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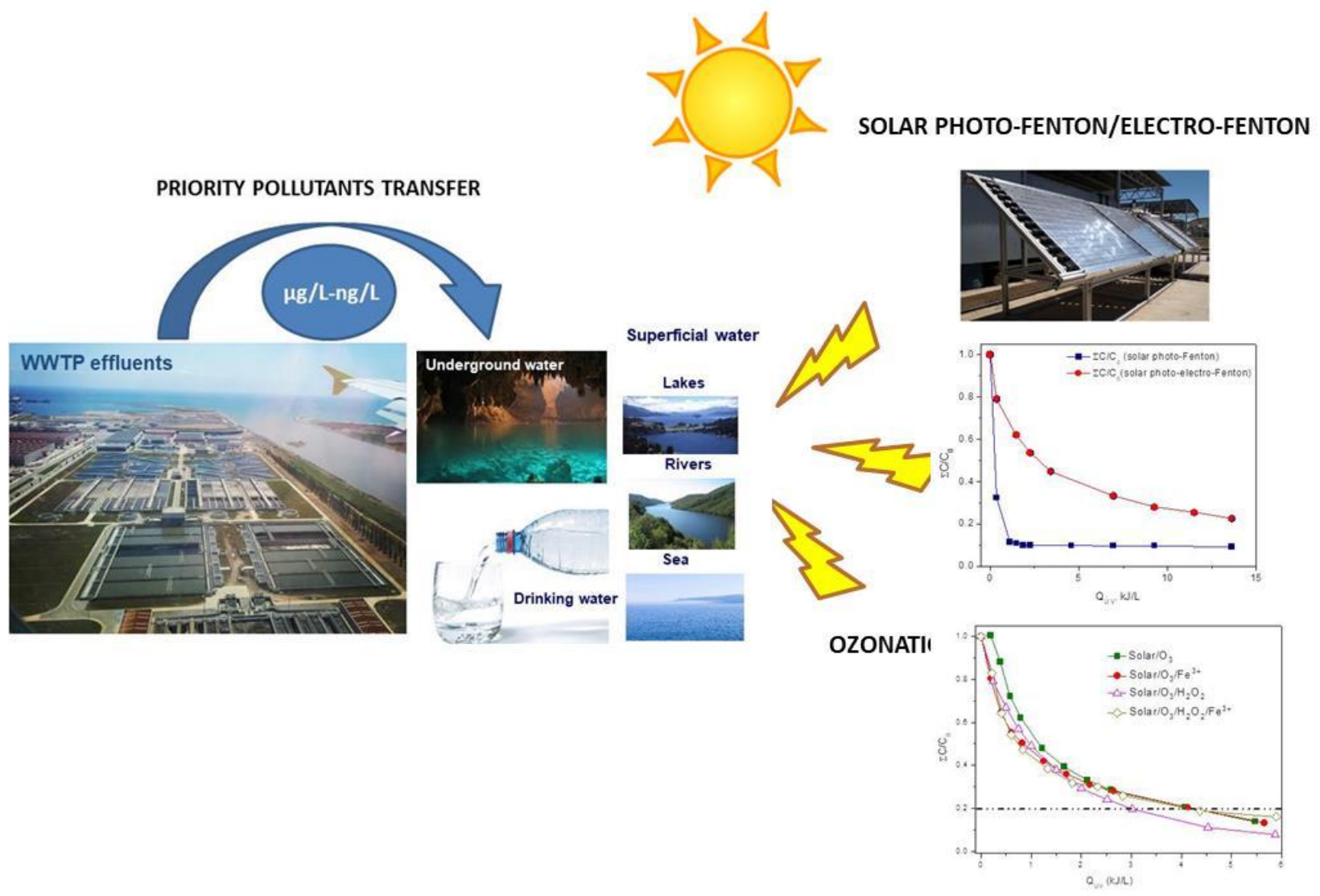
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Highlights

- New application of solar photo-electro-Fenton at neutral pH at pilot plant scale.
- Higher microcontaminants degradation rate in solar photo-Fenton compared to solar photo-electro-Fenton.
- No significant improvement detected when ozone was combined with Fenton's reagent.
- Significant low consumption of ozone was observed when combined with solar energy.



1 **New approaches to solar Advanced Oxidation Processes for elimination of**
2 **priority substances based on electrooxidation and ozonation at pilot plant**
3 **scale**

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8 **Abstract**

9 The main objective of this work is the comparison of various Advanced Oxidation
10 Processes based on solar photo-Fenton at circumneutral pH (by adding EDDS as iron
11 complexing agent), such as solar photo-electro-Fenton process and solar ozonation in
12 combination with Fenton like processes ($O_3/Fe^{2+}/H_2O_2$, $O_3/Fe^{3+}/H_2O_2$ and
13 $Solar/Fe^{3+}/O_3/H_2O_2$), for the elimination of four microcontaminants (Terbutryn,
14 chlorfenvinphos, pentachlorophenol and diclofenac) at 200 $\mu g/L$ each and in different water
15 matrices. These compounds were selected as Priority Substances listed in European
16 Commission directives (2013/39/EC and 2008/105/EC Directives). Research was carried
17 out at pilot plant scale in a 30 L electrochemical system (cells made by an anode of boron-
18 doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-
19 polytetrafluoroethylene (PTFE) GDE as the cathode), a 20 L ozone reactor and three
20 different solar photoreactors (39 L, 45L and 120 L) based on compound parabolic
21 collectors (CPC) and connected to the non-solar oxidation systems. Results showed
22 successful elimination of at least 80% of MCs for all the technologies tested. However,

23 solar photo-Fenton at circumneutral pH showed better performance than solar photo-
24 electro-Fenton and even electro-Fenton processes. In addition, the combination of ozone
25 with solar radiation showed promising results as almost complete elimination of MCs was
26 attained with a significant lower ozone consumption that when applying ozone in the dark
27 (with or without the assistance of Fenton's reagent).

28

29 **Keywords:** Mild Solar photo-Fenton; ozonation; photo-electro-Fenton, priority substances,
30 solar energy.

31 **1. Introduction**

32 The growing development of the personal care and pharmaceutical industry has led to the
33 presence of substances as antiseptics, pesticides, hormones, etc., in water bodies, for instance
34 in municipal wastewater treatment plant (MWWTP) effluents, in a very low concentration
35 that have being detected thanks to the development of advanced analytical methods [1].
36 Among these microcontaminants (MCs) there are pesticides, industrial compounds,
37 antibiotics, steroids, drugs, etc. Many of these trace contaminants are referred as
38 Contaminants of Emerging Concern (CECs) because they have recently been analysed, they
39 are not still regulated and are believed to affect the environment and human health, not only
40 for themselves but also for the degradation by-products that they can generate, sometimes
41 presenting even higher toxicity than the parent compounds. Although there are no discharge
42 limits for most MCs, some regulations have been published and therefore some CECs
43 identified with high risk (based on available data of acute and chronic effects to aquatic
44 environment and human health) entered in the regulations and therefore they are called

45 Priority substances (PS). A new strategy was defined by the European Directive
46 2000/60/EC identifying some PS. Later, a list of 33 PS was established by the Directive
47 2008/105/EC. The last Directive 2013/39/EU updated previous regulations introducing the
48 polluter pays principle. Therefore, the development of non-expensive-innovative
49 wastewater treatment technologies are needed [2] not only for removing PS but also CECs,
50 all of them considered MCs.

51 Considering that conventional wastewater treatments based on biological systems are
52 normally designed focusing on carbon, nitrogen and phosphorous elimination, only partial
53 MCs removal is usually achieved since most of the compounds cannot be metabolized by
54 microorganisms as source of carbon and may even inhibit the activity of the
55 microorganisms or produce their bioaccumulation in the food chain [3]. The application of
56 tertiary treatments for refining these treated waters so as to avoid PS and other CECs
57 reaching both irrigation water (as they could accumulate in crops products [4, 5], and water
58 natural bodies, and to prevent their bioaccumulation and the consequent aggravation of
59 their detrimental effects on human health, has been widely studied in the last years [6].

60 Recently, membrane separation and advanced oxidation processes (AOPs) are becoming
61 consolidated as effective technologies to remove MCs [[Westerhoff, P., Moon, H.,
62 Minakata, D., Crittenden, J. Oxidation of organics in retentates from reverse osmosis
63 wastewater reuse facilities. Water Research, 43, 3992-3998, 2009. Pérez-González, A.,
64 Urtiaga, A.M., Ibáñez, R., Ortiz, I. State of the art and review on the treatment technologies
65 of water reverse osmosis concentrates. Water Research, 46, 267-283, 2012. Justo, A.,
66 González, O., Aceña, J., Pérez, S., Barceló, D., Sans, C., Esplugas, S. Pharmaceuticals and
67 organic pollution mitigation in reclamation osmosis brines by UV/H₂O₂ and ozone.](#)

68 | [Journal of Hazardous Materials, 263, 268-274, 2013.](#) 7]. In this context, the treatment of
69 | membrane rejection streams (highly concentrated in salts and contaminants) has open the
70 | door to the application of electrochemical processes for MCs removal, as these processes
71 | need high conductivity in water to be effective [[Pérez, G., Fernández-Alba, A.R., Urtiaga,](#)
72 | [A.M., Ortiz, I. Electro-oxidation of reverse osmosis concentrates generated in tertiary water](#)
73 | [treatment. Water Research, 44, 2763-2772, 2010; Radjenovic, J., Bagastyo, A., Rozendal,](#)
74 | [R.A., Mu, Y., Keller, J., Rabaey, K. Electrochemical oxidation of trace organic](#)
75 | [contaminants in reverse osmosis concentrate using RuO₂/IrO₂-coated titanium anodes.](#)
76 | [Water Research, 45, 1579-1586, 2011. Urtiaga, A.M., Pérez, G., Ibáñez, R., Ortiz, I.](#)
77 | [Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse](#)
78 | [osmosis followed by electrochemical oxidation of the RO concentrate. Desalination, 331,](#)
79 | [pp. 26-34, 2013.;](#) 8]. Usually, wastewater containing MCs resembles to natural sweet
80 | waters in its physic-chemical characteristics, such as MWWTP effluents.

81 | Nowadays, it is booming the combination of processes looking for an increase in treatments
82 | effectiveness, therefore it has emerged a high trend on the application of electro-Fenton
83 | (EF) processes, based on the application of two oxidative systems simultaneously. On the
84 | one hand, $\cdot\text{OH}$ are electrogenerated on the anode surface by electrolysis of water, and on
85 | the other hand, hydrogen peroxide is electrogenerated in the cathode, so Fenton reaction
86 | takes place when adding iron [9]. According to the published works in this topic, there is a
87 | niche for research on the elimination of MCs by EF processes and so several challenges
88 | needs to be addressed [10-13]. [Critical challenges to wider adoption of electrochemical](#)
89 | [oxidation for wastewater treatment is the high cost of electrodes and that it is strongly pH](#)
90 | [dependent. Usually, the oxidation potential of an electrochemical system in acidic medium](#)

91 [is higher than that in alkaline medium. Boron-doped diamond \(BDD\) electrodes have been](#)
92 [studied extensively in recent years but the performance of the process in removing MCs is](#)
93 [affected by the presence of inorganic anions and DOM intrinsically present in wastewater,](#)
94 [which can react with the electro-generated hydroxyl radicals and other reactive oxygen](#)
95 [species \[Sirés I., Brillas E., 2012. Remediation of water pollution caused by pharmaceutical](#)
96 [residues based on electrochemical separation and degradation technologies: A review.](#)
97 [Environment International 40, 212-229\]. One of the challenges regards their](#)
98 [implementation in continuous mode to provide high H₂O₂ amounts from the start.](#)
99 [Moreover, EF operation at acidic pH is a known drawbacks that need to be solved. A](#)
100 [comprehensive review on the application of EF and other processes for the abatement of](#)
101 [MCs was recently published \[Francisca C. Moreira, Rui A.R. Boaventura, Enric Brillas,](#)
102 [Vítor J.P. Vilar. Electrochemical advanced oxidation processes: A review on their](#)
103 [application to synthetic and real wastewaters. Applied Catalysis B: Environmental Volume](#)
104 [202, March 2017, Pages 217-261\].](#)

105 Since most water bodies containing MCs come from MWWTP effluents and these are in
106 pH ranges near neutrality, it is necessary to consider that the ideal situation would be the
107 application of tertiary treatments which are known to be effective at natural pH such as
108 ozone based processes [14]. The treatment of MWWTP effluents with ozonation has
109 already been implemented in Switzerland with the target in the elimination of a selection of
110 CECs from a defined list of compounds. The studies evaluate the suitable process
111 configurations depending on the individual features of the treatment plants [15].

112 The wide diversity of MCs and local specificity of their composition indicates the need for
113 development and integration of different treatments. Therefore, the aim of this study is to

114 propose alternative solar treatments, all of them operated at circumneutral pH in
115 combination with electro-oxidation or O₃-based processes. The most tested solar-based
116 treatment in the recent years for elimination of MCs has been photo-Fenton, known to be
117 optimal at pH around 3, but successfully applied at circumneutral pH by using different
118 complexing agents such as citric acid, EDTA, EDDS, etc [16]. This statement has been
119 widely demonstrated in several works [17-20] so any other technology to be applied must
120 be successfully compared to photo-Fenton process at neutral pH.

121 The main objective of this work is the comparison of various AOPs based on solar photo-
122 Fenton at circumneutral pH, such as photo-electro-Fenton process and solar ozonation in
123 combination with Fenton like processes (O₃/Fe²⁺/H₂O₂, O₃/Fe³⁺/H₂O₂ and
124 Solar/Fe³⁺/O₃/H₂O₂), for the elimination of selected target MCs (terbutryn,
125 chlorfenvinphos, pentachlorophenol and diclofenac) at pilot plant scale contained in
126 different water matrices (demineralized water, natural water, simulated fresh water and
127 simulated MWWTP effluent). Conventional photo-Fenton process and ozonation were also
128 performed as a matter for comparison. Target MCs have been selected as PS included in
129 [Directive 2013/39/EU, including a set of compounds of different structure \(aromatic and](#)
130 [not aromatic\), considered highly toxic, with different heteroatoms \(Cl, N, P\) and possible to](#)
131 [analyze by HPLC/UV at low concentration \(LOQ < 5 µg/L\).](#)

132 **2. Materials and methods**

133 **2.1. Chemicals and wastewater characterization**

134 Pentachlorophenol (PCP), terbutryn (TBT), chlorfenvinphos (CFP) and diclofenac (DFC)
135 high-purity grade (>99%) all were purchased from Sigma-Aldrich. As iron source it was

136 used Iron (III) Sulphate ($\text{Fe}_2(\text{SO}_4)\cdot 3\text{H}_2\text{O}$, 75% purity) from Panreac. Anhydrous sodium
137 sulfate (Fluka) was employed as background electrolyte in electrochemical processes at
138 0.05 M. Reagent grade hydrogen peroxide (35% w/v), sulphuric acid and sodium hydroxide
139 (for pH adjustment) were acquired from J.T. Baker. [Ethylenediamine-N,N'-disuccinic acid](#)
140 [\(EDDS\)](#) 35% in H_2O was purchased from Aldrich. Acetonitrile (ACN) and formic acid for
141 the HPLC method were HPLC-grade from Panreac. Millipore 0.2 μm syringe-driven Millex
142 hydrophobic Fluoropore (PTFE) membrane filters were utilized for particles removal.

143 Experiments were conducted in demineralized water, natural water (NW) (pH 6.2 and
144 1.1 mS/cm of conductivity), ~~simulated fresh water (SW)~~ and simulated effluent from a
145 MWWTP (SE). ~~SW-SE~~ was ~~prepared according to~~ based in the following receipt [for](#)
146 [simulated water](#) [21]: 96 mg/L of NaHCO_3 , 60 mg/L of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, 60 mg/L of MgSO_4
147 and 4 mg/L of KCl. ~~A slightly modified~~ SE from the American Standard Methods [21] was
148 prepared by adding the following chemicals to [SWsimulated water](#): beef extract (1.8 mg/L),
149 peptone (2.7 mg/L), humic acid (4.2 mg/L), tannic acid (4.2 mg/L), sodium lignin sulfonate
150 (2.4 mg/L), sodium lauryle sulphate (0.9 mg/L), acacia gum powder (4.7 mg/L), Arabic
151 acid (5.0 mg/L), $(\text{NH}_4)_2\text{SO}_4$ (23.6 mg/L) and K_2HPO_4 (7.0 mg/L), contributing 10 mg/L of
152 dissolved organic carbon (DOC) [22].

153 **2.2. Analytical methods**

154 Hydrogen peroxide was measured by spectrophotometry at 410 nm by adding Ti(IV)
155 oxysulfate, according to DIN 38409 H15 and iron concentration was measured following
156 ISO 6332 using for both a Unicam UV/Vis UV2 spectrophotometer (at 510 nm).

157 Ozone concentration in solution was measured by the indigo method based on the
158 decolorization of indigo trisulfonate (600 nm) by ozone [21, 23].

159 ~~A Shimadzu TOC-VCSN analyzer was used to monitor Dissolved Organic Carbon (DOC)~~
160 ~~after sample filtration through a 0.22 µm Nylon filter.~~ The degradation rate of the MCs was
161 monitored by a UPLC/UV Agilent Technologies Series 1260, equipped with a C-18
162 ZORBAX XDB C-18 analytical column. The gradient started at 90/10 (v/v) ultrapure water
163 (with formic acid 25 mM) and acetonitrile (ACN) that progress till 100% ACN in 14 min at
164 a flow rate of 1 mL/min. The UV signal for each compound was: 220 nm for
165 Pentachlorophenol, 230 nm for Terbutryn, 240 nm for Chlorofenvinphos and 285 nm for
166 Diclofenac. Limits of quantification (LOQ) of Pentachlorophenol, Terbutryn,
167 Chlorofenvinphos and Diclofenac were 4.4, 3.8, 3.2 and 3.4 µg/L respectively. 9 mL of
168 sample was filtered with a 0.22 µm PTFE filter. The filter was washed with 1 ml of ACN
169 to extract any absorbed compound, mixing it with 9 mL of filtered sample before injection
170 in HPLC. Injection volume was 100µL. Mineralization of MCs (TOC results) was not
171 determined because treating MCs at 200 µg/L is out of the analytical limits of this
172 technique and/or not realible due to the presence of other organics.

173 Fe³⁺:EDDS concentration was measured by liquid chromatography (HPLC Agilent 1100
174 Series) by using an Ion-Pair method with a reversed-phase column (Luna C18, 150X3 mm,
175 5µm particle size) [24].

176 **2.3. Pilot plants and experimental procedures**

177 **2.3.1. Solar photo-Fenton treatment**

178 Compound parabolic collector (CPC) solar pilot plant used for solar photo-Fenton
179 experiments is located in Plataforma Solar de Almería (latitude 37°N, longitude 2.4°W).
180 ~~The volume inside the absorber tubes is 22 L being the total irradiated area 3.08 m² and the~~
181 ~~total volume 39 L. Table 1 describes the characteristics of CPC photo-reactor.~~ A global
182 solar UV radiometer (KIPP&ZONEN, Model CUV 3) tilted 37° as the CPC reactor
183 quantifies the solar ultraviolet radiation (UV). More details can be obtained in [25]. Solar
184 accumulated UV energy has been quantified according to Eq. 1 where:

$$185 \quad Q_{UV,n+1} = Q_{UV} + \Delta t_n \cdot \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_T}; \quad \Delta t_n = t_{n+1} - t_n \quad (1)$$

186 t_n : experimental time for each sample.

187 UV: average solar ultraviolet radiation measured during the period Δt_n .

188 A_i : illuminated area (m²).

189 $Q_{UV,n}$: accumulated energy per unit of volume (kJ/L) at t_n .

190 Solar photo-Fenton experiments at near neutral pH would require the addition of a
191 complexing agent such as EDDS for maintaining iron in solution [26]. In such a case, 5.5
192 mg/L of Fe³⁺ was complexed with EDDS maintaining the molar ratio 1:2 Fe³⁺: EDDS as
193 better operating condition according to Miralles-Cuevas et al. [27]. For the complex
194 formation in the dark, iron was dissolved in the minimum amount of acidified water, and
195 then the required amount of EDDS was added. The complex was immediately formed
196 showing a strong yellow color.

197

198 **2.3.2. Solar photo-electro-Fenton treatment**

199 Solar photo-electro-Fenton pilot plant consisted of four electrochemical cells acquired from
200 ElectroCell coupled to a CPC photo-reactor. Each cell was composed by an anode made of
201 boron-doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-
202 polytetrafluoroethylene (PTFE) GDE as the cathode, both with 0.01 m² effective area. The
203 GDE cathode was fed with compressed air (ABAC air compressor, 1.5 kW) at 10 L/min.
204 The experiments were carried at a constant j using a Delta Electronika power supply limited
205 to 70 V and 22 A.

206 Solar CPC photoreactor combined with the electro-Fenton plant [is described in Table 1](#),
207 consists of 10 borosilicate tubes mounted in an aluminum frame on a platform tilted 37°
208 (PSA, 37° N, 2.4° W) ~~with a total illuminated area of 2 m², and an irradiated volume of 23~~
209 [L](#). Scheme of the pilot plant is shown in elsewhere [28]. The working volume was 30 L for
210 electro-Fenton (EF) assays ~~and 75 L to perform the solar photo-electro-Fenton (SPEF)~~
211 [tests](#).

212 Accumulated UV energy in each experiment was obtained by using equation 1 (as
213 explained for solar photo-Fenton experiments previously).

214 Experiments were developed by using 50 mM solution of Na₂SO₄ (Sigma –Aldrich) as
215 supporting electrolyte dissolved on demineralized water. First of all, Fe:EDDS complex
216 prepared as described above, was added in a 1:2 ratio. Then, 200 µg/L of each target
217 contaminant was also added to directly to the recirculation tank of the pilot plant. Letting
218 homogenize the solution for a time equal to 3 times the recirculation of the total volume, a
219 sample was taken to check initial MCs concentration. After this, experiment started and

220 samples were taken in intervals of 5 minutes during the first 30 min, then every 15 min till
221 90 min of test and finally every 30 min.

222 **2.3.3. Ozonation treatment**

223 The ozonation system is an Anseros PAP-pilot plant (Ansero Klaus Nonnenmacher GmbH,
224 Germany) for batch operation. The reactor is a 20 L column with an inlet O₃ diffuser and a
225 gas dehumidifier in the sampling point. It was also equipped with an ozone destroyer, two
226 nondispersive UV analyzers (Ozomat GM-6000-OEM) to measure inlet and outlet ozone
227 gas concentration, a flow-meter for inlet air regulation, an [air-oxygen](#) generator (Anseros
228 SEP100) and an ozone generator (Anseros COM-AD02).

229 During experiments with ozonation, the mix of four MCs was added directly from stock
230 solution into the reactor. The samples were collected every 5-10 min and residual ozone
231 was removed with N₂ to stop the reaction. The ozone generator was set at 20% power with
232 a constant 1.5 g O₃/h production. Ozone gas was measured at the system inlet (C_{O₃,i}, g/
233 Nm³) and outlet (C_{O₃,o}, g/Nm³), so that ozone consumption of each sample O_{3cons,n}, g/L
234 could be calculated by Eq. (2) taking the inlet air flow Q_a Nm³/h of 0.06 Nm³/h and ozone
235 consumption in the previous sample into account:

$$236 \quad O_{3cons,n} \left(\frac{g}{L} \right) = O_{3cons,n-1} + \frac{Q_a \cdot (C_{O_{3,i,n}} - C_{O_{3,o,n}}) \cdot (t_n - t_{n-1})}{V_r} \quad (2)$$

237 In some experiments ozonation pilot plant was combined with a solar CPC photo-reactor
238 (different to that described in section 2.3.1.) for the assessment of Solar/Fe³⁺/O₃/H₂O₂

239 process (see Figure 1). Table 1 presents the characteristics of CPC photo-reactor used. Eq.
 240 1 was used to determine $Q_{UV,n}$.



241

242

Figure 1 - Ozonation Plant Pilot

243

244 **Table 1.** CPC solar photo-reactor used for Solar/Fe³⁺/O₃/H₂O₂the different tests-processes

PARAMETER	<u>photo-Fenton</u>	<u>photo-electro-Fenton</u>	<u>Solar/Fe³⁺/O₃/H₂O₂</u>
Illuminated volume	<u>22 L</u>	<u>23 L</u>	68.2 L
Reactor area	<u>3.08 m²</u>	<u>2 m²</u>	2 m ²
Glass tubes diameter	<u>32 mm</u>	<u>45 mm</u>	75 mm
CPC inclination	<u>37°</u>	<u>37°</u>	37°
Total volume	<u>39L</u>	<u>75 L</u>	120 L

245

246 3. Results and discussion

247 3.1. Solar pPhoto -electro-Fenton and photo/electro-Fenton processes treatment

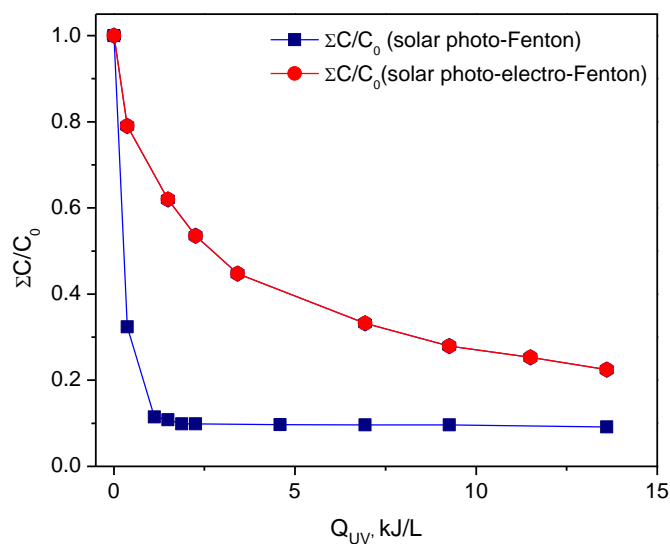
248 [3.1.a. Solar photo-Fenton and photo-electro-Fenton comparison](#)

249 Elimination of target MCs (200 µg/L of each) in demineralized water by solar photo-Fenton
250 process under well-known operating conditions [26], at pilot plant scale and at near neutral
251 pH by using Fe:EDDS 1:2, and 0.1 mM of Fe³⁺, was first evaluated (Figure 2 shows the
252 degradation profile of the sum of MCs). Diclofenac and Pentachlorophenol were
253 completely degraded after a solar-UV accumulated energy of 0.83 kJ/L (after around 5
254 minutes of solar illumination) and requiring 31 mg/L of H₂O₂, though Chlorfenvinphos and
255 Terbutryn were more resistant and 85% of elimination was attained after 11 kJ/L
256 (corresponding to around 60 minutes of solar illumination) and a H₂O₂ consumption of 60
257 mg/L. Final pH at the end of the experiment was 6.

258 The degradation of ~~the same concentration of selected~~ MCs was also tested by electro-
259 oxidation in demineralized water containing a required electrolyte, in this case Na₂SO₄
260 (50 mM), in the ~~electro-oxidation~~ pilot plant described in section 2.3.2. ~~Taking into account~~
261 ~~the p~~Previously reported results ~~related to the optimization of optimized~~ this experimental
262 system for in-situ electrogeneration of hydrogen peroxide [28] ~~and~~, 73.6 mA/cm² was
263 selected ~~with a hydrogen peroxide production rate between 30 and 60 mg/min for carrying~~
264 ~~out the degradation tests~~. However, though optimum pH obtained in the previous work was
265 3, in this occasion it was selected to operate at circumneutral pH. ~~and so, cathodic~~
266 ~~electrogeneration of hydrogen peroxide was checked under such new operating conditions.~~
267 ~~As a result, hydrogen peroxide production rate was observed to be between 30 and~~
268 ~~60 mg/min.~~ The following paragraphs discuss results obtained under these conditions
269 checking the stability of the complex Fe:EDDS in the dark and applying SPEF (Figure 2).

270 Before applying solar photoelectro-Fenton (SPEF) process by using also Fe:EDDS 1:2 at
271 circumneutral pH, it was required checking the stability of the complex Fe:EDDS in the
272 dark during electro-oxidation. Under our knowledge any previous study on the use of
273 EDDS in electro-oxidation systems has been reported. Therefore, an electro-Fenton (EF)
274 test was performed at 73.6 mA/cm^2 and pH 6 for 240 min monitoring Fe:EDDS complex at
275 0.1 mM of Fe^{3+} . During 120 minutes of treatment the complex remained stable and from
276 then it began to decay. After 180 minutes (14.9 kWh/m^3) Fe:EDDS complex showed a 18%
277 of decay and 40% at the end of the assay with an energy consumption of 20 kWh/m^3 . In
278 consequence, 180 minutes were considered as the maximum process time for the rest of
279 assays developed in the study to guaranty the stability of the complex and so at least 80%
280 of Fe^{3+} would be present as Fe:EDDS.

281 Then, SPEF experiment was carried out at a current density of 73.6 mA/cm^2 and 0.1 mM of
282 Fe^{3+} with Fe:EDDS 1:2 (Figure 2). It is important to highlight that the exposure of the
283 complex to sunlight promotes its degradation. Accordingly to this, iron in solution
284 decreased from 0.1 mM to 0.062 mM after 60 minutes of SPEF. Despite this, after 180
285 minutes, with 5.1 kWh/m^3 of energy consumption it was achieved 77.5% of MCs
286 degradation in the electro-oxidation process. At that point, iron dissolved in the system was
287 only 0.036 mM , confirming the instability of the complex and the degradation of EDDS.



288

289 **Figure 2.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by SPEF (j 73.6 mA/cm²) with 0.1 mM of
 290 Fe³⁺ at neutral pH by adding Fe:EDDS 1:2 in demineralized water ([Na₂SO₄ 50 mM in](#)
 291 [SPEF](#)).

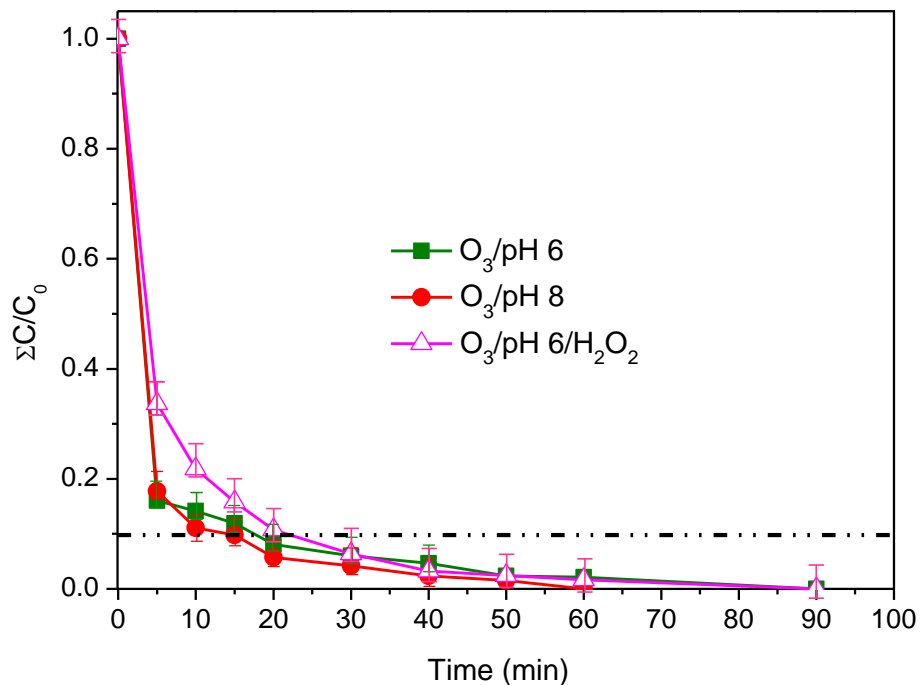
292 SPEF treatment showed less efficiency in the target MCs abatement compared with solar
 293 photo-Fenton process. Indeed initial reaction rate corresponding to the degradation of the
 294 sum of MCs was 77.8 $\mu\text{g/L}\cdot\text{min}$ for solar photo-Fenton against 10.6 $\mu\text{g/L}\cdot\text{min}$ for SPEF
 295 process. Both experiments were carried out in demineralized water though the presence of
 296 the electrolyte (Na₂SO₄ 50 mM) required for the adequate performance of SPEF provoked
 297 [the lower reduction on the removal rate in SPEF compared with solar photo-Fenton.](#)
 298 [Generation of hydroxyl radicals was lower because of \(i\) the formation of sulfato-Fe\(III\)](#)
 299 [complexes and \(ii\) scavenging of hydroxyl radicals by sulfate and formation of sulfate](#)
 300 [radicals which are less reactive than HO radicals.](#) In addition, the absence of an external
 301 source of hydrogen peroxide was also responsible of the removal rate slowed down and
 302 therefore, it must be stated that cathodic electrogeneration of hydrogen peroxide governed

303 MCs removal rate. Using higher amount of hydrogen peroxide, a better performance of the
304 electrochemical cells or advanced concepts and new materials of such cells, could increase
305 SPEF efficiency as H₂O₂ production rate is a key issue in this kind of AOPs.

306 [3.1.b. Electro-Fenton process](#)

307 EF experiments were also carried out in order to evaluate MCs degradation without
308 combining with solar energy. For that purpose, first, pure anodic oxidation (AO) was
309 carried out at 73.6 mA/cm². Afterwards, EF was applied also at 73.6 mA/cm² in the
310 presence of Fe³⁺ but testing different concentrations: 0.1, 0.2 and 0.5 mM (Figure 3 and
311 Table 2). In addition, and regarding the current density (j), 30, 73.6 and 100 mA/cm² were
312 tested at Fe³⁺ 0.1 mM. Lowest current density slowed down the generation of hydrogen
313 peroxide, though it also showed a lowest energy consumption (2.2 kWh/m³) for attaining
314 80% degradation of MCs after 150 minutes of EF treatment. This result brought to light the
315 necessity of increasing j to improve the ratio between energy consumption and MCs
316 elimination. Nevertheless, when applying the highest j value (100 mA/cm²), EF treatment
317 time was significantly reduced to 60 min due to the larger oxidizing power of the anode and
318 the higher production of hydrogen peroxide that favored the Fenton reaction and
319 consequently, MCs elimination. Nevertheless, that positive result was countered by the
320 important increase detected on the related energy consumption, attaining 6.5 kWh/m³. Best
321 compromise between MCs degradation and energy consumption was obtained when
322 applying j of 73.6 mA/cm², which did not entail a significant increase in current density,
323 compared with 30 mA/cm² but more than 80% degradation after 45 minutes of EF was
324 reached with an energy consumption of 3.45 kWh/m³.

325



326

327 **Figure 3.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by AO and EF (Fe:EDDS, 1:2) at neutral pH
 328 [in demineralized water \(\$\text{Na}_2\text{SO}_4\$ 50 mM in SPEF\).](#)

329

330 It must be noticed that an increase in Fe^{3+} concentration from 0.1mM to 0.2 and 0.5 mM at
 331 73.6 mA/cm^2 in the EF treatment always involves an increase in EDDS amount for
 332 maintaining the ratio Fe:EDDS of 1:2. In consequence, higher concentration of EDDS
 333 would mean also higher organic carbon in solution that would act as radicals' scavenger.
 334 This fact explains the increase on the energy required for attaining 80% of MCs removal
 335 associated to a higher concentration of Fe^{3+} (Figure 3). However, when Fe^{3+} was increased
 336 from 0.2 mM to 0.5 mM, the energy demanded was lower than when using Fe^{3+} 0.2 mM but
 337 still higher than at Fe^{3+} 0.1 mM. At higher Fe^{3+} concentration dark-Fenton process was so
 338 fast that all hydrogen peroxide generated was consumed rapidly.

339

340 Finally, the AO test at j 73.6 mA/cm² corroborated higher required treatment time and
 341 energy consumption compared to EF process with 0.1 mM of Fe³⁺. It should be highlighted
 342 that AO was very effective for Pentachlorophenol, Terbutryn and Diclofenac removal, but
 343 not for the more recalcitrant MC, Chlorofenvinphos (Table 2). [AO does not require iron](#)
 344 [removal after the treatment, which would simplify electrooxidation operation.](#)

345

346

347

348 **Table 2.** Summary of the results obtained in the electro-oxidation pilot plant to attain 80%
 349 of total MCs degradation at pH 6 by using AO or EF (with Fe:EDDS).

	0.1 mM Fe ³⁺			73.6 mA/cm ²		
	30 mA/cm ²	73.6 mA/cm ²	100 mA/cm ²	AO	0.2 mM Fe ³⁺	0.5 mM Fe ³⁺
Time (min.)	150	45	60	75	120	180
Energy consumption kWh/m³	2.2	3.5	6.5	5.0	12.1	8.1
MCs removal (%)						
Pentachlorophenol	87.8	78.8	91.7	100	89	85.8
Terbutryn	66.2	84.2	79.5	84.1	72.1	68.3
Chlorofenvinphos	58.4	57.4	57.3	46.2	61.5	62.9
Diclofenac	100	97.3	100	100	100	100

350

351 **3.32. ~~Solar ozonation treatment~~ Ozonation and solar ozonation systems**

3.2.a. Ozonation tests

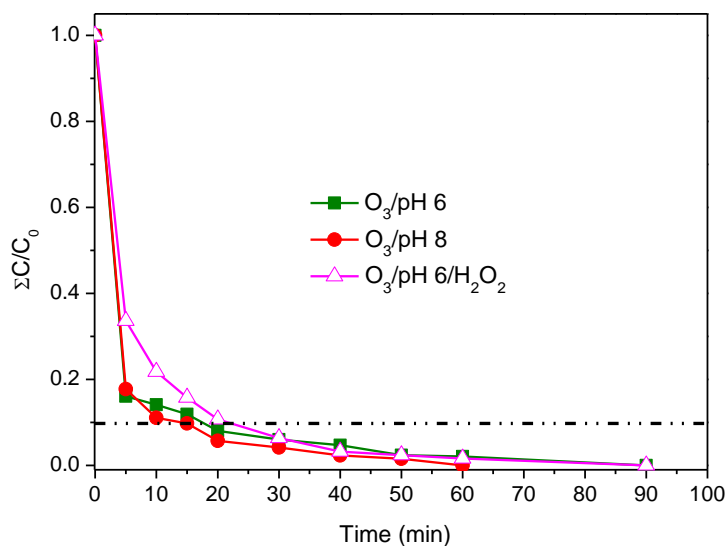
Ozonation treatment of the target MCs spiked on different types of water (demineralized water, NW and SE) was performed varying pH from 6 to 11 (direct ozonation and indirect free radical oxidation). Initial concentration of each target MC was maintained in 200 µg/L. The effect assessment of H₂O₂ addition (at 1.5 mM) as well as Fenton like reactions by using Fe²⁺ or Fe³⁺ at 0.1 mM, were also carried out. Same operating conditions were evaluated in combination with solar radiation.

Ozonation results in demineralized water at pH 6 and pH 11 showed more than 99% degradation of all contaminants (after 50 minutes of treatment) in both situations. It should be noted that, working at pH 11, ozone consumption was higher (32 mg O₃/L) than when working at lower pH (13 mg O₃/L) due to the reaction of ozone with generated hydroxyl radicals at high pH (Eq. 3). It is important to stress that more oxidizing conditions at pH 11 did not entail higher degradation rates due to the low concentration of MCs. Therefore, pH 11 was disregarded for further tests as indirect free radical oxidation route showed any substantial interest for this application. Lower pH (around 8) was selected instead as it is a normal value for natural waters and wastewater containing MCs.



Afterwards, ozonation was tested in NW at pH 6 and 8. It was observed an increment of the degradation rate and on the consumption of ozone, 14 mg O₃/L at pH 6 and 19 mg O₃/L at pH 8, for attaining more than 99% of MCs degradation (Figure 4). Substantially lower consumption of ozone was required to degrade 90% of MCs (1.8 mg O₃/L at pH 6 and 4.4 mg O₃/L at pH 8). It was clearly observed that higher pH resulted in higher reaction

374 rates but accompanied of higher ozone consumption. Consequently, it should be remarked
375 that application of ozone treatment for elimination of MCs must be always tested at pH
376 around 8 (normal pH of natural waters and MWWTP effluents) and not at pH 6. These
377 results are consistent with ozone application at large scale for treatment of MCs in
378 Switzerland, where a specific ozone dose of 1.5-2.5 mg/L is required for 80% of MCs
379 abatement [29]. It is important to highlight that when adding H₂O₂ at natural pH (8), the
380 consumption of O₃ slightly increased to 5 mg/L to degrade >90% of MCs, without an
381 improvement on the MCs elimination rate. The reaction of ozone with of H₂O₂ (peroxone
382 process) gives rise to the generation of •OH radicals [30] but, as in the case of ozonation at
383 pH 11, it did not provoke a better degradation rate due to the low concentration of MCs and
384 so ozone reacted with H₂O₂.



385

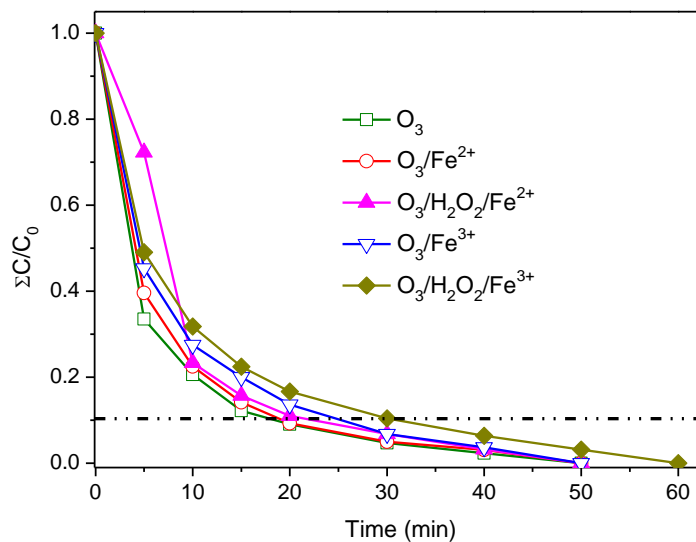
386 **Figure 4.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by ozonation in NW at two different pHs and
387 with addition of H₂O₂ (50 mg/L).

388 After demonstrating the bad performance of ozone at pH 11 for MCs elimination and that
 389 the process was efficient at pH close to the typical pH of MWWTP effluents (pH around 8)
 390 the final objective was to study if any combination between ozonation and Fenton ~~or photo-~~
 391 ~~Fenton~~ would be interesting for the enhancement of MCs removal. Figure 5 shows results
 392 with SE at natural pH (8) showing a consumption of ozone of 6.4 mg/L to degrade >90% of
 393 MCs. In Figure 5 it is also shown experimental results obtained in the presence of iron with
 394 and without its combination with H₂O₂. When applying Fe²⁺ or Fe³⁺ (both at 0.1 mM),
 395 ozone consumption was 6.6 and 9.6 mg O₃/L, respectively. Recent studies reported that the
 396 co-presence of O₃ and Fenton reagents favored the generation of •OH [31]. Experiments
 397 with addition of iron to the ozonation system have been carried out to evaluate the direct
 398 reaction of ozone with Fe²⁺ and reduction to Fe³⁺ with extra •OH generation according to
 399 Eqs. 4-7 [32]. But no improvement was observed in the reaction rate or in ozone
 400 consumption. Initial degradation rate was 61.7 µg/L.min for ozonation (pH 8) almost equal
 401 to those obtained when Fe²⁺ or Fe³⁺ were added (59.5 µg/L.min and 60.6 µg/L.min,
 402 respectively).



403 When testing ozonization in combination with Fenton process (Fe/H₂O₂), both consumption
 404 of ozone and treatment times were similar, so any significant improvement took place. In

405 addition, initial degradation rates were 58.6 $\mu\text{g/L}\cdot\text{min}$ and 50.2 $\mu\text{g/L}\cdot\text{min}$, when adding
406 H_2O_2 to Fe^{2+} and Fe^{3+} , respectively.



407

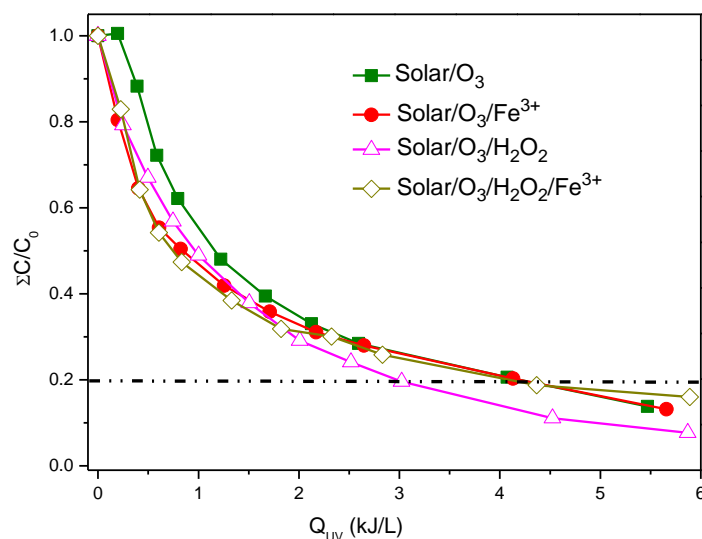
408 **Figure 5.** MCs degradation ($\Sigma\text{C}_0 \approx 800 \mu\text{g/L}$) by ozonation in SE at pH 8 with addition of
409 Fe^{2+} , Fe^{3+} (0.1 mM) and H_2O_2 (1.5 mM).

410 [3.2.b. Solar ozonation tests](#)

411 Finally, the combination of ozone with a solar CPC photo-reactor working at natural pH (8)
412 for the elimination of MCs in SE was performed (figure 6).

413 Dissolved ozone molecules absorb UV light with a peak absorbance at 260 nm and a molar
414 absorptivity of $3292 \pm 70 \text{ M/cm}$ [33]. Upon the irradiation of UV, the dissolved ozone
415 molecules undergo photolysis reactions to yield hydrogen peroxide [34]. The application of
416 ozone in the presence of solar radiation led to an enhancement of MCs removal as lower
417 consumption of ozone was required. Indeed, for 80% degradation of MCs the consumption
418 of ozone was 0.52 mg/L (O_3), 0.30 mg/L ($\text{O}_3/\text{Fe}^{3+}$), 0.23 mg/L ($\text{O}_3/\text{H}_2\text{O}_2$) and 0.6 mg/L
419 ($\text{O}_3/\text{Fe}^{3+}/\text{H}_2\text{O}_2$). The so important reduction in ozone consumption for solar/ O_3 compared

420 with results obtained with ozonation in the dark was due to a new source of $\bullet\text{OH}$ generated
 421 under solar UV ($\lambda < 315$ nm) from H_2O_2 photolysis as H_2O_2 could be produced by Eq. 8
 422 [35]. The consumption of ozone in solar/ O_3 / H_2O_2 was still low against an enhancement in
 423 the reaction rate. In that cases in which ozone was combined with iron under solar
 424 illumination, the contribution of photo-Fenton process was not clear as both ozone
 425 consumption and reaction rate were quite similar to solar/ O_3 process. It is interesting to
 426 remark that during solar treatments, the temperature in the photo-reactor increased (up to
 427 c.a. 40°C). This also favored MCs elimination since ozone reaction rates increase with
 428 temperature [36].



429

430 **Figure 6.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by ozonation combined with a CPC photo-
 431 reactor in SE at pH 8 with addition of Fe^{2+} , Fe^{3+} (0.1 mM) and H_2O_2 (50 mg/L).

432 It is important also to stress that initial degradation rate did not improve when combining
433 ozone with solar radiation, as it decreased to 28.3 $\mu\text{g/L}\cdot\text{min}$. Similar values were obtained
434 when Fe^{3+} or H_2O_2 were added separately (24.7 $\mu\text{g/L}\cdot\text{min}$ and 24.9 $\mu\text{g/L}\cdot\text{min}$, respectively),
435 or even in combination of both reagents, giving 30.4 $\mu\text{g/L}\cdot\text{min}$ of initial degradation rate.
436 These results expose the evidence that main advantage on combining ozonation with solar
437 radiation lays on the significant reduction on ozone consumption.

438

439

440 **4. Conclusions**

441 It has been demonstrated that Fe:EDDS complex is able to maintain iron in solution for EF
442 and SPEF treatments and so it can be considered a useful tool for performing
443 electrochemical processes at circumneutral pH.

444 SPEF treatment showed less efficiency compared with solar photo-Fenton process at
445 circumneutral pH due to the hydroxyl radicals' scavenger effect provoked by the necessity
446 of adding an electrolyte in wastewater with low ionic strength. SPEF was also less efficient
447 than EF treatment due to a limited electro-generation of H_2O_2 . An improvement on the in-
448 situ production rate of hydrogen peroxide would enhance SPEF process. Better
449 performance of target MCs elimination was obtained when applying EF with Fe^{3+} at
450 0.1 mM. These results bring to light the interest on EF, SPEF and electro-oxidation
451 processes in general as a suitable technology for MCs removal only when they are
452 contained on specific wastewaters characterized by high conductivity values, such as
453 membrane processes rejection streams.

454 Finally, Ozonation treatment demonstrated to be successful in the almost complete removal
455 of studied MCs present in different water matrices at different pH in dark conditions.
456 However, it is important to stress that higher pH values increased ozone consumption due
457 to the very low concentration of contaminants to be oxidized, and so the reaction of
458 generated H_2O_2 with O_3 .

459 In general, the removal of MCs do not need the generation of high concentrations of
460 hydroxyl radicals, this is why the combination of ozone with other treatments based on the
461 addition of iron and hydrogen peroxide in the dark did not show an enhancement in the
462 efficiency of the process. Nevertheless, the application of ozone in the presence of solar
463 radiation led to an improvement on the MCs degradation and a reduction on ozone
464 consumption compared with ozonation in the dark. This interesting result must be explored
465 in detail and optimized taking into account economic aspects such as electricity
466 requirements and the consequent depletion of ozone generation costs.

467 **Acknowledgements**

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1 **New approaches to solar Advanced Oxidation Processes for elimination of**
2 **priority substances based on electrooxidation and ozonation at pilot plant**
3 **scale**

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8 **Abstract**

9 The main objective of this work is to compare various Advanced Oxidation Processes
10 based on solar photo-Fenton at circumneutral pH (by adding EDDS as iron complexing
11 agent), such as solar photo-electro-Fenton process and solar ozonation in combination with
12 Fenton like processes ($O_3/Fe^{2+}/H_2O_2$, $O_3/Fe^{3+}/H_2O_2$ and $Solar/Fe^{3+}/O_3/H_2O_2$), for the
13 elimination of four microcontaminants (Terbutryn, chlorfenvinphos, pentachlorophenol and
14 diclofenac) at 200 $\mu\text{g/L}$ each and in different water matrices. These compounds were
15 selected as Priority Substances listed in European Commission directives (2013/39/EC and
16 2008/105/EC Directives). Research was carried out at pilot plant scale in a 30 L
17 electrochemical system (cells made by an anode of boron-doped diamond thin film on a
18 niobium mesh (Nb-BDD) and a carbon-polytetrafluoroethylene (PTFE) GDE as the
19 cathode), a 20 L ozone reactor and three different solar photoreactors (39 L, 45L and 120
20 L) based on compound parabolic collectors (CPC) and connected to the non-solar oxidation
21 systems. Results showed successful elimination of at least 80% of MCs for all the
22 technologies tested. However, solar photo-Fenton at circumneutral pH showed better

23 performance than solar photo-electro-Fenton and even electro-Fenton processes. In
24 addition, the combination of ozone with solar radiation showed promising results since
25 almost a complete elimination of MCs was attained with a significant lower ozone
26 consumption than when applying ozone in the dark (with or without the assistance of
27 Fenton's reagent).

28

29 **Keywords:** Mild Solar photo-Fenton; ozonation; photo-electro-Fenton, priority substances,
30 solar energy.

31 **1. Introduction**

32 The growing development of the personal care and pharmaceutical industry has led to the
33 presence of substances such as antiseptics, pesticides, hormones, etc., in water bodies, for
34 instance in municipal wastewater treatment plant (MWWTP) effluents, in such a low
35 concentration that they have been detected thanks to the development of advanced
36 analytical methods [1]. Among these microcontaminants (MCs) there are pesticides,
37 industrial compounds, antibiotics, steroids, drugs, etc. Many of these trace contaminants are
38 referred as Contaminants of Emerging Concern (CECs) because they have recently been
39 analysed, they are not still regulated and are believed to affect the environment and human
40 health, not only for themselves but also for the degradation by-products that they can
41 generate, sometimes presenting even higher toxicity than the parent compounds. Although
42 there are no discharge limits for most MCs, some regulations have been published and
43 therefore some CECs identified with high risk (based on available data of acute and chronic
44 effects to aquatic environment and human health) entered in the regulations and therefore

45 they are called Priority substances (PS). A new strategy was defined by the European
46 Directive 2000/60/EC identifying some PS. Later, a list of 33 PS was established by the
47 Directive 2008/105/EC. The last Directive 2013/39/EU updated previous regulations
48 introducing the polluter pays principle. Therefore, the development of non-expensive-
49 innovative wastewater treatment technologies are needed [2] not only for removing PS but
50 also CECs, all of them considered MCs.

51 Considering that conventional wastewater treatments based on biological systems are
52 normally designed focusing on carbon, nitrogen and phosphorous elimination, MCs are
53 only partially removed since most of the compounds cannot be metabolized by
54 microorganisms and may even inhibit their activity or produce their bioaccumulation in the
55 food chain [3]. The application of tertiary treatments for refining these treated waters so as
56 to avoid PS and other CECs reaching both irrigation water (as they could accumulate in
57 crop products [4, 5], and water natural bodies, and to prevent their bioaccumulation and the
58 consequent aggravation of their detrimental effects on human health, has been widely
59 studied in the last years [6].

60 Recently, membrane separation and advanced oxidation processes (AOPs) are becoming
61 consolidated as effective technologies to remove MCs [7-10]. In this context, the treatment
62 of membrane rejection streams (highly concentrated in salts and contaminants) has open the
63 door to the application of electrochemical processes for MCs removal, as these processes
64 need high conductivity in water to be effective [11-14]. Usually, wastewater containing
65 MCs resembles to natural sweet waters in its physic-chemical characteristics, such as
66 MWWTP effluents.

67 Nowadays, the combination of processes looking for an increase in treatments effectiveness
68 is booming, therefore a high trend on the application of electro-Fenton (EF) processes has
69 emerged, based on the simultaneous application of two oxidative systems. On the one hand,
70 $\cdot\text{OH}$ are electrogenerated on the anode surface by electrolysis of water, and on the other
71 hand, hydrogen peroxide is electrogenerated in the cathode, so Fenton reaction takes place
72 when adding iron [15]. According to the published works regarding this topic, there is a
73 niche for research on the elimination of MCs by EF processes and so, several challenges
74 need to be addressed [16-19]. Critical challenges in order to wider the adoption of
75 electrochemical oxidation for wastewater treatment are the high cost of electrodes and that
76 it is strongly pH dependent. Usually, the oxidation potential of an electrochemical system
77 in acidic medium is higher than in alkaline medium. Boron-doped diamond (BDD)
78 electrodes have been studied extensively in the recent years but their performance in the
79 process of removing MCs is affected by the presence of inorganic anions and DOM,
80 intrinsically present in wastewater, which can react with the electro-generated hydroxyl
81 radicals and other reactive oxygen species [20]. One of the challenges is their
82 implementation in a continuous mode in order to provide high H_2O_2 amounts from the start.
83 Moreover, EF operation at acidic pH is known as a drawback that needs to be solved. A
84 comprehensive review on the application of EF and other processes for the abatement of
85 MCs was recently published [21].

86 Since most water bodies containing MCs come from MWWTP effluents and these are in
87 pH ranges near neutrality, it is necessary to consider that the ideal situation would be the
88 application of tertiary treatments which are known to be effective at natural pH, such as
89 ozone based processes [22]. The treatment of MWWTP effluents with ozonation has

90 already been implemented in Switzerland with the aim of removing a selection of CECs
91 from a defined list of compounds. The studies evaluate the suitable process configurations
92 depending on the individual features of the treatment plants [23].

93 The wide diversity of MCs and local specificity of their composition indicates the need for
94 developing and integrating different treatments. Therefore, the aim of this study is to
95 propose alternative solar treatments, all of them operated at circumneutral pH in
96 combination with electro-oxidation or O₃-based processes. The most tested solar-based
97 treatment in the recent years for elimination of MCs has been photo-Fenton, known to be
98 optimal at pH around 3, but successfully applied at circumneutral pH by using different
99 complexing agents, such as citric acid, EDTA, EDDS, etc [24]. This statement has been
100 widely demonstrated in several works [25-28] so, any other technology applied, must be
101 successfully compared to photo-Fenton process at neutral pH.

102 The main objective of this work is the comparison of various AOPs based on solar photo-
103 Fenton at circumneutral pH, such as photo-electro-Fenton process and solar ozonation in
104 combination with Fenton like processes (O₃/Fe²⁺/H₂O₂, O₃/Fe³⁺/H₂O₂ and
105 Solar/Fe³⁺/O₃/H₂O₂), for the elimination of selected target MCs (terbutryn,
106 chlorfenvinphos, pentachlorophenol and diclofenac) at a pilot plant scale contained in
107 different water matrices (demineralized water, natural water, simulated fresh water and
108 simulated MWWTP effluent). Conventional photo-Fenton process and ozonation were also
109 performed for comparison. Target MCs have been selected as PS included in Directive
110 2013/39/EU, including a set of compounds with different structures (aromatic and not
111 aromatic), considered highly toxic, with different heteroatoms (Cl, N, P) and possible to
112 analyze by HPLC/UV at low concentration (LOQ < 5 µg/L).

113 2. Materials and methods

114 2.1. Chemicals and wastewater characterization

115 Pentachlorophenol (PCP), terbutryn (TBT), chlorfenvinphos (CFP) and diclofenac (DFC)
116 high-purity grade (>99%) were all purchased from Sigma-Aldrich. As iron source Iron (III)
117 Sulphate ($\text{Fe}_2(\text{SO}_4)\cdot 3\text{H}_2\text{O}$, 75% purity) from Panreac was used. Anhydrous sodium sulfate
118 (Fluka) was employed as background electrolyte in electrochemical processes at 0.05 M.
119 Reagent grade hydrogen peroxide (35% w/v), sulphuric acid and sodium hydroxide (for pH
120 adjustment) were acquired from J.T. Baker. Ethylenediamine- $\text{N,N}'$ -disuccinic acid (EDDS)
121 35% in H_2O was purchased from Aldrich. Acetonitrile (ACN) and formic acid for the
122 HPLC method were HPLC-grade from Panreac. Millipore 0.2 μm syringe-driven Millex
123 hydrophobic Fluoropore (PTFE) membrane filters were used for particles removal.

124 Experiments were conducted in demineralized water, natural water (NW) (pH 6.2 and
125 1.1 mS/cm of conductivity), and simulated effluent from a MWWTP (SE). SE was based in
126 the following receipt for simulated water [29]: 96 mg/L of NaHCO_3 , 60 mg/L of
127 $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, 60 mg/L of MgSO_4 and 4 mg/L of KCl. SE from the American Standard
128 Methods [29] was prepared by adding the following chemicals to simulated water: beef
129 extract (1.8 mg/L), peptone (2.7 mg/L), humic acid (4.2 mg/L), tannic acid (4.2 mg/L),
130 sodium lignin sulfonate (2.4 mg/L), sodium lauryle sulphate (0.9 mg/L), acacia gum
131 powder (4.7 mg/L), Arabic acid (5.0 mg/L), $(\text{NH}_4)_2\text{SO}_4$ (23.6 mg/L) and K_2HPO_4 (7.0
132 mg/L), contributing 10 mg/L of dissolved organic carbon (DOC) [30].

133 2.2. Analytical methods

134 Hydrogen peroxide was measured by spectrophotometry at 410 nm by adding Ti(IV)
135 oxysulfate, according to DIN 38409 H15 and iron concentration was measured following
136 ISO 6332 using for both a Unicam UV/Vis UV2 spectrophotometer (at 510 nm).

137 Ozone concentration in solution was measured by the indigo method based on the
138 decolorization of indigo trisulfonate (600 nm) by ozone [29,31].

139 The degradation rate of the MCs was monitored by a UPLC/UV Agilent Technologies
140 Series 1260, equipped with a C-18 ZORBAX XDB C-18 analytical column. The gradient
141 started at 90/10 (v/v) ultrapure water (with formic acid 25 mM) and acetonitrile (ACN) that
142 progress till 100% ACN in 14 min at a flow rate of 1 mL/min. The UV signal for each
143 compound was: 220 nm for Pentachlorophenol, 230 nm for Terbutryn, 240 nm for
144 Chlorofenvinphos and 285 nm for Diclofenac. Limits of quantification (LOQ) of
145 Pentachlorophenol, Terbutryn, Chlorofenvinphos and Diclofenac were 4.4, 3.8, 3.2 and
146 3.4 µg/L respectively. 9 mL of sample was filtered with a 0.22 µm PTFE filter. The filter
147 was washed with 1 ml of ACN to extract any absorbed compound, mixing it with 9 mL of
148 filtered sample before injection in HPLC. Injection volume was 100µL. Mineralization of
149 MCs (TOC results) was not determined because treating MCs at 200 µg/L is out of the
150 analytical limits of this technique and/or not realible due to the presence of other organics.

151 Fe³⁺:EDDS concentration was measured by liquid chromatography (HPLC Agilent 1100
152 Series) by using an Ion-Pair method with a reversed-phase column (Luna C18, 150X3 mm,
153 5µm particle size) [32].

154 **2.3. Pilot plants and experimental procedures**

155 **2.3.1. Solar photo-Fenton treatment**

156 Compound parabolic collector (CPC) solar pilot plant used for solar photo-Fenton
157 experiments is located at Plataforma Solar de Almería (latitude 37°N, longitude 2.4°W).
158 Table 1 describes the characteristics of CPC photo-reactor. A global solar UV radiometer
159 (KIPP&ZONEN, Model CUV 3) tilted 37° as the CPC reactor quantifies the solar
160 ultraviolet radiation (UV). More details can be obtained in [33]. Solar accumulated UV
161 energy has been quantified according to Eq. 1 where:

$$162 \quad Q_{UV,n+1} = Q_{UV} + \Delta t_n \cdot \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_T}; \quad \Delta t_n = t_{n+1} - t_n \quad (1)$$

163 t_n : experimental time for each sample.

164 UV: average solar ultraviolet radiation measured during the period Δt_n .

165 A_i : illuminated area (m^2).

166 $Q_{UV,n}$: accumulated energy per unit of volume (kJ/L) at t_n .

167 Solar photo-Fenton experiments at near neutral pH would require the addition of a
168 complexing agent, such as EDDS, for maintaining iron in solution [34]. In such a case,
169 5.5 mg/L of Fe^{3+} was complexed with EDDS maintaining the molar ratio 1:2 Fe^{3+} : EDDS
170 as better operating condition according to Miralles-Cuevas et al. [35]. For the complex
171 formation in the dark, iron was dissolved in the minimum amount of acidified water, and
172 then the required amount of EDDS was added. The complex was immediately formed
173 showing a strong yellow color.

174

175 **2.3.2. Solar photo-electro-Fenton treatment**

176 Solar photo-electro-Fenton pilot plant consisted of four electrochemical cells acquired from
177 ElectroCell coupled to a CPC photo-reactor. Each cell was composed by an anode made of
178 a boron-doped diamond thin film on a niobium mesh (Nb-BDD) and a carbon-
179 polytetrafluoroethylene (PTFE) GDE as the cathode, both with 0.01 m² effective area. The
180 GDE cathode was fed with compressed air (ABAC air compressor, 1.5 kW) at 10 L/min.
181 The experiments were carried at a constant j using a Delta Electronika power supply limited
182 to 70 V and 22 A.

183 Solar CPC photoreactor combined with the electro-Fenton plant is described in Table 1, it
184 consists of 10 borosilicate tubes mounted in an aluminum frame on a platform tilted 37°
185 (PSA, 37° N, 2.4° W). Scheme of the pilot plant is shown in elsewhere [36]. The working
186 volume was 30 L for electro-Fenton (EF) assays.

187 Accumulated UV energy in each experiment was obtained by using equation 1 (as
188 explained for solar photo-Fenton experiments previously).

189 Experiments were developed by using 50 mM solution of Na₂SO₄ (Sigma –Aldrich) as
190 supporting electrolyte dissolved on demineralized water. First of all, Fe:EDDS complex
191 prepared as described above, was added in a 1:2 ratio. Then, 200 µg/L of each target
192 contaminant was also added directly to the recirculation tank of the pilot plant. After
193 homogenizing the solution for a time equal to 3 times the recirculation of the total volume,
194 a sample was taken to check initial MCs concentration. After this, the experiment started
195 and samples were taken in intervals of 5 minutes during the first 30 min, then every 15 min
196 till 90 min of test and finally every 30 min.

197 **2.3.3. Ozonation treatment**

198 The ozonation system is an Anseros PAP-pilot plant (Ansero Klaus Nonnenmacher GmbH,
 199 Germany) for batch operation. The reactor is a 20 L column with an inlet O₃ diffuser and a
 200 gas dehumidifier in the sampling point. It was also equipped with an ozone destroyer, two
 201 nondispersive UV analyzers (Ozomat GM-6000-OEM) to measure inlet and outlet ozone
 202 gas concentration, a flow-meter for inlet air regulation, an oxygen generator (Anseros
 203 SEP100) and an ozone generator (Anseros COM-AD02).

204 During experiments with ozonation, the mix of four MCs was added directly from stock
 205 solution into the reactor. The samples were collected every 5-10 min and residual ozone
 206 was removed with N₂ to stop the reaction. The ozone generator was set at 20% power with
 207 a constant 1.5 g O₃/h production. Ozone gas was measured at the system inlet (C_{O₃,i}, g/
 208 Nm³) and outlet (C_{O₃,o}, g/Nm³), so that ozone consumption of each sample O_{3cons,n}, g/L
 209 could be calculated by Eq. (2) taking the inlet air flow Q_a Nm³/h of 0.06 Nm³/h and ozone
 210 consumption in the previous sample into account:

$$211 \quad O_{3cons,n} \left(\frac{g}{L} \right) = O_{3cons,n-1} + \frac{Q_a \cdot (C_{O_3,i,n} - C_{O_3,o,n}) \cdot (t_n - t_{n-1})}{V_r} \quad (2)$$

212 In some experiments, the ozonation pilot plant was combined with a solar CPC photo-
 213 reactor (different to that described in section 2.3.1.) for the assessment of
 214 Solar/Fe³⁺/O₃/H₂O₂ process (see Figure 1). Table 1 presents the characteristics of the CPC
 215 photo-reactor used. Eq. 1 was used to determine Q_{UV,n}.



216

217

Figure 1 - Ozonation Pilot plant

218

219 **Table 1.** CPC solar photo-reactors used in the different tested processes

PARAMETER	photo-Fenton	photo-electro-Fenton	Solar/Fe ³⁺ /O ₃ /H ₂ O ₂
Illuminated volume	22 L	23 L	68.2 L
Reactor area	3.08 m ²	2 m ²	2 m ²
Glass tubes diameter	32 mm	45 mm	75 mm
CPC inclination	37°	37°	37°
Total volume	39L	75 L	120 L

220

221 **3. Results and discussion**

222 **3.1. Photo-Fenton and photo/electro-Fenton processes**

223 *3.1.a. Solar photo-Fenton and photo-electro-Fenton comparison*

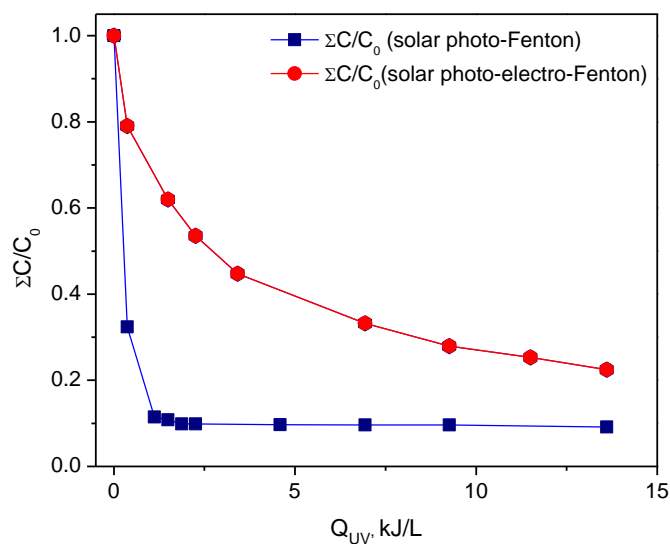
224 Elimination of target MCs (200 µg/L of each) in demineralized water by solar photo-Fenton
225 process under well-known operating conditions [34]; at pilot plant scale and at near neutral
226 pH by using Fe:EDDS 1:2, and 0.1 mM of Fe³⁺, was first evaluated (Figure 2 shows the
227 degradation profile of the sum of MCs). Diclofenac and Pentachlorophenol were
228 completely degraded after a solar-UV accumulated energy of 0.83 kJ/L (after around 5
229 minutes of solar illumination) and requiring 31 mg/L of H₂O₂, though Chlorfenvinphos and
230 Terbutryn were more resistant and 85% of elimination was attained after 11 kJ/L
231 (corresponding to around 60 minutes of solar illumination) and a H₂O₂ consumption of 60
232 mg/L. Final pH at the end of the experiment was 6.

233 The degradation of MCs was also tested by electro-oxidation in demineralized water
234 containing the required electrolyte, in this case Na₂SO₄ (50 mM), in the pilot plant
235 described in section 2.3.2. Previously reported results, optimized this experimental system
236 for in-situ electrogeneration of hydrogen peroxide [36] and 73.6 mA/cm² was selected with
237 a hydrogen peroxide production rate between 30 and 60 mg/min. However, though
238 optimum pH obtained in the previous work was 3, in this occasion it was selected to
239 operate at circumneutral pH. The following paragraphs discuss results obtained under these
240 conditions checking the stability of the complex Fe:EDDS in the dark and applying SPEF
241 (Figure 2).

242 Before applying solar photoelectro-Fenton (SPEF) process by using also Fe:EDDS 1:2 at
243 circumneutral pH, it was required to check the stability of the complex Fe:EDDS in the
244 dark during electro-oxidation. To our knowledge, no previous study on the use of EDDS in
245 electro-oxidation systems has been reported. Therefore, an electro-Fenton (EF) test was
246 performed at 73.6 mA/cm² and pH 6 for 240 min monitoring Fe:EDDS complex at 0.1 mM

247 of Fe^{3+} . During 120 minutes of treatment, the complex remained stable and from then it
 248 began to decay. After 180 minutes (14.9 kWh/m^3) Fe:EDDS complex showed a 18% of
 249 decay and 40% at the end of the assay, with an energy consumption of 20 kWh/m^3 . In
 250 consequence, 180 minutes were considered to be the maximum process time for the rest of
 251 assays developed in the study in order to guaranty the stability of the complex and so at
 252 least 80% of Fe^{3+} would be present as Fe:EDDS.

253 Then, SPEF experiment was carried out at a current density of 73.6 mA/cm^2 and 0.1 mM of
 254 Fe^{3+} with Fe:EDDS 1:2 (Figure 2). It is important to highlight that the exposure of the
 255 complex to sunlight promotes its degradation. Accordingly to this, iron in solution
 256 decreased from 0.1 mM to 0.062 mM after 60 minutes of SPEF. Despite this, after 180
 257 minutes, with 5.1 kWh/m^3 of energy consumption, 77.5% of MCs degradation was
 258 achieved in the electro-oxidation process. At that point, iron dissolved in the system was
 259 only 0.036 mM , confirming the instability of the complex and the degradation of EDDS.



260

261 **Figure 2.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by SPEF ($j 73.6 \text{ mA/cm}^2$) with 0.1 mM of
262 Fe^{3+} at neutral pH by adding Fe:EDDS 1:2 in demineralized water (Na_2SO_4 50 mM in
263 SPEF).

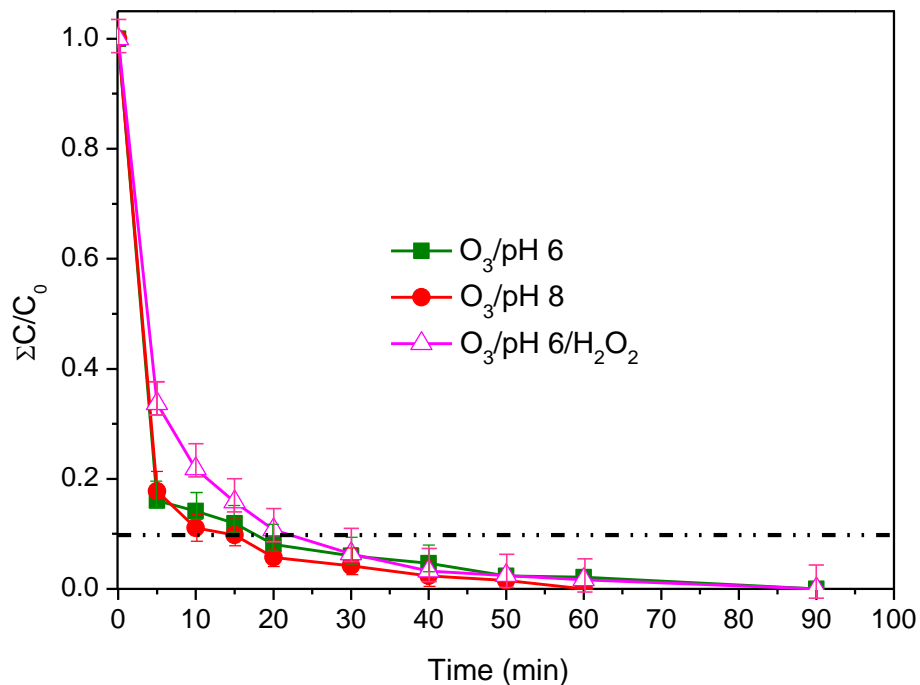
264 SPEF treatment showed less efficiency in MCs removal compared with solar photo-Fenton
265 process. Indeed initial reaction rate, corresponding to the degradation of the sum of MCs,
266 was $77.8 \mu\text{g/L}\cdot\text{min}$ for solar photo-Fenton against $10.6 \mu\text{g/L}\cdot\text{min}$ for SPEF process. Both
267 experiments were carried out in demineralized water though the presence of the electrolyte
268 (Na_2SO_4 50 mM) required for the adequate performance of SPEF provoked lower removal
269 rate in SPEF compared with solar photo-Fenton. Generation of hydroxyl radicals was lower
270 because of (i) the formation of sulfato-Fe(III) complexes and (ii) scavenging of hydroxyl
271 radicals by sulfate and the formation of sulfate radicals which are less reactive than HO
272 radicals. In addition, the absence of an external source of hydrogen peroxide was also
273 responsible of the removal rate slow down and therefore, it must be stated that cathodic
274 electrogeneration of hydrogen peroxide governed MCs removal rate. Using higher amount
275 of hydrogen peroxide, a better performance of the electrochemical cells or advanced
276 concepts and new materials of such cells, could increase SPEF efficiency as H_2O_2
277 production rate is a key issue in this kind of AOPs.

278 *3.1.b. Electro-Fenton process*

279 EF experiments were also carried out in order to evaluate MCs degradation without
280 combining with solar energy. For that purpose, first, pure anodic oxidation (AO) was
281 carried out at 73.6 mA/cm^2 . Afterwards, EF was applied also at 73.6 mA/cm^2 in the
282 presence of Fe^{3+} but testing different concentrations: 0.1, 0.2 and 0.5 mM (Figure 3 and

283 Table 2). In addition, and regarding the current density (j), 30, 73.6 and 100 mA/cm² were
284 tested at Fe³⁺ 0.1 mM. Lowest current density slowed down the generation of hydrogen
285 peroxide, though it also showed the lowest energy consumption (2.2 kWh/m³) for attaining
286 80% degradation of MCs after 150 minutes of EF treatment. This result brought to light the
287 necessity of increasing j in order to improve the ratio between energy consumption and
288 MCs elimination. Nevertheless, when applying the highest j value (100 mA/cm²), EF
289 treatment time was significantly reduced to 60 min due to the larger oxidizing power of the
290 anode and the higher production of hydrogen peroxide that favored the Fenton reaction and
291 consequently, MCs elimination. Nevertheless, that positive result was countered by the
292 important increase detected on the related energy consumption, attaining 6.5 kWh/m³. Best
293 compromise between MCs degradation and energy consumption was obtained when
294 applying j of 73.6 mA/cm², which did not entail a significant increase in current density,
295 compared with 30 mA/cm², but more than 80% degradation after 45 minutes of EF was
296 reached with an energy consumption of 3.45 kWh/m³.

297



298

299 **Figure 3.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by AO and EF (Fe:EDDS, 1:2) at neutral pH
 300 in demineralized water (Na_2SO_4 50 mM in SPEF).

301

302 It must be noticed that an increase in Fe^{3+} concentration from 0.1mM to 0.2 and 0.5 mM at
 303 73.6 mA/cm^2 in the EF treatment always involves an increase in EDDS amount for
 304 maintaining the ratio Fe:EDDS of 1:2. In consequence, a higher concentration of EDDS
 305 would mean also higher organic carbon in solution that would act as radicals' scavenger.
 306 This fact explains the increase on the energy required for attaining 80% of MCs removal
 307 associated to a higher concentration of Fe^{3+} (Figure 3). However, when Fe^{3+} was increased
 308 from 0.2 mM to 0.5 mM, the energy demand was lower than when using Fe^{3+} 0.2 mM,
 309 although still higher than at Fe^{3+} 0.1 mM. At higher Fe^{3+} concentration, dark-Fenton process
 310 was so fast that all hydrogen peroxide generated was consumed rapidly.

311

312 Finally, the AO test at j 73.6 mA/cm² corroborated that higher treatment time and energy
 313 consumption was required compared to EF process with 0.1 mM of Fe³⁺. It should be
 314 highlighted that AO was very effective for Pentachlorophenol, Terbutryn and Diclofenac
 315 removal, but not for the more recalcitrant MC, Chlorofenvinphos (Table 2). AO does not
 316 require iron removal after the treatment, which would simplify electrooxidation operation.

317

318

319

320 **Table 2.** Summary of the results obtained in the electro-oxidation pilot plant to attain 80%
 321 of total MCs degradation at pH 6 by using AO or EF (with Fe:EDDS).

	0.1 mM Fe ³⁺			73.6 mA/cm ²		
	30 mA/cm ²	73.6 mA/cm ²	100 mA/cm ²	AO	0.2 mM Fe ³⁺	0.5 mM Fe ³⁺
Time (min.)	150	45	60	75	120	180
Energy consumption kWh/m³	2.2	3.5	6.5	5.0	12.1	8.1
MCs removal (%)						
Pentachlorophenol	87.8	78.8	91.7	100	89	85.8
Terbutryn	66.2	84.2	79.5	84.1	72.1	68.3
Chlorofenvinphos	58.4	57.4	57.3	46.2	61.5	62.9
Diclofenac	100	97.3	100	100	100	100

322

323 **3.2. Ozonation and solar ozonation systems**

324 3.2.a. Ozonation tests

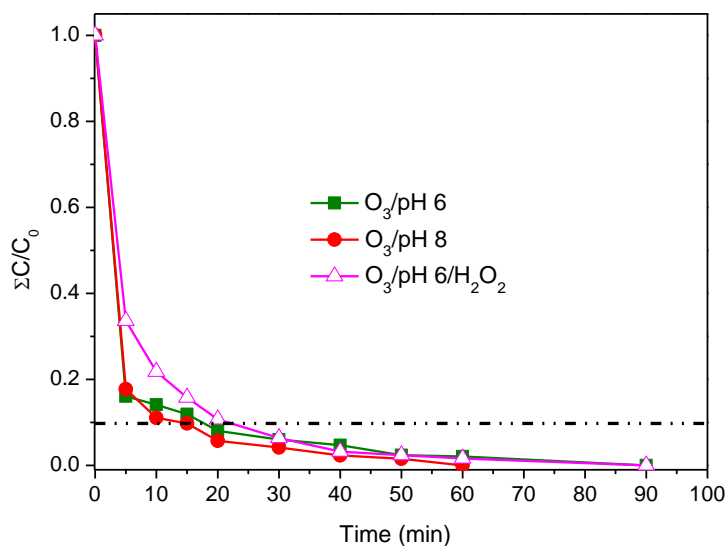
325 Ozonation treatment of the target MCs spiked on different types of water (demineralized
326 water, NW and SE) was performed varying pH from 6 to 11 (direct ozonation and indirect
327 free radical oxidation). Initial concentration of each target MC was maintained in 200 µg/L.
328 The effect assessment on H₂O₂ addition (at 1.5 mM) as well as Fenton like reactions by
329 using Fe²⁺ or Fe³⁺ at 0.1 mM, were also carried out. Same operating conditions were
330 evaluated in combination with solar radiation.

331 Ozonation results in demineralized water at pH 6 and pH 11 showed more than 99%
332 degradation of all contaminants (after 50 minutes of treatment) in both situations. It should
333 be noted that, working at pH 11, ozone consumption was higher (32 mg O₃/L) than when
334 working at lower pH (13 mg O₃/L) due to the reaction of ozone with generated hydroxyl
335 radicals at high pH (Eq. 3). It is important to stress that more oxidizing conditions at pH 11
336 did not entail higher degradation rates due to the low concentration of MCs. Therefore, pH
337 11 was disregarded for further tests as indirect free radical oxidation route showed no
338 substantial interest for this application. Lower pH (around 8) was selected instead as it is a
339 normal value for natural water and wastewater containing MCs.



341 Afterwards, ozonation was tested in NW at pH 6 and 8. An increment of the degradation
342 rate and on the consumption of ozone was observed, 14 mg O₃/L at pH 6 and 19 mg O₃/L at
343 pH 8, for attaining more than 99% of MCs degradation (Figure 4). Substantially lower
344 consumption of ozone was required to degrade 90% of MCs (1.8 mg O₃/L at pH 6 and
345 4.4 mg O₃/L at pH 8). It was clearly observed that higher pH resulted in higher reaction

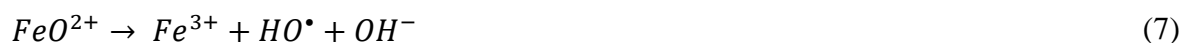
346 rates but accompanied with a higher ozone consumption. Consequently, it should be
 347 remarked that application of ozone treatment for elimination of MCs must be always tested
 348 at pH around 8 (normal pH of natural waters and MWWTP effluents) and not at pH 6.
 349 These results are consistent with ozone application at large scale for treatment of MCs in
 350 Switzerland, where a specific ozone dose of 1.5-2.5 mg/L is required for 80% of MCs
 351 abatement [37]. It is important to highlight that when adding H₂O₂ at natural pH (8), the
 352 consumption of O₃ slightly increased to 5 mg/L to degrade >90% of MCs, without an
 353 improvement on the MCs elimination rate. The reaction of ozone with of H₂O₂ (peroxone
 354 process) rises the generation of •OH radicals [38] but, as in the case of ozonation at pH 11,
 355 it did not provoke a better degradation rate due to the low concentration of MCs and so
 356 ozone reacted with H₂O₂.



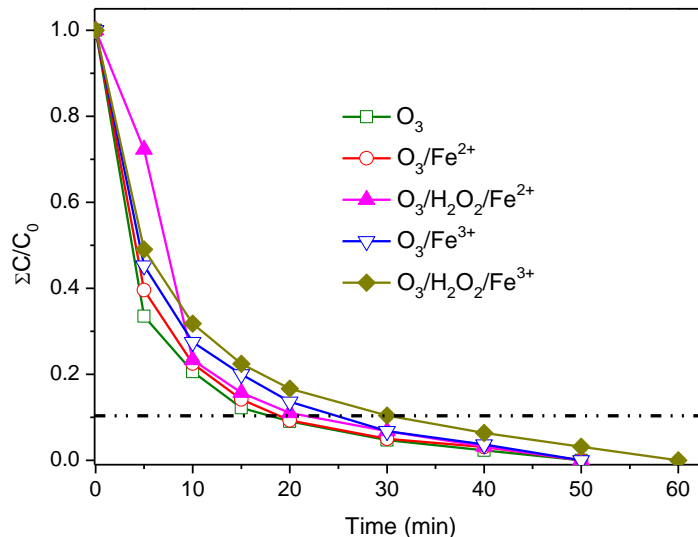
357

358 **Figure 4.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by ozonation in NW at two different pHs and
 359 with addition of H₂O₂ (50 mg/L).

360 After demonstrating the bad performance of ozone at pH 11 for MCs elimination and that
 361 the process was efficient at pH close to the typical pH of MWWTP effluents (pH around 8)
 362 the final objective was to study if any combination between ozonation and Fenton would be
 363 interesting for the enhancement of MCs removal. Figure 5 shows results with SE at natural
 364 pH (8) showing a consumption of ozone of 6.4 mg/L to degrade >90% of MCs. In Figure 5,
 365 the experimental results obtained in the presence of iron with and without its combination
 366 with H₂O₂ are shown. When applying Fe²⁺ or Fe³⁺ (both at 0.1 mM), ozone consumption
 367 was 6.6 and 9.6 mg O₃/L, respectively. Recent studies reported that the co-presence of O₃
 368 and Fenton reagents favored the generation of •OH [39]. Experiments with addition of iron
 369 to the ozonation system have been carried out to evaluate the direct reaction of ozone with
 370 Fe²⁺ and reduction to Fe³⁺ with extra •OH generation according to Eqs. 4-7 [40], but no
 371 improvement was observed in the reaction rate or in the ozone consumption. Initial
 372 degradation rate was 61.7 µg/L.min for ozonation (pH 8), almost equal to those obtained
 373 when Fe²⁺ or Fe³⁺ were added (59.5 µg/L.min and 60.6 µg/L.min, respectively).



374 When testing ozonization in combination with Fenton process (Fe/H₂O₂) both, consumption
 375 of ozone and treatment times, were similar so no significant improvement took place. In
 376 addition, initial degradation rates were 58.6 µg/L.min and 50.2 µg/L.min, when adding
 377 H₂O₂ to Fe²⁺ and Fe³⁺, respectively.



378

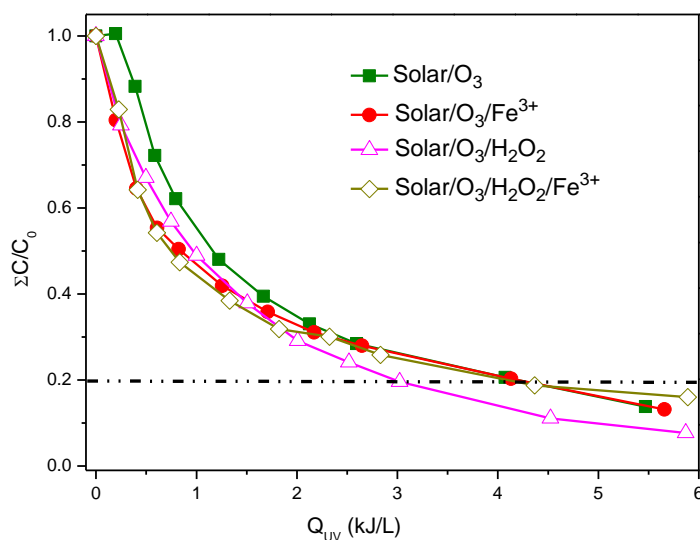
379 **Figure 5.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by ozonation in SE at pH 8 with addition of
 380 Fe^{2+} , Fe^{3+} (0.1 mM) and H_2O_2 (1.5 mM).

381 *3.2.b. Solar ozonation tests*

382 Finally, the combination of ozone with a solar CPC photo-reactor working at natural pH (8)
 383 for the elimination of MCs in SE was performed (figure 6).

384 As it has been previously reported, dissolved ozone molecules absorb UV light with a peak
 385 absorbance at 260 nm and a molar absorptivity of $3292 \pm 70 \text{ M/cm}$ [41]. Upon the irradiation
 386 of UV, the dissolved ozone molecules undergo photolysis reactions to yield hydrogen
 387 peroxide [42]. The application of ozone in the presence of solar radiation led to an
 388 enhancement of MCs removal as lower consumption of ozone was required. Indeed, to
 389 obtain 80% degradation of MCs the consumption of ozone was 0.52 mg/L (O_3), 0.30 mg/L
 390 ($\text{O}_3/\text{Fe}^{3+}$), 0.23 mg/L ($\text{O}_3/\text{H}_2\text{O}_2$) and 0.6 mg/L ($\text{O}_3/\text{Fe}^{3+}/\text{H}_2\text{O}_2$). The so important reduction
 391 in ozone consumption for solar/ O_3 compared with results obtained with ozonation in the
 392 dark was due to a new source of $\bullet\text{OH}$ generated under solar UV ($\lambda < 315 \text{ nm}$) from H_2O_2

393 photolysis as H_2O_2 could be produced by Eq. 8 [43]. The consumption of ozone in
 394 solar/ O_3/H_2O_2 was still low against an enhancement in the reaction rate. In the cases in
 395 which ozone was combined with iron under solar illumination, the contribution of photo-
 396 Fenton process was not clear as both ozone consumption and reaction rate were quite
 397 similar to solar/ O_3 process. It is interesting to remark that during solar treatments, the
 398 temperature in the photo-reactor increased (up to c.a. 40° C). This also favored MCs
 399 elimination since ozone reaction rates increase with temperature [44].



400

401 **Figure 6.** MCs degradation ($\Sigma C_0 \approx 800 \mu\text{g/L}$) by ozonation combined with a CPC photo-
 402 reactor in SE at pH 8 with addition of Fe^{2+} , Fe^{3+} (0.1 mM) and H_2O_2 (50 mg/L).

403 It is important also to stress that initial degradation rate did not improve when combining
 404 ozone with solar radiation, as it decreased to 28.3 $\mu\text{g/L}\cdot\text{min}$. Similar values were obtained
 405 when Fe^{3+} or H_2O_2 were added separately (24.7 $\mu\text{g/L}\cdot\text{min}$ and 24.9 $\mu\text{g/L}\cdot\text{min}$, respectively),

406 or even combining both reagents, giving 30.4 $\mu\text{g/L}\cdot\text{min}$ of initial degradation rate. These
407 results show that the main advantage in combining ozonation with solar radiation lays on
408 the significant reduction on ozone consumption.

409

410 **4. Conclusions**

411 It has been demonstrated that Fe:EDDS complex is able to maintain iron in solution for EF
412 and SPEF treatments and so, it can be considered a useful tool for performing
413 electrochemical processes at circumneutral pH.

414 SPEF treatment showed less efficiency compared with solar photo-Fenton process at
415 circumneutral pH due to the hydroxyl radicals' scavenger effect provoked by the need of
416 adding an electrolyte in wastewater with low ionic strength. SPEF was also less efficient
417 than EF treatment due to a limited electro-generation of H_2O_2 . An improvement on the in-
418 situ production rate of hydrogen peroxide would enhance the SPEF process. A better
419 performance of target MCs elimination was obtained when applying EF with Fe^{3+} at
420 0.1 mM. These results bring to light the interest on EF, SPEF and electro-oxidation
421 processes in general as a suitable technology for MCs removal only when they are
422 contained in specific wastewaters characterized by high conductivity values, such as
423 membrane processes rejection streams.

424 Finally, Ozonation treatment demonstrated to be successful in almost the complete removal
425 of studied MCs present in different water matrices at different pH in dark conditions.
426 However, it is important to stress that higher pH values increased ozone consumption due

427 to the very low concentration of contaminants to be oxidized, and the reaction of generated
428 H₂O₂ with O₃.

429 In general, the removal of MCs does not need the generation of high concentrations of
430 hydroxyl radicals, this is why the combination of ozone with other treatments based on the
431 addition of iron and hydrogen peroxide in the dark did not show an enhancement in the
432 efficiency of the process. Nevertheless, the application of ozone in the presence of solar
433 radiation led to an improvement on the MCs degradation and a reduction on ozone
434 consumption compared with ozonation in the dark. This interesting result must be explored
435 in detail and optimized taking into account economic aspects, such as electricity
436 requirements and the consequent depletion of ozone generation costs.

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