 122–159. https://doi.org/10.1016/j.aquatox.2005.09.009
498 García-Fernández, I., Miralles-Cuevas, S., Oller, I., Malato, S., Fernández-Ibáñez, P., Polo-
499 López, M.I., 2019. Inactivation of E. coli and E. faecalis by solar photo-Fenton with
500 EDDS complex at neutral pH in municipal wastewater effluents. Journal of Hazardous
501 Materials, SI: Photocatalysis:Future Trend 372, 85–93.
502 https://doi.org/10.1016/j.jhazmat.2018.07.037
503 Giannakis, S., 2018. Analogies and differences among bacterial and viral disinfection by the
504 photo-Fenton process at neutral pH: a mini review. Environ Sci Pollut Res 25, 27676–
505 27692. https://doi.org/10.1007/s11356-017-0926-x
506 Giannakis, S., Polo López, M.I., Spuhler, D., Sánchez Pérez, J.A., Fernández Ibáñez, P.,
507 Pulgarin, C., 2016. Solar disinfection is an augmentable, in situ-generated photo-
508 Fenton reaction—Part 1: A review of the mechanisms and the fundamental aspects of
509 the process. Applied Catalysis B: Environmental 199, 199–223.
510 https://doi.org/10.1016/j.apcatb.2016.06.009
511 Giannakis, S., Rtimi, S., Pulgarin, C., 2017. Light-Assisted Advanced Oxidation Processes for
512 the Elimination of Chemical and Microbiological Pollution of Wastewaters in
513 Developed and Developing Countries. Molecules 22, 1070.
514 https://doi.org/10.3390/molecules22071070
515 Gómez-López, V.M., Lannoo, A.-S., Gil, M.I., Allende, A., 2014. Minimum free chlorine
516 residual level required for the inactivation of Escherichia coli O157:H7 and
517 trihalomethane generation during dynamic washing of fresh-cut spinach. Food Control
518 42, 132–138. https://doi.org/10.1016/j.foodcont.2014.01.034

519 Lahlou, F.-Z., Mackey, H.R., Al-Ansari, T., 2021. Wastewater reuse for livestock feed
520 irrigation as a sustainable practice: A socio-environmental-economic review. Journal
521 of Cleaner Production 294, 126331. https://doi.org/10.1016/j.jclepro.2021.126331
522 Leonel, L.P., Tonetti, A.L., 2021. Wastewater reuse for crop irrigation: Crop yield, soil and
523 human health implications based on giardiasis epidemiology. Science of The Total
524 Environment 775, 145833. https://doi.org/10.1016/j.scitotenv.2021.145833
525 Liao, Z., Chen, Z., Xu, A., Gao, Q., Song, K., Liu, J., Hu, H.-Y., 2021. Wastewater treatment
526 and reuse situations and influential factors in major Asian countries. Journal of
527 Environmental Management 282, 111976.
528 https://doi.org/10.1016/j.jenvman.2021.111976
529 Malato, S., Blanco, J., Campos, A., Cáceres, J., Guillard, C., Herrmann, J.M., Fernández-
530 Alba, A.R., 2003. Effect of operating parameters on the testing of new industrial
531 titania catalysts at solar pilot plant scale. Applied Catalysis B: Environmental 42, 349–
532 357. https://doi.org/10.1016/S0926-3373(02)00270-9
533 Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J., Gernjak, W., 2009.
534 Decontamination and disinfection of water by solar photocatalysis: Recent overview
535 and trends. Catalysis Today, MONOGRAPH: Decontamination and disinfection of
536 water by solar photocatalysis: Recent overview and trends 147, 1–59.
537 https://doi.org/10.1016/j.cattod.2009.06.018
538 Maniakova, G., Salmerón, I., Aliste, M., Inmaculada Polo-López, M., Oller, I., Malato, S.,
539 Rizzo, L., 2022. Solar photo-Fenton at circumneutral pH using Fe(III)-EDDS
540 compared to ozonation for tertiary treatment of urban wastewater: Contaminants of
541 emerging concern removal and toxicity assessment. Chemical Engineering Journal
542 431, 133474. https://doi.org/10.1016/j.cej.2021.133474
543 Maniakova, G., Salmerón, I., Nahim-Granados, S., Malato, S., Oller, I., Rizzo, L., Polo-
544 López, M.I., 2021a. Sunlight advanced oxidation processes vs ozonation for

wastewater disinfection and safe reclamation. Science of The Total Environment 787, 147531. https://doi.org/10.1016/j.scitotenv.2021.147531

Maniakova, G., Salmerón, I., Polo-López, M.I., Oller, I., Rizzo, L., Malato, S., 2021b. Simultaneous removal of contaminants of emerging concern and pathogens from urban wastewater by homogeneous solar driven advanced oxidation processes. Science of The Total Environment 766, 144320. https://doi.org/10.1016/j.scitotenv.2020.144320

Miralles-Cuevas, S., Oller, I., Ruíz-Delgado, A., Cabrera-Reina, A., Cornejo-Ponce, L., Malato, S., 2019. EDDS as complexing agent for enhancing solar advanced oxidation processes in natural water: Effect of iron species and different oxidants. Journal of Hazardous Materials, SI: Photocatalysis:Future Trend 372, 129–136. https://doi.org/10.1016/j.jhazmat.2018.03.018

Moreira, N.F.F., Narciso-da-Rocha, C., Polo-López, M.I., Pastrana-Martínez, L.M., Faria, J.L., Manaia, C.M., Fernández-Ibáñez, P., Nunes, O.C., Silva, A.M.T., 2018. Solar treatment (H2O2, TiO2-P25 and GO-TiO2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related genes in urban wastewater. Water Research 135, 195–206. https://doi.org/10.1016/j.watres.2018.01.064

Nahim-Granados, S., Sánchez Pérez, J.A., Polo-Lopez, M.I., 2018. Effective solar processes in fresh-cut wastewater disinfection: Inactivation of pathogenic E. coli O157:H7 and Salmonella enteritidis. Catalysis Today, 5th European Conference on Environmental Applications of Advanced Oxidation Processes 313, 79–85. https://doi.org/10.1016/j.cattod.2017.10.042

Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry.

570 Critical Reviews in Environmental Science and Technology 36, 1–84.
571 https://doi.org/10.1080/10643380500326564
572 Rincón, A.-G., Pulgarin, C., 2004. Effect of pH, inorganic ions, organic matter and H2O2 on
573 E. coli K12 photocatalytic inactivation by TiO2: Implications in solar water
574 disinfection. Applied Catalysis B: Environmental 51, 283–302.
575 https://doi.org/10.1016/j.apcatb.2004.03.007
576 Rodríguez-Chueca, J., Mosteo, R., Ormad, M.P., Ovelleiro, J.L., 2012. Factorial experimental
577 design applied to Escherichia coli disinfection by Fenton and photo-Fenton processes.
578 Solar Energy 86, 3260–3267. https://doi.org/10.1016/j.solener.2012.08.015
579 Sánchez-Montes, I., Salmerón García, I., Rivas Ibañez, G., Aquino, J.M., Polo-López, M.I.,
580 Malato, S., Oller, I., 2020. UVC-based advanced oxidation processes for simultaneous
581 removal of microcontaminants and pathogens from simulated municipal wastewater at
582 pilot plant scale. Environ. Sci.: Water Res. Technol. 6, 2553–2566.
583 https://doi.org/10.1039/D0EW00279H
584 Scheierling, S., Bartone, C., Mara, D., Drechsel, P., 2011. Towards an agenda for improving
585 wastewater use in agriculture. Water International 36, 420–440.
586 https://doi.org/10.1080/02508060.2011.594527
587 Soriano-Molina, P., García Sánchez, J.L., Alfano, O.M., Conte, L.O., Malato, S., Sánchez
588 Pérez, J.A., 2018. Mechanistic modeling of solar photo-Fenton process with Fe3+-
589 EDDS at neutral pH. Applied Catalysis B: Environmental 233, 234–242.
590 https://doi.org/10.1016/j.apcatb.2018.04.005
591 Soriano-Molina, P., Plaza-Bolaños, P., Lorenzo, A., Agüera, A., García Sánchez, J.L., Malato,
592 S., Sánchez Pérez, J.A., 2019. Assessment of solar raceway pond reactors for removal
593 of contaminants of emerging concern by photo-Fenton at circumneutral pH from very
594 different municipal wastewater effluents. Chemical Engineering Journal 366, 141–
595 149. https://doi.org/10.1016/j.cej.2019.02.074

596 Wu, X., Conkle, J.L., Ernst, F., Gan, J., 2014. Treated Wastewater Irrigation: Uptake of
597 Pharmaceutical and Personal Care Products by Common Vegetables under Field
598 Conditions. Environ. Sci. Technol. 48, 11286–11293.
599 https://doi.org/10.1021/es502868k
600 Zhang, Y., Zhou, M., 2019. A critical review of the application of chelating agents to enable
601 Fenton and Fenton-like reactions at high pH values. Journal of Hazardous Materials
602 362, 436–450. https://doi.org/10.1016/j.jhazmat.2018.09.035
603