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Title: Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents.

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Keywords: Micropollutants, ozonization, photo-Fenton, photocatalysis, toxicity

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Abstract: Conventional municipal wastewater treatment plants are not able to entirely degrade some organic pollutants that end up in the environment. Within this group of contaminants, Emerging Contaminants are mostly unregulated compounds that may be candidates for future regulation. In this work, different advanced technologies: solar heterogeneous photocatalysis with TiO₂, solar photo-Fenton and ozonation, are studied as tertiary treatments for the remediation of micropollutants present in real municipal wastewater treatment plants effluents at pilot plant scale. Contaminants elimination was followed by Liquid Chromatography/ Quadrupole ion trap Mass Spectrometry analysis after a pre-concentration 100:1 by automatic solid phase extraction. 66 target micropollutants were identified and quantified. 16 of those contaminants at initial concentrations over 1000 ng L⁻¹, made up over 88% of the initial total effluent pollutant load. The order of micropollutants elimination efficiency under the experimental conditions evaluated was solar photo-Fenton > ozonation > solar heterogeneous photocatalysis with TiO₂. Toxicity analyses by *Vibrio fischeri* and respirometric tests showed no significant changes in the effluent toxicity after the three tertiary treatments application. Solar photo-Fenton and ozonation treatments were also compared from an economical point of view.

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48 **1. Introduction**

49 Emerging contaminants (ECs) are mostly unregulated compounds that may be
50 candidates for future regulation depending on research on their potential effects on
51 health, and monitoring data regarding their occurrence (Petrovic et al., (2003); Hansen
52 (2007); Jelic et al., (2011)). ECs do not need to persist in the environment to cause a
53 detrimental effect, because their high transformation/removal rates are compensated by
54 their continuous introduction into the environment. Pharmaceuticals, personal-care
55 products, steroid sex hormones, illicit drugs, flame retardants and perfluorinated
56 compounds, enter the wastewater network after use in households and industry.
57 Moreover, they have been detected in sewage treatment plant influents and effluents in
58 many countries (Lapwortha et al., (2012); Camacho Muñoz et al., (2010); Pal et al.,
59 (2010)). In view of their widespread occurrence and potential impact, ECs must be
60 removed from treated water before discharge or reuse.

61 Conventional municipal wastewater treatment plants are not able to entirely degrade
62 ECs and other pollutants present at $\mu\text{g-ng L}^{-1}$ concentrations (Martinez-Bueno et al.
63 (2007); Escher et al., (2011)). Consequently, they end up in the aquatic environment and
64 may cause ecological risks (Hansen (2007); Pal (2010)), such as feminization of higher
65 organisms, microbiological resistance and finally, accumulation of these contaminants
66 in soil, plants and animals (Bolong et al., (2009)). The effect of these micropollutants in
67 the environment does not only depend on their concentration, but also on other factors,
68 such as their increased lipofility or persistence, bioaccumulation, exposure time and
69 biotransformation and elimination mechanisms. Once in the environment, some
70 substances undergo biotransformation, releasing metabolites or degradation products
71 more harmful than the original compounds (Celiz et al., (2009)).

72 The continuous detection of a wide variety of these compounds in MWTP effluents
73 shows how poor the removal efficiency of commonly applied wastewater treatments is
74 (Bolong et al., (2009)). Consequently, simple advanced technologies which are already
75 at hand are necessary to definitively eliminate these contaminants from water. Activated
76 carbon, nanofiltration, reverse osmosis membranes or air stripping may all be used for
77 their treatment. However, such technologies are only phase-transfer techniques which
78 do not destroy micropollutants. In this sense, advanced oxidation processes (AOPs)
79 have been proposed as tertiary MWTP treatments due to their versatility and ability to
80 increase biodegradability, and detoxify effluent streams containing polar and
81 hydrophilic chemicals. (Nakada et al., (2007); Rosal et al., (2008); Wert et al., (2009)).
82 The main drawback of AOPs is that their operating costs are much higher than
83 conventional treatments due to the high electricity demand of the UV lamps used for
84 them. Therefore, in recent years, the attention of research has focused on AOPs that can
85 be driven by solar radiation (photo-Fenton and heterogeneous catalysis with TiO₂)
86 (Herrmann (2005); Braham et. al., (2009); Malato et al., (2009)). In addition, another
87 important drawback of AOPs is the possible formation of oxidation intermediates more
88 toxic than the parent compounds. This highlights the necessity of performing toxicity
89 and biodegradability analyses during the AOPs application.

90 On the other hand, ozone is well established and widely used, even commercially, as an
91 oxidant for drinking water treatment and disinfection (Von Gunten (2003)), and also for
92 the elimination of organic micropollutants contained in MWTP (Hollender et al.,
93 (2009)). Therefore, its comparison with solar AOPs is of interest. However, it should
94 also be considered that the removal of low pollutant concentrations ($\mu\text{g L}^{-1}$ range) from
95 water containing other organics in the mg L^{-1} range (e.g., MWTP effluents) could
96 involve the use of large amounts of ozone (Stackelberg et al., (2007); Broséus et al.,

97 (2009)). In this technology application, evidence that the formed ozonation by-products
98 are either harmless or easily degradable is also needed (Joss et al.,(2008)).

99 This study compared conventional ozonation and AOPs that can be powered by solar
100 radiation (i.e., light at wavelengths over 300 nm), homogeneous photocatalysis by
101 photo-Fenton and heterogeneous photocatalysis with TiO₂, for the elimination of
102 micropollutants contained in MWTP effluents at pilot plant scale. The efficiency of
103 these three remediation technologies in the elimination of contaminants measured were
104 compared in terms of energy consumed, treatment time and reagent consumption (H₂O₂
105 for photo-Fenton and O₃ for ozonation). A hybrid triple-quadrupole/linear ion trap
106 (QTRAP) was employed for monitoring contaminant removal. Toxicity during each
107 tertiary treatment studied was also assessed.

108 **2. Materials and methods**

109 *2.1. Reagents and wastewater*

110 Real wastewater effluents were taken from the El Ejido MWTP (Almería Province,
111 Spain) designed for 62,300 inhabitants with an inlet flow of 12,500 m³ day⁻¹. Effluents
112 were collected downstream of the MWTP secondary biological treatment and used
113 within the next 4 days. Initial concentrations of the micropollutants detected were
114 different depending on the day collected (40-80 µg L⁻¹) due to the inherent variability of
115 real MWTP effluents. Dissolved organic carbon (DOC), total inorganic carbon (TIC)
116 and chemical oxygen demand (COD) ranges were 13-23, 89-132 and 32-63 mg L⁻¹,
117 respectively. Effluent pH was around 8.

118 All reagents used for chromatographic analyses were HPLC grade. Analytical standards
119 for chromatography analyses were purchased from Sigma-Aldrich.

120 Heterogeneous photocatalytic experiments were carried out using a slurry suspension
121 (20 mg L⁻¹) of Evonik P-25 titanium dioxide (surface area 51-55 m² g⁻¹). Photo-Fenton

122 experiments were performed using iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and reagent-grade
123 hydrogen peroxide (30%, w/v). In both cases, sulphuric acid (supplied by Panreac) was
124 used for carbonate stripping and pH adjustment. For ozonation experiments, pure
125 oxygen was used for ozone generation and N_2 to stop the reaction by removing residual
126 dissolved O_3 present in samples.

127 2.2. Solar photoreactors

128 Solar experiments were performed at the Plataforma Solar de Almería in compound
129 parabolic collector (CPC) solar pilot plants designed for solar photocatalytic
130 applications (Malato et al., (2009)). TiO_2 experiments were performed in a
131 photoreactor comprised of two modules with twelve Pyrex glass tubes (30 mm o.d.,
132 11 L) and mounted on a fixed platform tilted 37° (local latitude). The water flowed
133 (20 L min^{-1}) directly from one module to the other and finally to a 10 L reservoir
134 tank. The total illuminated area is 3 m^2 , the total volume (two modules, reservoir
135 tank, piping and valves) is 35 L (V_T), and the irradiated volume is 22 L (V_i). The
136 temperature was continuously recorded by a temperature probe (Crioterm PT-100
137 3H) inserted in the piping. Photo-Fenton experiments were also performed in a CPC
138 solar pilot-plant with a temperature control system. The reactor consists of a
139 continuously stirred tank, a centrifugal recirculation pump (25 L min^{-1}), collectors
140 and connecting tubing and valves. The solar collector consists of four 1.04 m^2 CPC
141 units (total area 4.16 m^2). The total volume of the reactor is 75 L (V_T) and the total
142 illuminated volume inside the absorber tubes is 44.6 L (V_i). The temperature inside
143 the reactor was kept at 35°C . Solar ultraviolet radiation (UV) was measured by a
144 global UV radiometer (KIPP&ZONEN, model CUV 3). Using Eq.1 and 2,
145 combination of the data from several days' experiments and their comparison with
146 other photocatalytic experiments is possible:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n UV \frac{A_r}{V_T} \quad (1)$$

$$\Delta t_n = t_n - t_{n-1}$$

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T} \quad (2)$$

147

148 where t_n is the experimental time for each sample, UV is the average solar
 149 ultraviolet radiation measured during Δt_n , and t_{30W} is the “normalized illumination
 150 time”. t_{30W} refers to the average solar UV irradiance of 30 W m^{-2} (typical solar UV
 151 power on a perfectly sunny day around noon); A_r is the illuminated area of collectors
 152 (m^2), and $Q_{UV,n}$ is the accumulated energy (per unit of volume, kJ L^{-1}) incident on
 153 the reactor for each sample taken during the experiment.

154 2.3. Ozonation pilot plant

155 The ozonation reactor consists of an ozone generator (TRAILIGAZ Labo 5 LOX,
 156 maximum ozone production 20 g h^{-1}), an ozone analyzer (BMT 964), an oxygen
 157 supply bottle with a pressure controller ($0\text{-}10, \text{ kg cm}^{-2}$), a contact column (1800 mm
 158 high water column, 50 L maximum capacity), and a thermal ozone destructor
 159 (TRAILIGAZ). Ozone generator power was set to 20 W and oxygen flow was
 160 100 L h^{-1} , ensuring a constant supply of O_3 (0.69 g h^{-1}) to the contact column.
 161 During the test, residual ozone was measured at the outlet of the contact column.
 162 0.69 g h^{-1} Ozone supply was selected in order to measure the minimum constant
 163 residual ozone concentration in the outlet until the treatment finished and ozone
 164 concentration clearly increased. During the whole batch mode experiment the
 165 effluent was continuously recirculated for correct mixing at 900 L h^{-1} by a Pan
 166 World Magnetic Pump, model NH-100PX.

167 2.4. Experimental procedure

168 MWTP secondary biological treatment effluents were pre-treated when received
169 with concentrated H₂SO₄ (around 80 mL) in a 500 L tank to lower the pH enough to
170 remove carbonates, which are widely known to be hydroxyl radical scavengers
171 (Pignatello et al., (2006)). Effluents were considered ready for the application of
172 AOPs when the total inorganic carbon (TIC) was below 2 mg L⁻¹ (keeping pH
173 around 6). This procedure was not applied for ozonation experiments.

174 Three types of experiments were performed:

175 i) *Solar heterogeneous photocatalysis with 20 mg L⁻¹ of TiO₂ at an initial pH*
176 *of 6.* The solar pilot plant was filled with 35 L of the MWTP secondary
177 biological treatment effluent after carbonate elimination and mixed with
178 20 mg L⁻¹ of TiO₂ by turbulent recirculation in the dark for 30 minutes.
179 Then the reactor was uncovered and solar photocatalysis began.

180 ii) *Homogeneous photocatalysis by solar photo-Fenton performed at pH 2.8*
181 *with 5 mg L⁻¹ of Fe²⁺ and initial H₂O₂ of 60 mg L⁻¹.* The solar pilot plant
182 was filled with 75 L of MWTP effluent after carbonate elimination and pH
183 was adjusted to 2.8 (by adding H₂SO₄ 2N). After 15 minutes of
184 homogenization, iron salt was added (5 mg L⁻¹ of Fe²⁺ as FeSO₄·7H₂O) and
185 homogenized for another 15 minutes. Then the reactor was uncovered,
186 hydrogen peroxide was added in a single dose of 60 mg L⁻¹, and the process
187 began. Samples were taken every five minutes, and after adjusting the
188 sample pH to 7, the reaction was immediately stopped when residual H₂O₂
189 was removed by adding catalase (2500 U/mg bovine liver, 100 mg L⁻¹)
190 acquired from Fluka Chemie AG (Buchs, Switzerland).

191 iii) *Ozonation treatment at pH 8 (natural pH)*. MWTP effluent was used as
192 received without stripping carbonates or adjusting pH. The column was
193 charged with 50 L of MWTP effluent and the recirculation system was
194 switched on for homogenization. After 15 minutes, the O₃ generator was
195 turned on at 20 W (0.69 g h⁻¹), and the reaction began. Residual O₃ was
196 measured at the outlet to evaluate consumption of ozone and detect the end
197 of treatment.

198 2.5. Toxicity analyses

199 Toxicity was evaluated using two methods (Gutiérrez et al., (2002)) (after sampling
200 pH, adjusting it to 6.5-7.5, and filtering):

- 201 i) A commercial assay marketed as Biofix[®]Lumi-10, which measures the
202 sample's inhibition of the bioluminescence emitted by the marine bacteria
203 *Vibrio fischeri* after a 30-minute contact period compared to a toxicant-free
204 control (2% sodium chloride solution). The reagent is a freeze-dried
205 preparation of a specially selected strain of the marine bacterium *V. fischeri*
206 (*Photobacterium phosphoreum*, NRRL number B-11177).
- 207 ii) A respirometry assay carried out with a BM-T respirometer (SURCIS S.L.,
208 Spain) provided with an oxygen probe (Hamilton), which monitors the
209 sample's effect on the oxygen uptake rate (mg oxygen L⁻¹ h⁻¹) of activated
210 sludge taken from the same MWTP as the effluent water for the
211 experiments. The respirometer was loaded with the required amount of
212 activated sludge (700 mL). Then, continuous aeration and agitation were
213 applied to the respirometer reactor flask at a constant 20°C. To attain the
214 maximum oxygen uptake rate, 0.5 g of sodium acetate per gram of volatile
215 suspended solids (VSS) was added. Then 300 mL of the sample were

216 added. The oxygen uptake rate starts to fall when the toxicity effect is
217 observed. This fall gives the percentage of inhibition by comparing dilution
218 from adding the sample to a reference test (300 mL of demineralised water
219 added to the same activated sludge).

220 *2.6. Analytical equipment and methods*

221 DOC was measured by direct injection of samples filtered with 0.2 µm syringe-driven
222 filters into a Shimadzu 5050A TOC analyzer. During photo-Fenton experiments, total
223 iron concentration was determined with 1,10-phenantroline following ISO 6332; and
224 hydrogen peroxide concentration was measured in a spectrophotometer at 410 nm
225 based on the formation of a yellow complex from the reaction of titanium (IV)
226 oxysulfate with H₂O₂ following DIN 38409 H15.

227 The concentration profile of each compound during degradation was determined by LC-
228 MS analysis. Solid-phase extraction (SPE) was applied using commercial Oasis HLB
229 (divinylbenzene/N-vinylpyrrolidone copolymer) cartridges (200 mg, 6 cm³). The
230 automated sample processor used was an ASPEC GX-271 equipped with a 406 Single
231 Syringe pump and a VALVEMATE® II valve actuator, all supplied by Gilson. The
232 HPLC-QTRAP-MS analytical method for the target compounds (Martinez Bueno et al.,
233 (2007)) was developed for the 3200 QTRAP MS/MS system (Applied Biosystems,
234 Concord, ON, Canada). Separation of the analytes was performed using an HPLC
235 (series 1100, Agilent Technologies) equipped with a reversed-phase C-18 analytical
236 column (Zorbax SB, Agilent Technologies) 250 mm long, and 3.0 mm i.d. The analyses
237 were carried out using a turbo ion spray source in positive and negative modes, and
238 Applied Biosystems/MDS Sciex Analyst software was used for data acquisition and
239 processing.

240

241 3. Results and discussion

242 It is clear that the presence of ECs and other micropollutants at minute concentrations
243 and world concern for environmental risks coincided with the need to develop more
244 sophisticated and less demanding analytical tools for their accurate determination at
245 micro scale (Hogenboom et al., (2009); Richardson (2010)). Liquid chromatography
246 and mass spectrometry, which can analyse polar analites, such as the many organic
247 pollutants, their metabolites and degradation products contained in MWTP effluents,
248 have emerged in recent years as the techniques of choice for this purpose. In this study,
249 MWTP secondary biological treatment effluents taken during two months were
250 analyzed by HPLC-QTRAP-MS. It is important to highlight that 66 target
251 micropollutants were identified and quantified. 16 of those contaminants at initial
252 concentrations over 1000 ng L⁻¹, made up over 88% of the initial total effluent pollutant
253 load (PL, sum of concentration of all contaminants identified). The PL varied depending
254 on the day the effluent was collected although it remained in the 40-80 µg L⁻¹ range. Of
255 these 16, most were pharmaceuticals, such as Ibuprofen, hydrochlorothiazide, atenolol,
256 ofloxacin, trimethoprim, and naproxen. Other groups formed from dipyrone metabolites
257 (N-(3,4-dimethoxycinnamonyl) anthranilic acid⁴ (DAA); 4-methylaminoantipyrine
258 (MAA); 4-formylaminoantipyrine (FAA); and 4-aminoantipyrine (AA); 4-
259 acetylaminoantipyrine (AAA)), pesticides (such as Atrazine, even though now
260 prohibited), metabolites and others, complete the list of 66 contaminants found and
261 quantified. Table 1 shows these 66 micropollutants in the different effluents treated and
262 the range of concentrations found.

263 3.1. Solar heterogeneous photocatalysis with TiO₂

264 Elimination of the 66 contaminants detected in the MWTP secondary biological
265 treatment effluent by solar heterogeneous photocatalysis with TiO₂ was studied.

266 Although, it is widely known that the appropriate catalyst concentration in solar CPC
267 photoreactors for industrial wastewater treatment is several hundred milligrams per litre
268 (Malato et al., (2009)), since the contaminants in MWTP effluents were present at
269 extremely low concentrations, we decided to use a much lower catalyst concentration
270 (Prieto-Rodriguez et al., (2012)). This way, the catalyst is easier to recover and reuse
271 and the addition of high amounts of TiO₂ to relatively clean water already treated in the
272 MWTP is also avoided. Following these criteria, a TiO₂ concentration of 20 mg L⁻¹ was
273 compared with mild solar photo-Fenton and ozonation treatments. In Figure 1, the
274 degradation of 16 contaminants with concentrations over 1000 ng L⁻¹ may be observed,
275 as well as the sum of the rest of contaminants found in MWTP effluents. Contaminant
276 degradation in this photocatalytic process ($Q_{UV} = 200 \text{ kJ L}^{-1}$) was over 85%, although
277 some contaminants such as caffeine and 4-AAA were hardly degraded at all.

278 The starting DOC in the real MWTP effluent after carbonate stripping was 23.2 mg L⁻¹
279 and remained almost constant during the whole photocatalytic treatment. However, this
280 was not within the scope of this study, because DOC in MWTP effluents (excluding
281 micropollutants), which is very often formed by natural organic matter or compounds
282 originating during biological oxidation, is not generally considered harmful.

283 Intermediate contaminants generated during photocatalytic treatment and remaining in
284 the effluent might be thought to cause some changes in toxicity, as mineralization was
285 not complete. However, toxicity analyses performed showed zero inhibition of *V. fischeri*
286 bioluminescence emission or activated sludge oxygen uptake rate.

287 *3.2. Solar photo-Fenton homogeneous photocatalysis*

288 Degradation of contaminants (usually in industrial wastewater) with conventional
289 photo-Fenton (iron in the mM range at pH 2.8 (Pignatello et al., (2006))) is not the best
290 choice for eliminating micropollutants in MWTP effluents at extremely low

291 concentrations, because too much iron would remain in the effluent, impeding its safe
292 reuse. Therefore, in this study, Fe^{2+} was used at a concentration of 5 mg L^{-1} . Even at this
293 low concentration, degradation of the micropollutants (with an H_2O_2 consumption of
294 54 mg L^{-1}) was over 98% in only a few minutes of irradiation. Indeed, 84% of
295 degradation had already been attained with only 15 mg L^{-1} of H_2O_2 (5 mg L^{-1} of Fe^{2+})
296 after just 3 minutes of illumination ($Q_{\text{UV}} = 0.56 \text{ kJ L}^{-1}$). Solar UV/ H_2O_2 control test was
297 not performed as the radiation wavelength transmitted by the solar photoreactor glass
298 tubes is higher than 315 nm and for that values hydroxyl radicals generation by solar
299 radiation/ H_2O_2 system does not occur.

300 Figure 2 shows the degradation of the 16 micropollutants with the highest
301 concentrations, as well as the sum of the rest of micropollutants detected, over the
302 normalized illuminated reaction time (t_{30w}). It may be observed that after 14 minutes of
303 illumination time (2.30 kJ L^{-1}), 98% of contaminants had been eliminated. 90% of
304 micropollutants degradation was attained after 6.8 minutes of illumination time (1 kJ L^{-1})
305 and a consumption of 37.8 mg L^{-1} of H_2O_2). Although MWTP effluent treated by
306 solar photo-Fenton contained a lower PL than the effluent treated by TiO_2 , it was still
307 within the same range (tens of $\mu\text{g L}^{-1}$), and taking into account the important difference
308 in the treatment time, the conclusion can still be considered sufficiently consistent. On
309 the other hand, based on previous experience with application of AOPs to this kind of
310 pollutant elimination, and taking into consideration the type of intermediates that could
311 be generated from micropollutant degradation (Trovó et al., (2009); Radjenovic et al.,
312 (2010)), it should be mentioned that substantial mineralisation was achieved (DOC
313 decreased from 7.5 mg L^{-1} to 4.3 mg L^{-1}). This is reinforced by the qualitative results
314 shown in Figure 1 from the *Supplementary Data*, showing LC-MS chromatograms of
315 the initial and final photo-Fenton samples. These chromatograms show that only

316 insignificant concentrations of micropollutants and their degradation products remained
317 after solar photo-Fenton. This was also demonstrated by toxicity bioassays. The last
318 stage of photo-Fenton treatment showed extremely low (non-toxic) inhibition: <23% for
319 *Vibrio fischeri* and <7% for activated sludge in respirometric analysis, meaning that no
320 significant changes in the MWTP effluent toxicity were detected after this tertiary
321 treatment.

322 3.3. Ozonation treatment

323 MWTP effluents were treated by conventional ozonation as received without carbonate
324 stripping or pH adjustment (natural pH was around 8). Previous publications (Rosal et
325 al., (2010); Rodríguez et al., (2012)) have already reported EC degradation by
326 ozonation, in which 6.2 mg L⁻¹ and 12 mg L⁻¹ of O₃ were used, respectively, to remove
327 some persistent contaminants at higher concentrations (1.5 to 3.6 mg L⁻¹). Figure 4
328 shows the degradation profile of the group of 16 micropollutants as well as the sum of
329 the rest of contaminants found in the MWTP effluent over ozonation reaction time.
330 After a treatment time of 60 minutes and an ozone consumption of 9.5 mg L⁻¹, 98% of
331 the sum of the micropollutant concentration had been degraded, which is quite similar
332 to the amount required in the abovementioned studies for eliminating much higher
333 contaminant concentrations. 90% of micropollutants degradation was achieved after 20
334 minutes of treatment and an ozone consumption of 3.4 mg L⁻¹. In addition, Electrical
335 Energy per Order (EEOs) for the ozonation treatment has been also obtained. 0.8-
336 3.4 kWh m⁻³ corresponding to 0.8-9.5 g O₃ m⁻³. For further economic estimations and
337 according to Hansen et al., (2010), the relation between EEO_{exp} and EEO_{real} (EEO_{real} is
338 0.3 times EEO_{exp}), has been used for large ozone generators at full-scale treatment
339 processes. In any case, O₃ consumption is usually related to oxidation of DOC and not
340 specifically related to the low concentration of micropollutants. As far as mineralisation

341 is concerned, real MWTP effluent DOC before ozonation was 12.6 mg L⁻¹ and was still
342 11.8 mg L⁻¹ after treatment. Micropollutant intermediates were probably formed during
343 the treatment, as neither complete degradation nor mineralisation was attained. This can
344 be observed in the ozonation sample chromatograms in Figure 2 from the
345 *Supplementary Data* at the beginning and after 60 minutes of treatment. The MS signal
346 is also observed to be very low at the end of the treatment, but remarkably higher than
347 after photo-Fenton. Nevertheless, toxicity assays during ozonation showed zero
348 inhibition of *Vibrio fischeri* bioluminescence emissions. On the other hand, 12%
349 inhibition (which is not considered toxic) observed in respirometric assays with
350 conventional activated sludge at the beginning of ozonation, was reduced to 0% at the
351 end of the treatment.

352 *3.4. Treatments comparison*

353 The three tertiary treatments tested, solar heterogeneous photocatalysis with TiO₂, solar
354 photo-Fenton and ozonation, were compared by means of the main operating parameters
355 which must be evaluated when scaling up the technology to real applications. In Table
356 2, treatment time and accumulated solar energy (related to plant size, and therefore,
357 investment costs), reagent consumption (related to operating costs) and the percentage
358 degradation of the sum of contaminant concentrations are summarized.

359 First of all, when the solar photocatalytic treatments are compared, it is quite clear that
360 heterogeneous photocatalysis with TiO₂ is much less efficient than solar photo-Fenton
361 in terms of accumulated energy and illumination time required to remove
362 micropollutants. Considering that the most important investment cost in a solar-driven
363 treatment is the CPC field, which is directly related to the accumulated energy needed
364 for the treatment, photocatalysis with TiO₂ demands by far the larger solar collector

365 field. Therefore, photocatalysis with TiO_2 is not compared to ozonation in the
366 paragraphs below.

367 In a comparison of photo-Fenton with ozonation, it is important to highlight that solar
368 photo-Fenton required 54 mg L^{-1} of H_2O_2 and ozonation 9.5 mg L^{-1} of O_3 for the same
369 percentage of micropollutant degradation (see Table 2). However, it is also quite
370 relevant that only 20 minutes (14 min $t_{30\text{W}}$) were necessary for solar photo-Fenton to
371 remove 98% of the initial micropollutant concentration, while 60 minutes were needed
372 for ozonation.

373 At this point, the economics of these two tertiary treatments, in terms of electricity
374 consumption (and the inherent advantage of using solar energy), operating and
375 investment costs (where the solar CPC field becomes more important), should also be
376 compared.

377 3.5. Brief economic considerations

378 The economics of the solar photo-Fenton and ozonation treatments were also compared.
379 Target economic parameters, such as reagent consumption, labour, electricity, and
380 investment costs were used to roughly estimate the cost of treated water in Euros per
381 m^3 .

382 The target economic parameters were estimated based on a design flow of $5,000 \text{ m}^3\text{day}^{-1}$

383 ¹ and the following operating costs based on the active substances (industrial grade
384 prices): H_2O_2 0.45 € L^{-1} , Fe(II)^{2+} 0.72 € Kg^{-1} , H_2SO_4 0.10 € L^{-1} , NaOH 0.12 € Kg^{-1} ,
385 electricity 0.07 € Kwh^{-1} , O_2 0.15 € Kg^{-1} and labour 18.8 € h^{-1} . According to the data
386 provided by the ozonation system manufacturer, $23.1 \text{ € Kg}^{-1}\text{O}_3$ produced (at 20W of
387 power and with 100 L h^{-1} of oxygen flow supply) was the price assumed in the
388 corresponding operating costs estimation.

389 Table 3 presents the main mild solar photo-Fenton and ozonation operating and
390 investment costs per m^3 of treated water (MWTP effluent) necessary to remove 98% of
391 micropollutants. The economic aspects for a removal percentage over 90% were also
392 considered in order to observe the evolution of both treatment costs at two different
393 stages of the treatment. Notice the low solar photo-Fenton investment cost (0.15 € m^{-3})
394 due to the CPC solar field (in this case $14,000 \text{ m}^2$) against the ozonation one ($0.9\text{-}0.27 \text{ €}$
395 m^{-3}). Regarding reagents consumption, solar photo-Fenton process operating costs
396 includes H_2SO_4 (0.25 L m^{-3} effluent) and NaOH (0.2 g m^{-3} effluent) required for pH
397 adjustments (to 2.8 and 6 before and after the treatment, respectively). Besides,
398 ozonation operating costs ($0.31\text{-}0.290 \text{ € m}^{-3}$) are higher than for solar photo-Fenton
399 (0.208 € m^{-3}) due to the costs of ozone generation (O_2 and electricity). Furthermore, it is
400 also important to highlight that when contaminant removal increases to 98%, the solar
401 photo-Fenton investment cost significantly increases, as the CPC solar field is directly
402 proportional to the accumulated energy required to eliminate the contaminants. In the
403 case of ozonation, it is the reagent and electricity which are affected by the increase in
404 micropollutant elimination and therefore treatment costs are quite similar.

405 ~~As expected, the~~The main difference in the two treatments is the ~~much~~ higher electricity
406 ~~investment~~ costs ~~demande~~d ~~by~~related to ozonation for contaminants degradation
407 ~~percentage~~ similar to solar photo-Fenton process. ~~In addition and as expected,~~
408 ~~differences can be also observed from the electricity costs demanded by ozonation~~
409 ~~compared to solar hoto-Fenton.~~ From this viewpoint and also technically, solar photo-
410 Fenton is very competitive with a commercial treatment for this kind of effluent
411 containing such a low concentration of contaminants.

412 4. Conclusions

- 413 • Three potential tertiary treatments: mild solar photocatalysis with TiO₂, mild
414 solar photo-Fenton, and ozonation, were demonstrated to be able to eliminate
415 micropollutants found in real MWTP effluents at a concentration range of 40 to
416 80 µg L⁻¹ with no change in effluent acute toxicity. Accordingly, chronic
417 toxicity tests must be performed in order to really evaluate micropollutants and
418 possible by-products long-term effect on the environment.
- 419 • Photocatalysis with TiO₂ is very inefficient in terms of treatment time and
420 accumulative energy compared to solar photo-Fenton and ozonation.
- 421 • Both photo-Fenton and ozonation substantially eliminate the contaminants and
422 their degradation products, but ozonation, because it is a milder oxidation
423 process, has a higher MS signal at the end of the treatment, as revealed by
424 HPLC-QTRAP-MS (*Supplementary Data*).
- 425 • Photo-Fenton is economically competitive with ozonation, the investment cost
426 of which (solar CPC field) is offset by the operating cost of ozonation. In this
427 sense, it is important to highlight the effect of the treatment design flow rate on
428 investment costs. If higher design flow rates are considered, solar photo-Fenton
429 investment costs per m³ of water to be treated would decrease (CPCs field costs
430 are lower as higher the plant required m² are), but ozonisation costs (highly
431 affected by operation costs as electricity consumption) would not significantly
432 change.
- 433 • Solar photo-Fenton is a potential tertiary treatment in MWTPs with treatment
434 costs in the range of <0.4 € m⁻³ for eliminating micropollutants and degradation
435 products, which is very competitive with more mature processes.

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561 **Table 1.** List of micropollutants found and quantified by HPLC-QTRAP-MS in MWTP
 562 effluent samples taken on different days. Minimum and maximum concentrations found
 563 during the study are also given.

Micropollutant	ng L ⁻¹	Micropollutant	ng/L	Micropollutant	ng L ⁻¹
4-AA	35-1315-	Codeine	126-999	Nadolol	0-6
4-AAA	1134-12702	Cotinine	162-301	Naproxen	367-2968
4-DAA	0-11	Diazepan	9-68	Nicotine	65-450
4-FAA	4617-5234	Diclofenac	414-1466	Norfloxacin	29-60
4-MAA	243-2824	Diuron	103-1081	Ofloxacin	324-1614
Acetaminophen	0-73	Epoxide Carbm.	0-15	Paraxanthine	5851-17750
Antipyrine	263-545	Erythromycin	41-78	Pravastatin	44-75
Atenolol	386-1235	Famotidine	19-61	Primidone	50-57
Atrazine	35-843	Fenofibric Acid	25-142	Propranolol	16-19
Azithromycin	35-161	Furosemide	213-504	Propyphenazone	0-32
Benzafibrate	44-57	Gemfibrozil	963-2862	Ranitidine	313-726
Biphenylol	0-565	Hydrochlorothiazide	281-1339	Salbutamol	0-81
Bisphenol A	0-3495	Ibuprofen	162-5620	Simazine	3-704
Caffeine	3322-15457	Ifosfamide	0-8	Sotalol	3-12
Carbamazepine	50-114	Indomethacine	47-437	Sulfadiazine	0-36
Cefotaxime	0-985	Isoproturon	37-172	Sulfamethazine	0-236
Chlorfenvinphos	29-522	Ketoprofen	178-428	Sulfamethoxazole	603-780
Chlorophene	0-105	Lincomycin	73-192	Sulfapyridine	72-131
Ciprofloxacin	305-538	Mefenamic Acid	7-18	Sulfathiazole	0-25
Citalopram HBr	17-98	Mepivacaine	10-28	Terbutaline	0-85
Clarithromycin	24-54	Metoprolol	0-21	Trimethoprim	97-1661
Clofibric Acid	3-6	Metronidazole	17-67	Velafaxime	169-539

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565 **Table 2.** Summary of the main operating parameters for achieving over 85%, 98% and
 566 98% micropollutants degradation by solar photocatalysis with TiO₂, solar photo-Fenton
 567 and ozonation, respectively.

	Solar photocatalysis with TiO₂	Solar photo-Fenton	Ozonation
Treatment time, min	475	20	60
Accumulated solar energy, kJ L ⁻¹	212	2.3	-
Reagent Consumption	-	H ₂ O ₂ <u>54 mg L⁻¹</u>	O ₃ 9.5 mg L ⁻¹
PL, µg L ⁻¹	80	<u>Fe(II)</u> 5 mg L ⁻¹	48

Tabla con formato

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590 **Table 3.** Costs of solar photo-Fenton and ozonation tertiary treatments for 90% and
 591 98% elimination of micropollutants.

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	Solar Photo-Fenton		Ozonation	
	90%	98%	90%	98%
	€m^{-3}			
Reagent	0.064	0.148	0.16	0.22
Labour	0.03	0.05	0.05	0.05
Electricity	0.004	0.010	0.035 0.010	0.042 0.020
Investment	0.09	0.15	0.78 0.23	0.90 0.27
Total	0.188	0.358	<u>1.025</u> 0.450	<u>1.212</u> 0.560

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617 **Figures caption**

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619 **Figure. 1.** Degradation profile of 16 contaminants with an initial concentration over
620 1000 ng L⁻¹ and the sum of the rest of contaminants (ΣC) at less than 1000 ng L⁻¹ (1-
621 Bisphenol A; 2-Ibuprofen; 3-Hydrochlorothiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-
622 Diclofenac; 8-Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen;
623 13-4-FAA; 14- ΣC ; 15-4-AAA; 16-Caffeine; 17-Paraxanthine) using solar
624 heterogeneous photocatalysis with TiO₂.

625 **Figure. 2.** Photo-Fenton degradation profile of the same 16 contaminants shown in
626 figure 1 and the sum of the rest of micropollutants (ΣC) at less than 1000 ng L⁻¹. (1-
627 Bisphenol A; 2-Ibuprofen; 3-Hydrochlorothiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-
628 Diclofenac; 8-Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen;
629 13-4-FAA; 14- ΣC ; 15-4-AAA; 16-Caffeine; 17-Paraxanthine).

630 **Figure 3.** Ozonation degradation profile of the same 16 contaminants shown in figure 1
631 and the sum of the rest of micropollutants (ΣC) at less than 1000 ng L⁻¹. (1-Bisphenol A;
632 2-Ibuprofen; 3-Hydrochlorothiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-Diclofenac; 8-
633 Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen; 13-4-FAA; 14-
634 ΣC ; 15-4-AAA; 16-Caffeine; 17-Paraxanthine).

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Highlights

- Solar photo-Fenton as a promising tertiary treatment for MWTP effluents.
- A QTRAP was employed for monitoring micropollutants removal.
- Photocatalysis with TiO₂ is very inefficient compared to solar photo-Fenton.
- Photo-Fenton is economically competitive with ozonation.
- Solar photo-Fenton investment cost is offset by the operating cost of ozonation.

Graphical abstract

In this work, different advanced technologies: solar heterogeneous photocatalysis with TiO₂, solar photo-Fenton and ozonation, are studied as tertiary treatments for the remediation of micropollutants present in real municipal wastewater treatment plants (MWTPs) effluents at pilot plant scale (66 target micropollutants were identified and quantified, in the range of 40-80 µg L⁻¹). The order of micropollutants elimination efficiency under the experimental conditions evaluated was solar photo-Fenton > ozonation > solar heterogeneous photocatalysis with TiO₂. Toxicity analyses by *Vibrio fischeri* and respirometric tests showed no significant changes in the MWTP effluent toxicity after the three tertiary treatments application. Solar photo-Fenton is a very competitive technology with commercial treatments like ozonation, with treatment costs in the range of <0.4 € m⁻³ for eliminating micropollutants and degradation products contained in MWTP effluents.

	Solar photo-Fenton	Ozonation
	€m⁻³	
	98%	98%
Reagent	0.148	0.22
Labour	0.05	0.05
Electricity	0.01	0.020
Investment	0.15	0.27
Total	0.358	0.560

26 **Abstract**

27 Conventional municipal wastewater treatment plants are not able to entirely degrade
28 some organic pollutants that end up in the environment. Within this group of
29 contaminants, Emerging Contaminants are mostly unregulated compounds that may be
30 candidates for future regulation. In this work, different advanced technologies: solar
31 heterogeneous photocatalysis with TiO₂, solar photo-Fenton and ozonation, are studied
32 as tertiary treatments for the remediation of micropollutants present in real municipal
33 wastewater treatment plants effluents at pilot plant scale. Contaminants elimination was
34 followed by Liquid Chromatography/ Quadrupole ion trap Mass Spectrometry analysis
35 after a pre-concentration 100:1 by automatic solid phase extraction. 66 target
36 micropollutants were identified and quantified. 16 of those contaminants at initial
37 concentrations over 1000 ng L⁻¹, made up over 88% of the initial total effluent pollutant
38 load. The order of micropollutants elimination efficiency under the experimental
39 conditions evaluated was solar photo-Fenton > ozonation > solar heterogeneous
40 photocatalysis with TiO₂. Toxicity analyses by *Vibrio fischeri* and respirometric tests
41 showed no significant changes in the effluent toxicity after the three tertiary treatments
42 application. Solar photo-Fenton and ozonation treatments were also compared from an
43 economical point of view.

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47 **Keywords:** Micropollutants, ozonization, photo-Fenton, photocatalysis, toxicity.

48 **1. Introduction**

49 Emerging contaminants (ECs) are mostly unregulated compounds that may be
50 candidates for future regulation depending on research on their potential effects on
51 health, and monitoring data regarding their occurrence (Petrovic et al., (2003); Hansen
52 (2007); Jelic et al., (2011)). ECs do not need to persist in the environment to cause a
53 detrimental effect, because their high transformation/removal rates are compensated by
54 their continuous introduction into the environment. Pharmaceuticals, personal-care
55 products, steroid sex hormones, illicit drugs, flame retardants and perfluorinated
56 compounds, enter the wastewater network after use in households and industry.
57 Moreover, they have been detected in sewage treatment plant influents and effluents in
58 many countries (Lapworth et al., (2012); Camacho Muñoz et al., (2010); Pal et al.,
59 (2010)). In view of their widespread occurrence and potential impact, ECs must be
60 removed from treated water before discharge or reuse.

61 Conventional municipal wastewater treatment plants are not able to entirely degrade
62 ECs and other pollutants present at $\mu\text{g-ng L}^{-1}$ concentrations (Martinez-Bueno et al.
63 (2007); Escher et al., (2011)). Consequently, they end up in the aquatic environment and
64 may cause ecological risks (Hansen (2007); Pal (2010)), such as feminization of higher
65 organisms, microbiological resistance and finally, accumulation of these contaminants
66 in soil, plants and animals (Bolong et al., (2009)). The effect of these micropollutants in
67 the environment does not only depend on their concentration, but also on other factors,
68 such as their increased lipofility or persistence, bioaccumulation, exposure time and
69 biotransformation and elimination mechanisms. Once in the environment, some
70 substances undergo biotransformation, releasing metabolites or degradation products
71 more harmful than the original compounds (Celiz et al., (2009)).

72 The continuous detection of a wide variety of these compounds in MWTP effluents
73 shows how poor the removal efficiency of commonly applied wastewater treatments is
74 (Bolong et al., (2009)). Consequently, simple advanced technologies which are already
75 at hand are necessary to definitively eliminate these contaminants from water. Activated
76 carbon, nanofiltration, reverse osmosis membranes or air stripping may all be used for
77 their treatment. However, such technologies are only phase-transfer techniques which
78 do not destroy micropollutants. In this sense, advanced oxidation processes (AOPs)
79 have been proposed as tertiary MWTP treatments due to their versatility and ability to
80 increase biodegradability, and detoxify effluent streams containing polar and
81 hydrophilic chemicals. (Nakada et al., (2007); Rosal et al., (2008); Wert et al., (2009)).
82 The main drawback of AOPs is that their operating costs are much higher than
83 conventional treatments due to the high electricity demand of the UV lamps used for
84 them. Therefore, in recent years, the attention of research has focused on AOPs that can
85 be driven by solar radiation (photo-Fenton and heterogeneous catalysis with TiO_2)
86 (Herrmann (2005); Braham et. al., (2009); Malato et al., (2009)). In addition, another
87 important drawback of AOPs is the possible formation of oxidation intermediates more
88 toxic than the parent compounds. This highlights the necessity of performing toxicity
89 and biodegradability analyses during the AOPs application.

90 On the other hand, ozone is well established and widely used, even commercially, as an
91 oxidant for drinking water treatment and disinfection (Von Gunten (2003)), and also for
92 the elimination of organic micropollutants contained in MWTP (Hollender et al.,
93 (2009)). Therefore, its comparison with solar AOPs is of interest. However, it should
94 also be considered that the removal of low pollutant concentrations ($\mu\text{g L}^{-1}$ range) from
95 water containing other organics in the mg L^{-1} range (e.g., MWTP effluents) could
96 involve the use of large amounts of ozone (Stackelberg et al., (2007); Broséus et al.,

97 (2009)). In this technology application, evidence that the formed ozonation by-products
98 are either harmless or easily degradable is also needed (Joss et al.,(2008)).

99 This study compared conventional ozonation and AOPs that can be powered by solar
100 radiation (i.e., light at wavelengths over 300 nm), homogeneous photocatalysis by
101 photo-Fenton and heterogeneous photocatalysis with TiO₂, for the elimination of
102 micropollutants contained in MWTP effluents at pilot plant scale. The efficiency of
103 these three remediation technologies in the elimination of contaminants measured were
104 compared in terms of energy consumed, treatment time and reagent consumption (H₂O₂
105 for photo-Fenton and O₃ for ozonation). A hybrid triple-quadrupole/linear ion trap
106 (QTRAP) was employed for monitoring contaminant removal. Toxicity during each
107 tertiary treatment studied was also assessed.

108 **2. Materials and methods**

109 *2.1. Reagents and wastewater*

110 Real wastewater effluents were taken from the El Ejido MWTP (Almería Province,
111 Spain) designed for 62,300 inhabitants with an inlet flow of 12,500 m³ day⁻¹. Effluents
112 were collected downstream of the MWTP secondary biological treatment and used
113 within the next 4 days. Initial concentrations of the micropollutants detected were
114 different depending on the day collected (40-80 µg L⁻¹) due to the inherent variability of
115 real MWTP effluents. Dissolved organic carbon (DOC), total inorganic carbon (TIC)
116 and chemical oxygen demand (COD) ranges were 13-23, 89-132 and 32-63 mg L⁻¹,
117 respectively. Effluent pH was around 8.

118 All reagents used for chromatographic analyses were HPLC grade. Analytical standards
119 for chromatography analyses were purchased from Sigma-Aldrich.

120 Heterogeneous photocatalytic experiments were carried out using a slurry suspension
121 (20 mg L⁻¹) of Evonik P-25 titanium dioxide (surface area 51-55 m² g⁻¹). Photo-Fenton

122 experiments were performed using iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and reagent-grade
123 hydrogen peroxide (30%, w/v). In both cases, sulphuric acid (supplied by Panreac) was
124 used for carbonate stripping and pH adjustment. For ozonation experiments, pure
125 oxygen was used for ozone generation and N_2 to stop the reaction by removing residual
126 dissolved O_3 present in samples.

127 2.2. *Solar photoreactors*

128 Solar experiments were performed at the Plataforma Solar de Almería in compound
129 parabolic collector (CPC) solar pilot plants designed for solar photocatalytic
130 applications (Malato et al., (2009)). TiO_2 experiments were performed in a
131 photoreactor comprised of two modules with twelve Pyrex glass tubes (30 mm o.d.,
132 11 L) and mounted on a fixed platform tilted 37° (local latitude). The water flowed
133 (20 L min^{-1}) directly from one module to the other and finally to a 10 L reservoir
134 tank. The total illuminated area is 3 m^2 , the total volume (two modules, reservoir
135 tank, piping and valves) is 35 L (V_T), and the irradiated volume is 22 L (V_i). The
136 temperature was continuously recorded by a temperature probe (Crioterm PT-100
137 3H) inserted in the piping. Photo-Fenton experiments were also performed in a CPC
138 solar pilot-plant with a temperature control system. The reactor consists of a
139 continuously stirred tank, a centrifugal recirculation pump (25 L min^{-1}), collectors
140 and connecting tubing and valves. The solar collector consists of four 1.04 m^2 CPC
141 units (total area 4.16 m^2). The total volume of the reactor is 75 L (V_T) and the total
142 illuminated volume inside the absorber tubes is 44.6 L (V_i). The temperature inside
143 the reactor was kept at 35°C . Solar ultraviolet radiation (UV) was measured by a
144 global UV radiometer (KIPP&ZONEN, model CUV 3). Using Eq.1 and 2,
145 combination of the data from several days' experiments and their comparison with
146 other photocatalytic experiments is possible:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n UV \frac{A_r}{V_T} \quad (1)$$

$$\Delta t_n = t_n - t_{n-1}$$

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T} \quad (2)$$

147

148 where t_n is the experimental time for each sample, UV is the average solar
 149 ultraviolet radiation measured during Δt_n , and t_{30W} is the “normalized illumination
 150 time”. t_{30W} refers to the average solar UV irradiance of 30 W m^{-2} (typical solar UV
 151 power on a perfectly sunny day around noon); A_r is the illuminated area of collectors
 152 (m^2), and $Q_{UV,n}$ is the accumulated energy (per unit of volume, kJ L^{-1}) incident on
 153 the reactor for each sample taken during the experiment.

154 2.3. Ozonation pilot plant

155 The ozonation reactor consists of an ozone generator (TRAILIGAZ Labo 5 LOX,
 156 maximum ozone production 20 g h^{-1}), an ozone analyzer (BMT 964), an oxygen
 157 supply bottle with a pressure controller ($0\text{-}10, \text{ kg cm}^{-2}$), a contact column (1800 mm
 158 high water column, 50 L maximum capacity), and a thermal ozone destructor
 159 (TRAILIGAZ). Ozone generator power was set to 20 W and oxygen flow was
 160 100 L h^{-1} , ensuring a constant supply of O_3 (0.69 g h^{-1}) to the contact column.
 161 During the test, residual ozone was measured at the outlet of the contact column.
 162 0.69 g h^{-1} Ozone supply was selected in order to measure the minimum constant
 163 residual ozone concentration in the outlet until the treatment finished and ozone
 164 concentration clearly increased. During the whole batch mode experiment the
 165 effluent was continuously recirculated for correct mixing at 900 L h^{-1} by a Pan
 166 World Magnetic Pump, model NH-100PX.

167 2.4. Experimental procedure

168 MWTP secondary biological treatment effluents were pre-treated when received
169 with concentrated H₂SO₄ (around 80 mL) in a 500 L tank to lower the pH enough to
170 remove carbonates, which are widely known to be hydroxyl radical scavengers
171 (Pignatello et al., (2006)). Effluents were considered ready for the application of
172 AOPs when the total inorganic carbon (TIC) was below 2 mg L⁻¹ (keeping pH
173 around 6). This procedure was not applied for ozonation experiments.

174 Three types of experiments were performed:

175 i) *Solar heterogeneous photocatalysis with 20 mg L⁻¹ of TiO₂ at an initial pH*
176 *of 6.* The solar pilot plant was filled with 35 L of the MWTP secondary
177 biological treatment effluent after carbonate elimination and mixed with
178 20 mg L⁻¹ of TiO₂ by turbulent recirculation in the dark for 30 minutes.
179 Then the reactor was uncovered and solar photocatalysis began.

180 ii) *Homogeneous photocatalysis by solar photo-Fenton performed at pH 2.8*
181 *with 5 mg L⁻¹ of Fe²⁺ and initial H₂O₂ of 60 mg L⁻¹.* The solar pilot plant
182 was filled with 75 L of MWTP effluent after carbonate elimination and pH
183 was adjusted to 2.8 (by adding H₂SO₄ 2N). After 15 minutes of
184 homogenization, iron salt was added (5 mg L⁻¹ of Fe²⁺ as FeSO₄·7H₂O) and
185 homogenized for another 15 minutes. Then the reactor was uncovered,
186 hydrogen peroxide was added in a single dose of 60 mg L⁻¹, and the process
187 began. Samples were taken every five minutes, and after adjusting the
188 sample pH to 7, the reaction was immediately stopped when residual H₂O₂
189 was removed by adding catalase (2500 U/mg bovine liver, 100 mg L⁻¹)
190 acquired from Fluka Chemie AG (Buchs, Switzerland).

191 iii) *Ozonation treatment at pH 8 (natural pH)*. MWTP effluent was used as
192 received without stripping carbonates or adjusting pH. The column was
193 charged with 50 L of MWTP effluent and the recirculation system was
194 switched on for homogenization. After 15 minutes, the O₃ generator was
195 turned on at 20 W (0.69 g h⁻¹), and the reaction began. Residual O₃ was
196 measured at the outlet to evaluate consumption of ozone and detect the end
197 of treatment.

198 2.5. Toxicity analyses

199 Toxicity was evaluated using two methods (Gutiérrez et al., (2002)) (after sampling
200 pH, adjusting it to 6.5-7.5, and filtering):

201 i) A commercial assay marketed as Biofix[®]Lumi-10, which measures the
202 sample's inhibition of the bioluminescence emitted by the marine bacteria
203 *Vibrio fischeri* after a 30-minute contact period compared to a toxicant-free
204 control (2% sodium chloride solution). The reagent is a freeze-dried
205 preparation of a specially selected strain of the marine bacterium *V. fischeri*
206 (Photobacterium phosphoreum, NRRL number B-11177).

207 ii) A respirometry assay carried out with a BM-T respirometer (SURCIS S.L.,
208 Spain) provided with an oxygen probe (Hamilton), which monitors the
209 sample's effect on the oxygen uptake rate (mg oxygen L⁻¹ h⁻¹) of activated
210 sludge taken from the same MWTP as the effluent water for the
211 experiments. The respirometer was loaded with the required amount of
212 activated sludge (700 mL). Then, continuous aeration and agitation were
213 applied to the respirometer reactor flask at a constant 20°C. To attain the
214 maximum oxygen uptake rate, 0.5 g of sodium acetate per gram of volatile
215 suspended solids (VSS) was added. Then 300 mL of the sample were

216 added. The oxygen uptake rate starts to fall when the toxicity effect is
217 observed. This fall gives the percentage of inhibition by comparing dilution
218 from adding the sample to a reference test (300 mL of demineralised water
219 added to the same activated sludge).

220 *2.6. Analytical equipment and methods*

221 DOC was measured by direct injection of samples filtered with 0.2 µm syringe-driven
222 filters into a Shimadzu 5050A TOC analyzer. During photo-Fenton experiments, total
223 iron concentration was determined with 1,10-phenantroline following ISO 6332; and
224 hydrogen peroxide concentration was measured in a spectrophotometer at 410 nm
225 based on the formation of a yellow complex from the reaction of titanium (IV)
226 oxysulfate with H₂O₂ following DIN 38409 H15.

227 The concentration profile of each compound during degradation was determined by LC-
228 MS analysis. Solid-phase extraction (SPE) was applied using commercial Oasis HLB
229 (divinylbenzene/N-vinylpyrrolidone copolymer) cartridges (200 mg, 6 cm³). The
230 automated sample processor used was an ASPEC GX-271 equipped with a 406 Single
231 Syringe pump and a VALVEMATE® II valve actuator, all supplied by Gilson. The
232 HPLC-QTRAP-MS analytical method for the target compounds (Martinez Bueno et al.,
233 (2007)) was developed for the 3200 QTRAP MS/MS system (Applied Biosystems,
234 Concord, ON, Canada). Separation of the analytes was performed using an HPLC
235 (series 1100, Agilent Technologies) equipped with a reversed-phase C-18 analytical
236 column (Zorbax SB, Agilent Technologies) 250 mm long, and 3.0 mm i.d. The analyses
237 were carried out using a turbo ion spray source in positive and negative modes, and
238 Applied Biosystems/MDS Sciex Analyst software was used for data acquisition and
239 processing.

240

241 **3. Results and discussion**

242 It is clear that the presence of ECs and other micropollutants at minute concentrations
243 and world concern for environmental risks coincided with the need to develop more
244 sophisticated and less demanding analytical tools for their accurate determination at
245 micro scale (Hogenboom et al., (2009); Richardson (2010)). Liquid chromatography
246 and mass spectrometry, which can analyse polar analites, such as the many organic
247 pollutants, their metabolites and degradation products contained in MWTP effluents,
248 have emerged in recent years as the techniques of choice for this purpose. In this study,
249 MWTP secondary biological treatment effluents taken during two months were
250 analyzed by HPLC-QTRAP-MS. It is important to highlight that 66 target
251 micropollutants were identified and quantified. 16 of those contaminants at initial
252 concentrations over 1000 ng L⁻¹, made up over 88% of the initial total effluent pollutant
253 load (PL, sum of concentration of all contaminants identified). The PL varied depending
254 on the day the effluent was collected although it remained in the 40-80 µg L⁻¹ range. Of
255 these 16, most were pharmaceuticals, such as Ibuprofen, hydrochlorothiazide, atenolol,
256 ofloxacin, trimethoprim, and naproxen. Other groups formed from dipyrone metabolites
257 (N-(3,4-dimethoxycinnamonyl) anthranilic acid⁴ (DAA); 4-methylaminoantipyrine
258 (MAA); 4-formylaminoantipyrine (FAA); and 4-aminoantipyrine (AA); 4-
259 acetylaminoantipyrine (AAA)), pesticides (such as Atrazine, even though now
260 prohibited), metabolites and others, complete the list of 66 contaminants found and
261 quantified. Table 1 shows these 66 micropollutants in the different effluents treated and
262 the range of concentrations found.

263 *3.1. Solar heterogeneous photocatalysis with TiO₂*

264 Elimination of the 66 contaminants detected in the MWTP secondary biological
265 treatment effluent by solar heterogeneous photocatalysis with TiO₂ was studied.

266 Although, it is widely known that the appropriate catalyst concentration in solar CPC
267 photoreactors for industrial wastewater treatment is several hundred milligrams per litre
268 (Malato et al., (2009)), since the contaminants in MWTP effluents were present at
269 extremely low concentrations, we decided to use a much lower catalyst concentration
270 (Prieto-Rodriguez et al., (2012)). This way, the catalyst is easier to recover and reuse
271 and the addition of high amounts of TiO₂ to relatively clean water already treated in the
272 MWTP is also avoided. Following these criteria, a TiO₂ concentration of 20 mg L⁻¹ was
273 compared with mild solar photo-Fenton and ozonation treatments. In Figure 1, the
274 degradation of 16 contaminants with concentrations over 1000 ng L⁻¹ may be observed,
275 as well as the sum of the rest of contaminants found in MWTP effluents. Contaminant
276 degradation in this photocatalytic process ($Q_{UV} = 200 \text{ kJ L}^{-1}$) was over 85%, although
277 some contaminants such as caffeine and 4-AAA were hardly degraded at all.
278 The starting DOC in the real MWTP effluent after carbonate stripping was 23.2 mg L⁻¹
279 and remained almost constant during the whole photocatalytic treatment. However, this
280 was not within the scope of this study, because DOC in MWTP effluents (excluding
281 micropollutants), which is very often formed by natural organic matter or compounds
282 originating during biological oxidation, is not generally considered harmful.
283 Intermediate contaminants generated during photocatalytic treatment and remaining in
284 the effluent might be thought to cause some changes in toxicity, as mineralization was
285 not complete. However, toxicity analyses performed showed zero inhibition of *V. fischeri*
286 bioluminescence emission or activated sludge oxygen uptake rate.

287 3.2. Solar photo-Fenton homogeneous photocatalysis

288 Degradation of contaminants (usually in industrial wastewater) with conventional
289 photo-Fenton (iron in the mM range at pH 2.8 (Pignatello et al., (2006))) is not the best
290 choice for eliminating micropollutants in MWTP effluents at extremely low

291 concentrations, because too much iron would remain in the effluent, impeding its safe
292 reuse. Therefore, in this study, Fe^{2+} was used at a concentration of 5 mg L^{-1} . Even at this
293 low concentration, degradation of the micropollutants (with an H_2O_2 consumption of
294 54 mg L^{-1}) was over 98% in only a few minutes of irradiation. Indeed, 84% of
295 degradation had already been attained with only 15 mg L^{-1} of H_2O_2 (5 mg L^{-1} of Fe^{2+})
296 after just 3 minutes of illumination ($Q_{\text{UV}} = 0.56 \text{ kJ L}^{-1}$). Solar UV/ H_2O_2 control test was
297 not performed as the radiation wavelength transmitted by the solar photoreactor glass
298 tubes is higher than 315 nm and for that values hydroxyl radicals generation by solar
299 radiation/ H_2O_2 system does not occur.

300 Figure 2 shows the degradation of the 16 micropollutants with the highest
301 concentrations, as well as the sum of the rest of micropollutants detected, over the
302 normalized illuminated reaction time (t_{30w}). It may be observed that after 14 minutes of
303 illumination time (2.30 kJ L^{-1}), 98% of contaminants had been eliminated. 90% of
304 micropollutants degradation was attained after 6.8 minutes of illumination time (1 kJ L^{-1})
305 and a consumption of 37.8 mg L^{-1} of H_2O_2 . Although MWTP effluent treated by solar
306 photo-Fenton contained a lower PL than the effluent treated by TiO_2 , it was still within
307 the same range (tens of $\mu\text{g L}^{-1}$), and taking into account the important difference in the
308 treatment time, the conclusion can still be considered sufficiently consistent. On the
309 other hand, based on previous experience with application of AOPs to this kind of
310 pollutant elimination, and taking into consideration the type of intermediates that could
311 be generated from micropollutant degradation (Trovó et al., (2009); Radjenovic et al.,
312 (2010)), it should be mentioned that substantial mineralisation was achieved (DOC
313 decreased from 7.5 mg L^{-1} to 4.3 mg L^{-1}). This is reinforced by the qualitative results
314 shown in Figure 1 from the *Supplementary Data*, showing LC-MS chromatograms of
315 the initial and final photo-Fenton samples. These chromatograms show that only

316 insignificant concentrations of micropollutants and their degradation products remained
317 after solar photo-Fenton. This was also demonstrated by toxicity bioassays. The last
318 stage of photo-Fenton treatment showed extremely low (non-toxic) inhibition: <23% for
319 *Vibrio fischeri* and <7% for activated sludge in respirometric analysis, meaning that no
320 significant changes in the MWTP effluent toxicity were detected after this tertiary
321 treatment.

322 3.3. Ozonation treatment

323 MWTP effluents were treated by conventional ozonation as received without carbonate
324 stripping or pH adjustment (natural pH was around 8). Previous publications (Rosal et
325 al., (2010); Rodríguez et al., (2012)) have already reported EC degradation by
326 ozonation, in which 6.2 mg L⁻¹ and 12 mg L⁻¹ of O₃ were used, respectively, to remove
327 some persistent contaminants at higher concentrations (1.5 to 3.6 mg L⁻¹). Figure 4
328 shows the degradation profile of the group of 16 micropollutants as well as the sum of
329 the rest of contaminants found in the MWTP effluent over ozonation reaction time.
330 After a treatment time of 60 minutes and an ozone consumption of 9.5 mg L⁻¹, 98% of
331 the sum of the micropollutant concentration had been degraded, which is quite similar
332 to the amount required in the abovementioned studies for eliminating much higher
333 contaminant concentrations. 90% of micropollutants degradation was achieved after 20
334 minutes of treatment and an ozone consumption of 3.4 mg L⁻¹. In addition, Electrical
335 Energy per Order (EEOs) for the ozonation treatment has been also obtained. 0.8-
336 3.4 kWh m⁻³ corresponding to 0.8-9.5 g O₃ m⁻³. For further economic estimations and
337 according to Hansen et al., (2010), the relation between EEO_{exp} and EEO_{real} (EEO_{real} is
338 0.3 times EEO_{exp}), has been used for large ozone generators at full-scale treatment
339 processes. In any case, O₃ consumption is usually related to oxidation of DOC and not
340 specifically related to the low concentration of micropollutants. As far as mineralisation

341 is concerned, real MWTP effluent DOC before ozonation was 12.6 mg L⁻¹ and was still
342 11.8 mg L⁻¹ after treatment. Micropollutant intermediates were probably formed during
343 the treatment, as neither complete degradation nor mineralisation was attained. This can
344 be observed in the ozonation sample chromatograms in Figure 2 from the
345 *Supplementary Data* at the beginning and after 60 minutes of treatment. The MS signal
346 is also observed to be very low at the end of the treatment, but remarkably higher than
347 after photo-Fenton. Nevertheless, toxicity assays during ozonation showed zero
348 inhibition of *Vibrio fischeri* bioluminescence emissions. On the other hand, 12%
349 inhibition (which is not considered toxic) observed in respirometric assays with
350 conventional activated sludge at the beginning of ozonation, was reduced to 0% at the
351 end of the treatment.

352 *3.4. Treatments comparison*

353 The three tertiary treatments tested, solar heterogeneous photocatalysis with TiO₂, solar
354 photo-Fenton and ozonation, were compared by means of the main operating parameters
355 which must be evaluated when scaling up the technology to real applications. In Table
356 2, treatment time and accumulated solar energy (related to plant size, and therefore,
357 investment costs), reagent consumption (related to operating costs) and the percentage
358 degradation of the sum of contaminant concentrations are summarized.

359 First of all, when the solar photocatalytic treatments are compared, it is quite clear that
360 heterogeneous photocatalysis with TiO₂ is much less efficient than solar photo-Fenton
361 in terms of accumulated energy and illumination time required to remove
362 micropollutants. Considering that the most important investment cost in a solar-driven
363 treatment is the CPC field, which is directly related to the accumulated energy needed
364 for the treatment, photocatalysis with TiO₂ demands by far the larger solar collector

365 field. Therefore, photocatalysis with TiO_2 is not compared to ozonation in the
366 paragraphs below.

367 In a comparison of photo-Fenton with ozonation, it is important to highlight that solar
368 photo-Fenton required 54 mg L^{-1} of H_2O_2 and ozonation 9.5 mg L^{-1} of O_3 for the same
369 percentage of micropollutant degradation (see Table 2). However, it is also quite
370 relevant that only 20 minutes (14 min $t_{30\text{W}}$) were necessary for solar photo-Fenton to
371 remove 98% of the initial micropollutant concentration, while 60 minutes were needed
372 for ozonation.

373 At this point, the economics of these two tertiary treatments, in terms of electricity
374 consumption (and the inherent advantage of using solar energy), operating and
375 investment costs (where the solar CPC field becomes more important), should also be
376 compared.

377 *3.5. Brief economic considerations*

378 The economics of the solar photo-Fenton and ozonation treatments were also compared.
379 Target economic parameters, such as reagent consumption, labour, electricity, and
380 investment costs were used to roughly estimate the cost of treated water in Euros per
381 m^3 .

382 The target economic parameters were estimated based on a design flow of $5,000 \text{ m}^3 \text{ day}^{-1}$
383 and the following operating costs based on the active substances (industrial grade
384 prizes): H_2O_2 0.45 € L^{-1} , Fe(II) 0.72 € Kg^{-1} , H_2SO_4 0.10 € L^{-1} , NaOH 0.12 € Kg^{-1} ,
385 electricity 0.07 € Kwh^{-1} , O_2 0.15 € Kg^{-1} and labour 18.8 € h^{-1} . According to the data
386 provided by the ozonation system manufacturer, $23.1 \text{ € Kg}^{-1} \text{O}_3$ produced (at 20W of
387 power and with 100 L h^{-1} of oxygen flow supply) was the price assumed in the
388 corresponding operating costs estimation. Table 3 presents the main mild solar photo-
389 Fenton and ozonation operating and investment costs per m^3 of treated water (MWTP

390 effluent) necessary to remove 98% of micropollutants. The economic aspects for a
391 removal percentage over 90% were also considered in order to observe the evolution of
392 both treatment costs at two different stages of the treatment. Notice the low solar photo-
393 Fenton investment cost (0.15 € m⁻³) due to the CPC solar field (in this case 14,000 m²)
394 against the ozonation one (0.0.27 € m⁻³). Regarding reagents consumption, solar photo-
395 Fenton process operating costs includes H₂SO₄ (0.25 L m⁻³ effluent) and NaOH (0.2 g
396 m⁻³ effluent) required for pH adjustments (to 2.8 and 6 before and after the treatment,
397 respectively). Besides, ozonation operating costs (0.290 € m⁻³) are higher than for solar
398 photo-Fenton (0.208 € m⁻³) due to the costs of ozone generation (O₂ and electricity).
399 Furthermore, it is also important to highlight that when contaminant removal increases
400 to 98%, the solar photo-Fenton investment cost significantly increases, as the CPC solar
401 field is directly proportional to the accumulated energy required to eliminate the
402 contaminants. In the case of ozonation, it is the reagent and electricity which are
403 affected by the increase in micropollutant elimination and therefore treatment costs are
404 quite similar.

405 The main difference in the two treatments is the higher investment costs related to
406 ozonation for contaminants degradation percentage similar to solar photo-Fenton
407 process. In addition and as expected, differences can be also observed from the
408 electricity costs demanded by ozonation compared to solar hoto-Fenton. From this
409 viewpoint and also technically, solar photo-Fenton is very competitive with a
410 commercial treatment for this kind of effluent containing such a low concentration of
411 contaminants.

412 **4. Conclusions**

- 413 • Three potential tertiary treatments: mild solar photocatalysis with TiO₂, mild
414 solar photo-Fenton, and ozonation, were demonstrated to be able to eliminate

415 micropollutants found in real MWTP effluents at a concentration range of 40 to
416 80 $\mu\text{g L}^{-1}$ with no change in effluent acute toxicity. Accordingly, chronic
417 toxicity tests must be performed in order to really evaluate micropollutants and
418 possible by-products long-term effect on the environment.

419 • Photocatalysis with TiO_2 is very inefficient in terms of treatment time and
420 accumulative energy compared to solar photo-Fenton and ozonation.

421 • Both photo-Fenton and ozonation substantially eliminate the contaminants and
422 their degradation products, but ozonation, because it is a milder oxidation
423 process, has a higher MS signal at the end of the treatment, as revealed by
424 HPLC-QTRAP-MS (*Supplementary Data*).

425 • Photo-Fenton is economically competitive with ozonation, the investment cost
426 of which (solar CPC field) is offset by the operating cost of ozonation. In this
427 sense, it is important to highlight the effect of the treatment design flow rate on
428 investment costs. If higher design flow rates are considered, solar photo-Fenton
429 investment costs per m^3 of water to be treated would decrease (CPCs field costs
430 are lower as higher the plant required m^2 are), but ozonisation costs (highly
431 affected by operation costs as electricity consumption) would not significantly
432 change.

433 • Solar photo-Fenton is a potential tertiary treatment in MWTPs with treatment
434 costs in the range of $<0.4 \text{ € m}^{-3}$ for eliminating micropollutants and degradation
435 products, which is very competitive with more mature processes.

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561 **Table 1.** List of micropollutants found and quantified by HPLC-QTRAP-MS in MWTP
 562 effluent samples taken on different days. Minimum and maximum concentrations found
 563 during the study are also given.

Micropollutant	ng L⁻¹	Micropollutant	ng/L	Micropollutant	ng L⁻¹
4-AA	35-1315-	Codeine	126-999	Nadolol	0-6
4-AAA	1134-12702	Cotinine	162-301	Naproxen	367-2968
4-DAA	0-11	Diazepan	9-68	Nicotine	65-450
4-FAA	4617-5234	Diclofenac	414-1466	Norfloxacin	29-60
4-MAA	243-2824	Diuron	103-1081	Ofloxacin	324-1614
Acetaminophen	0-73	Epoxide Carbm.	0-15	Paraxanthine	5851-17750
Antipyrine	263-545	Erythromycin	41-78	Pravastatin	44-75
Atenolol	386-1235	Famotidine	19-61	Primidone	50-57
Atrazine	35-843	Fenofibric Acid	25-142	Propranolol	16-19
Azithromycin	35-161	Furosemide	213-504	Propyphenazone	0-32
Benzafibrate	44-57	Gemfibrozil	963-2862	Ranitidine	313-726
Biphenylol	0-565	Hydrochlorothiazide	281-1339	Salbutamol	0-81
Bisphenol A	0-3495	Ibuprofen	162-5620	Simazine	3-704
Caffeine	3322-15457	Ifosfamide	0-8	Sotalol	3-12
Carbamazepine	50-114	Indomethacine	47-437	Sulfadiazine	0-36
Cefotaxime	0-985	Isoproturon	37-172	Sulfamethazine	0-236
Chlorfenvinphos	29-522	Ketoprofen	178-428	Sulfamethoxazole	603-780
Chlorophene	0-105	Lincomycin	73-192	Sulfapyridine	72-131
Ciprofloxacin	305-538	Mefenamic Acid	7-18	Sulfathiazole	0-25
Citalopram HBr	17-98	Mepivacaine	10-28	Terbutaline	0-85
Clarithromycin	24-54	Metoprolol	0-21	Trimethoprim	97-1661
Clofibric Acid	3-6	Metronidazole	17-67	Velafaxime	169-539

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565 **Table 2.** Summary of the main operating parameters for achieving over 85%, 98% and
 566 98% micropollutants degradation by solar photocatalysis with TiO₂, solar photo-Fenton
 567 and ozonation, respectively.

	Solar photocatalysis with TiO₂	Solar photo-Fenton		Ozonation
Treatment time, min	475	20		60
Accumulated solar energy, kJ L ⁻¹	212	2.3		-
Reagent Consumption	-	H ₂ O ₂ 54 mg L ⁻¹	Fe(II) 5 mg L ⁻¹	O ₃ 9.5 mg L ⁻¹
PL, µg L ⁻¹	80	40		48

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590 **Table 3.** Costs of solar photo-Fenton and ozonation tertiary treatments for 90% and
 591 98% elimination of micropollutants.

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	Solar Photo-Fenton		Ozonation	
	90%	98%	90%	98%
	€m⁻³			
Reagent	0.064	0.148	0.16	0.22
Labour	0.03	0.05	0.05	0.05
Electricity	0.004	0.010	0.010	0.020
Investment	0.09	0.15	0.23	0.27
Total	0.188	0.358	0.450	0.560

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617 **Figures caption**

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619 **Figure. 1.** Degradation profile of 16 contaminants with an initial concentration over
620 1000 ng L⁻¹ and the sum of the rest of contaminants (ΣC) at less than 1000 ng L⁻¹ (1-
621 Bisphenol A; 2-Ibuprofen; 3-Hydrochlorothiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-
622 Diclofenac; 8-Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen;
623 13-4-FAA; 14- ΣC ; 15-4-AAA; 16-Caffeine; 17-Paraxanthine) using solar
624 heterogeneous photocatalysis with TiO₂.

625 **Figure. 2.** Photo-Fenton degradation profile of the same 16 contaminants shown in
626 figure 1 and the sum of the rest of micropollutants (ΣC) at less than 1000 ng L⁻¹. (1-
627 Bisphenol A; 2-Ibuprofen; 3-Hydrochlorothiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-
628 Diclofenac; 8-Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen;
629 13-4-FAA; 14- ΣC ; 15-4-AAA; 16-Caffeine; 17-Paraxanthine).

630 **Figure 3.** Ozonation degradation profile of the same 16 contaminants shown in figure 1
631 and the sum of the rest of micropollutants (ΣC) at less than 1000 ng L⁻¹. (1-Bisphenol A;
632 2-Ibuprofen; 3-Hydrochlorothiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-Diclofenac; 8-
633 Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen; 13-4-FAA; 14-
634 ΣC ; 15-4-AAA; 16-Caffeine; 17-Paraxanthine).

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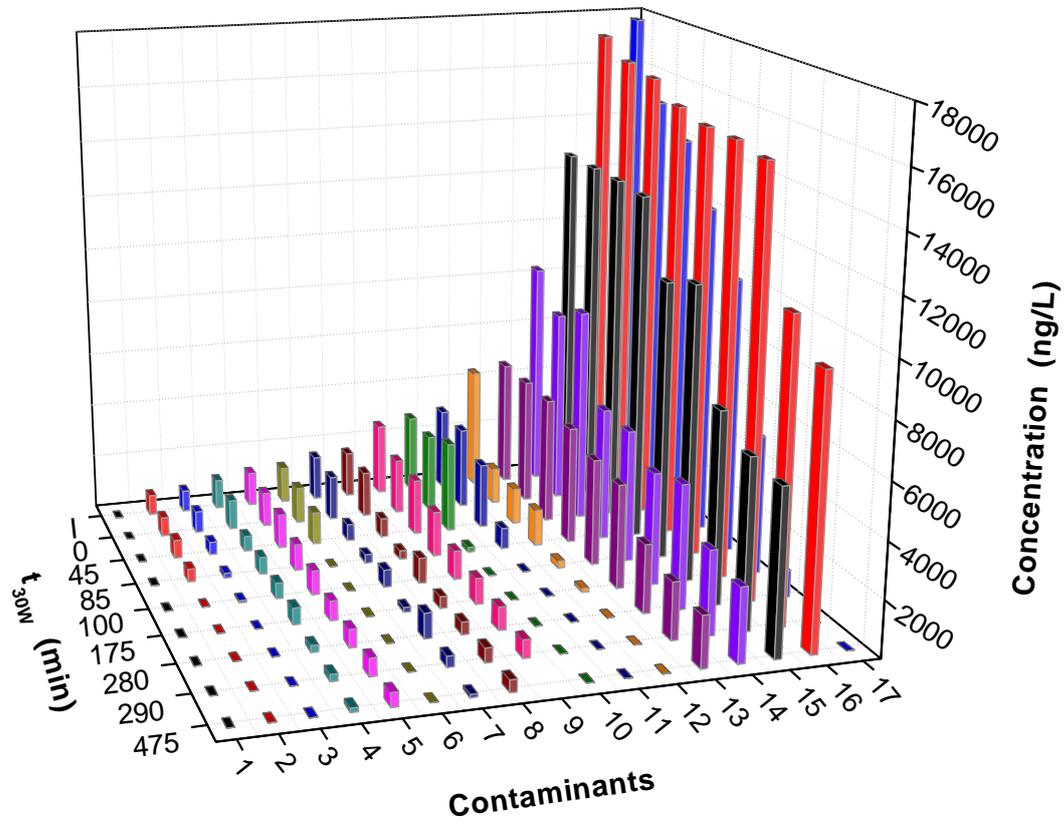
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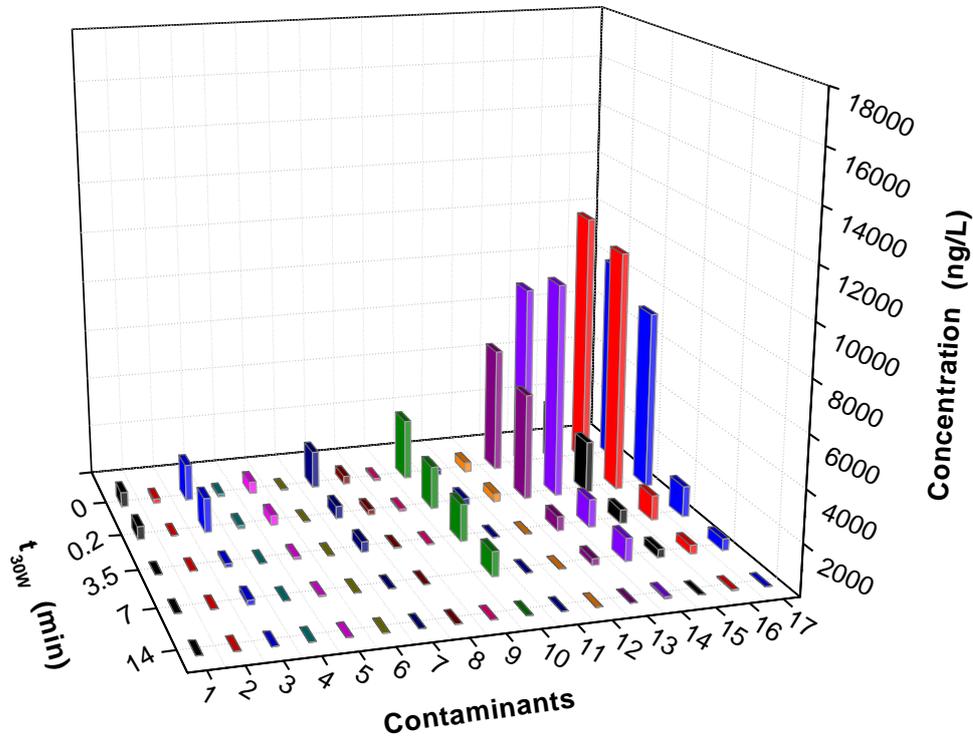
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1 **Figure 1.**



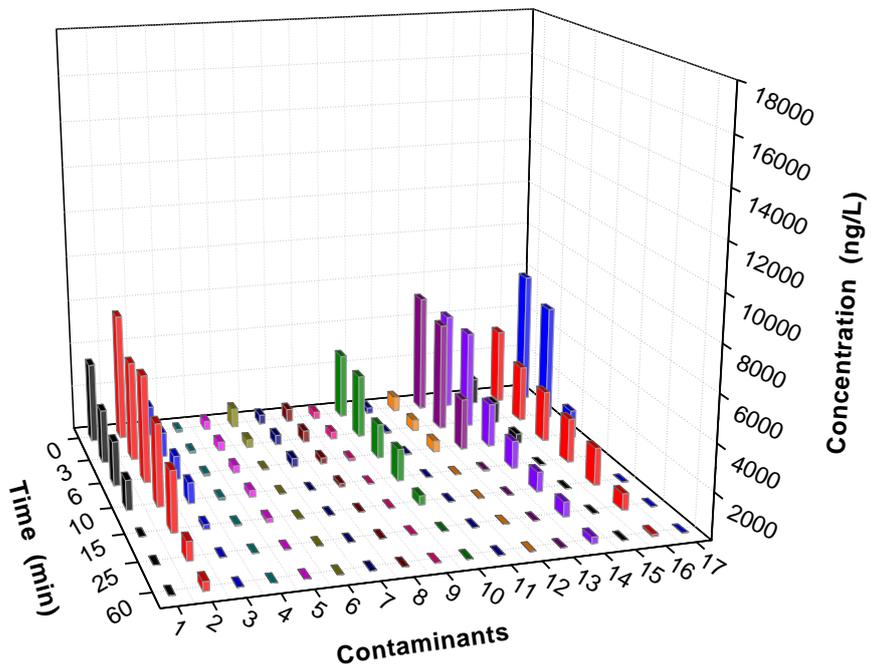
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1 **Figure 2.**



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1 **Figure 3.**



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