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Abstract

A comparative analysis is presented of light-driven advanced oxidation processes in terms of environmental sustainability. Photochemical oxidation has proven a viable option for treating emerging and priority pollutants at laboratory scale. Nevertheless, as a nascent technology, photocatalysis is yet to be widely applied at large-scale water treatment plants. This paper presents a powerful tool that should enable stakeholders to develop sustainable, large-scale, photocatalytic treatment plants by providing knowledge of environmental sustainability and hotspots (where technological flaws

have high environmental impact) and understanding as to how process sustainability can be improved through scenario analyses. The following processes were examined: natural and simulated solar photolysis, solar photo-Fenton without hydrogen peroxide addition (solar/Fe), solar photo-Fenton (solar/Fe/H_2O_2), photolysis under UV-A irradiation (UV-A), titania-mediated photocatalysis (UV-A/TiO_2), photolysis under UV-C irradiation (UV-C), and UV-C treatment with hydrogen peroxide addition (UV-C/H_2O_2). Actual life cycle inventory data were collected at bench scale, and the environmental performances estimated by means of life cycle assessment. Effective removal of 1μg of 17α-ethynylestradiol per liter of wastewater, a commonly occurring micropollutant and endocrine disrupting chemical, was used as the functional unit. Solar photolysis exhibited an environmental footprint about 23 times higher than solar/Fe. Solar/Fe/H_2O_2 minimized the environmental footprint. Being energy intensive, simulated solar irradiation had a much higher (~ 5-fold) environmental footprint than natural solar light. UV photolysis exhibited low environmental impact, with UV-C found to be about 3 times more environmentally friendly than UV-A photolysis. Addition of TiO_2 to UV-A and H_2O_2 to UV-C caused their total environmental impacts to decrease by about 97% and 88%, implying that UV-A/TiO_2 was better than UV-C/H_2O_2. In terms of total environmental footprint, the advanced oxidation processes descend in the following order: solar photolysis > UV-A > UV-C > solar/Fe > UV-A/TiO_2 > UV-C/H_2O_2 > solar/Fe/H_2O_2. The environmental sustainability of all processes was directly proportional to treatment efficiency but inversely proportional to treatment time (due to the large energy input per unit time). Although reagent use (i.e. titania, iron, and hydrogen peroxide) was not associated with high environmental impact, its addition greatly improved process efficiency as well as environmental sustainability. For all examined light-driven processes, the main

environmental hotspot was electricity consumption. Introduction of renewable energy sources could reduce the environmental footprint of oxidation processes by up to 87.5%.

Keywords: water purification; estrogens; photocatalysis; LCA; EDCs; EE2

1. Introduction

Trace- or micro-pollutants are synthetic chemicals of emerging environmental and health concern that have recently been detected in the aquatic environment (Tiedeken, 2017). Several hundred endocrine-disrupting chemicals (EDCs) have been measured in humans and wildlife, even in such remote places as the Arctic (Birnbaum, 2013). There is growing evidence that these pollutants have adverse effects on human health and living organisms. Trace-pollutants can act, or have the potential to act, as EDCs that cumulatively interfere with the endocrine system of living organisms and cause genetic abnormalities, infertility, feminization, increased cancer rates, trigger Alzheimer disease, etc. (Rochester, 2013). EDCs derive from the chemical processing industry in the form of drugs, surfactants, cosmetics, and other personal care products, which usually end up in the sewage system. Synthetic estrogens are EDCs that are found in increasing concentrations in natural waters (Zhang et al., 2014) and wastewater (Mohagheghian et al., 2014). A representative synthetic estrogen is 17α-ethynylestradiol (EE2), which is the basic component of the contraceptive pill. EE2 is

more stable in an aqueous environment and has greater estrogenic potency (~11–27 times) than natural estrone (E1) and estradiol (E2). Continuous exposure to EE2, even to concentrations of μg/L, has been found to cause bodyweight loss, accelerate vaginal opening, alter estrous cycles in young animals, and damage fish populations (Frontistis et al., 2015).

Due to their xenobiotic and non-biodegradable nature, conventional biological wastewater treatment plants (WWTPs) cannot effectively remove EDCs, which in turn are discharged into receiving waters. To overcome this, it is necessary to add robust tertiary treatment technologies to existing WWTPs. Of the technologies available for the removal of EDCs, light-driven advanced oxidation processes (AOPs) offer considerable promise. The effectiveness of AOPs is mainly due to the formation of reactive oxygen species (ROS), such as hydroxyl radicals ($HO^{\bullet}$), which subsequently oxidize the organic content of water samples. AOPs include solar, UV-A and UV-C photolysis and photocatalysis, usually accelerated by adding titania (TiO_2) (i.e. heterogeneous catalysis) (Lee et al., 2017), hydrogen peroxide (H_2O_2) and/or iron (Fe^{2+}) to form the photo-Fenton reagent (i.e. homogeneous catalysis) (Clarizia et al., 2017). To date, several studies have investigated the treatment of EE2-contaminated water by means of UV and solar photocatalysis or photolysis. Marinho et al. (2013) observed that TiO_2-mediated photocatalysis, under solar or UVA irradiation permitted efficient degradation of EE2, usually at reaction times lower than 15 min. Koutantou et al. (2013) used a zinc oxide photocatalyst immobilized onto a glass substrate to degrade EE2 by simulated solar light. They found that at the best conditions assayed, treatment time was only 50 min. Madsen and Søgaard (2012) found that photocatalysis with TiO_2 was the best method for removal of EE2 compared to UVC lamps. Experiments were carried out in a mobile test unit with wastewater volumes of 30 L. Even so, apart from UV-C

96 photolysis, other light-driven AOPs are still nascent technologies, not yet applied at
97 industrial-scale.

98 AOPs are energy intensive, with high operating cost and elevated environmental
99 footprint (Chatzisymeon et al., 2013). Solar photo-Fenton AOPs have high chemical
100 demand, and generate residual fluxes with negative environmental impacts, such as
101 sludge contaminated by metal ions, exhausted solid catalysts, etc. (Rodríguez et al.,
102 2016). Previous research has focused on the degradation efficiency and techno-
103 economic feasibility of AOPs, without detailed consideration of environmental
104 sustainability (Rodríguez et al., 2016). A brief review of existing studies on AOPs
105 environmental sustainability is given by (Ioannou-Ttofa et al., 2017).

106 In order for AOP technology to reach prototype-scale applications, it must be
107 acceptable from an environmental perspective. To achieve this, the environmental
108 sustainability of each AOP should first be assessed at bench- or pilot-scale, in order to
109 identify merits and drawbacks, establish the main environmental impact hotspots, and
110 assess ways of reducing the total environmental footprint through scenario and
111 sensitivity analyses. By determining the optimal environmental performance of AOPs,
112 the technology could be effectively scaled up to sustainable, large-scale applications in
113 water treatment works.

114 This paper describes a comparative life cycle assessment (LCA) of seven well-
115 established light-driven AOPs, namely: solar, solar/Fe, solar/Fe/H_2O_2, UVA,
116 UVA/TiO_2, UVC, and UVC/H_2O_2. The aim is to identify the strengths and weaknesses
117 of AOPs from an environmental sustainability perspective, thus enabling process scale
118 up. LCA methodology is employed, in accordance with ISO 14040 and ISO 14044
119 (ISO, 2006a, b), using SimaPro 8. The assessment was made using life cycle inventory

120 (LCI) data collected from bench-scale experiments, rather than extracted from a
121 database. The results should provide researchers, decision- and policy-makers, and the
122 water treatment industry with a better understanding of the environmental sustainability
123 of light-driven AOPs, which in turn should help advance the technology so that it
124 becomes ready for industrial-scale application. To the best of the authors' knowledge
125 this is the first study to date dealing with LCA of several light-driven oxidation
126 processes. Many publications focus on comparing several irradiation sources in terms
127 of ability to decontaminate/disinfect water and wastewater. Assessment of
128 environmental sustainability of such processes, including both solar and UV-irradiated
129 techniques, is presently missing from the literature.

130 Of the various methodologies used to assess the environmental sustainability of
131 a product or process, the most commonly utilized are multi-criteria analysis (MCA),
132 environmental performance indicators (EPIs), and life cycle assessment (LCA)
133 (Hermann et al., 2007). MCA compares and ranks alternative options, and evaluates
134 environmental consequences according to established criteria. However, its weakness
135 lies in the subjectivity of the weighting step, necessary to evaluate different criteria.
136 EPIs estimate the current or past environmental performance of an organisation and
137 compare it against a set of targets; however, the usefulness of EPIs is limited by
138 insufficient data availability (Hermann et al., 2007). LCA offers an effective means of
139 including environmental considerations in the design, production, use, and disposal of
140 a product (Foteinis et al., 2011). LCA is a tool for the systematic evaluation of
141 environmental impacts, which provides insight into the overall performance and
142 relative contributions of different stages within the product lifespan (Hermann et al.,
143 2007).

144

2. Materials and methods

Data used in the comparative LCA analysis were obtained from laboratory experiments, described by Frontistis et al. (2011, 2012, 2015). All experiments were carried out under the same ambient temperature and water conditions. Table 1 lists the optimum operating conditions assayed for each light-driven process. In all cases, the wastewater sample was stirred by a 50 W magnetic stirrer and the ambient temperature kept constant at 25±2 ^{o}C. Energy required to keep the temperature constant was external to system boundaries, while the stirrer was assumed to operate at 30 W (i.e. not at full power). At industry scale, wastewater pumping would replace the magnetic stirrer. Simulated solar irradiation was emitted by a Newport, model 96000, 150 W solar simulator system. The UV-A and UV-C experiments were conducted in an immersion well, batch type, laboratory-scale photoreactor (Ace Glass, Vineland, NJ, USA). UV-A irradiation was provided by a 9 W lamp (Radium Ralutec, 9W/78, 350–400 nm). UV-C irradiation was provided by an 11 W low-pressure mercury lamp (Phillips, TUV PL-S). The Fe^{2+} ionic solution used in the experiments was in the form of $FeSO_4 \cdot 7H_2O$ (≥ 99%, Sigma-Aldrich). H_2SO_4 was added in order to regulate the initial water pH. TiO_2 P25 was donated by Evonik Industries, and H_2O_2 (35% w/w) was purchased from Merck.

3. Environmental sustainability analysis

To assess the environmental sustainability of light-driven AOPs, LCA methodology was employed, as detailed in ISO 14040 and 14044 (ISO, 2006a, b). Bench-scale experimental results were utilized by the environmental model. The timespan covered 2010 to the present date, the geographical boundaries encompassed Greece and similar countries, and average technology was assumed. For the foreground system, primary

169 inventory data were collected for laboratory-scale experiments, while, for the
170 background system, data were used regarding the most recent average technology (e.g.
171 for electricity the average technology mix in Greece was imported from the ecoinvent
172 database).

173

174 **3.1 Functional unit**

175 The functional unit selected to quantify the performance of a light-driven AOP was the
176 effective removal of 1 μg EE2 per liter of treated wastewater. The life cycle inventory
177 (LCI) for each AOP under study was then normalized per functional unit (ISO, 2006a,
178 b) in order to study the environmental performance of the different technologies.
179 Attributional life cycle assessment (ALCA) was used because it estimates the
180 environmental impacts of a product or system according to the delivery of a specified
181 quantity of the functional unit (Chatzisymeon et al., 2016).

182 **3.2 System boundaries and life cycle inventory (LCI)**

183 The system boundaries define which unit processes (the smallest elements for which
184 input and output data are quantified in the LCI) are included within the LCA (ISO,
185 2006a). Energy and raw material requirements, waterborne emissions, and the
186 materials' disposal or recycling are included within system boundaries.

187 For the AOPs photoreactor, LCI data could not be identified and so their
188 primary materials, i.e. glass, lamps, and the stirrer, were taken into account. It was
189 assumed that solar and UV photoreactors have similar dimensions and materials, and
190 that all experiments were carried out at the same ambient temperature. Two different
191 scenarios were examined for the solar AOPs. The first scenario comprised the
192 photoreactor and lamp (i.e. simulated solar irradiation), whereas the second scenario

193 did not include the lamp (i.e. natural solar irradiation). The latter scenario is closer to
194 actual operating conditions of solar AOPs. Following Ioannou-Ttofa et al. (2017), the
195 photoreactor glass was assigned a useful lifespan of five years (10 h/d operation, all
196 year round). Recycling was also incorporated. Photoreactor lamps are not included in
197 SimaPro's proprietary life cycle inventory (LCI) databases, and so the LCI data were
198 obtained from relevant literature (Garrett and Collins, 2009; OSRAM, 2016). The data
199 were re-scaled according to the power requirements of each process and input to
200 SimaPro in order to simulate the environmental impact of each lamp under study. Data
201 on the stirrer used to mix effluent were not available in SimaPro's proprietary LCI
202 databases, and so were substituted by relevant data concerning the LCI of a low-power
203 motor (AAB, 2002), re-scaled to fit the rated output of the stirrer under study, and used
204 as input to SimaPro.

205 Information on the Fe^{2+} ion as iron sulphate was supplied from the SimaPro LCI
206 databases. Residual Fe^{2+} in the treated wastewater was also taken into account as
207 waterborne emission. Data on H_2O_2 and H_2SO_4 reagents were obtained from proprietary
208 LCI databases. Energy used to drive each process was supplied as electricity from the
209 Greek energy grid, which is fossil fuel-dependent and comprises 54% lignite, 11%
210 crude oil, 17% natural gas, and 18% renewable energy (Ioannou-Ttofa et al., 2017). To
211 carry out the comparative analysis, from an environmental perspective, of light-driven
212 AOPs, the final use and disposal route of treated effluent was taken to be external to
213 system boundaries. In other words, cradle-to-gate (treated effluent) was used.

214

215 Table 1.

216

3.3 Life cycle impact assessment (LCIA)

Life cycle impact assessment (LCIA) relates the data inventory to specific environmental impacts and damages (ISO, 2006a, b). ReCiPe was chosen for the LCIA as a robust method that comprises both midpoint and endpoint impact/damage approaches which examine different stages in the cause-effect chain to calculate impact (Chatzisymeon et al., 2016). The endpoint, or damage-oriented, approach translates environmental impacts into issues of concern, such as human health, natural environment, and natural resources. Endpoint results are associated with higher levels of statistical uncertainty, compared to midpoint, due to data gaps and assumptions stacking up along the cause-effect chain, but are easier for decision- and policy-makers to comprehend (Chatzisymeon et al., 2016). Given that this is a comparative LCA, results are compared using the following three endpoint damage categories: "Human Health", "Resources", and "Ecosystems". These can be also aggregated into a single score, which makes interpretation simpler.

A hierarchist perspective (H), based on the most common policy principles, was invoked within ReCiPe along with European normalization and average weighting. Decisions whether or not to include information in the H model are based on mean scientific consensus, and it assumes that, with proper management, environmental impacts can be avoided (Chatzisymeon et al., 2016), thus fitting better the goal and scope of the comparative analysis.

Moreover, in order to ensure accuracy and transparency of the LCA, the primary LCI data along with data used for the background system were verified against information from the open literature (Chatzisymeon et al., 2013; Gimenez et al 2015). Light-driven AOPs comprise a nascent technology for wastewater treatment, and so

241 comparative environmental studies based on similar operating conditions and similar
242 initial organic loads are needed; however, information on these important parameters is
243 scarce.

244

245 **3.4 Energy consumption**

246 The energy consumption of artificial lighting constitutes a major fraction of the
247 operating costs in UV treatment. Bolton et al. (2001) introduced the electric energy per
248 order, E_{EO}, defined as the energy required for 90% degradation of a pollutant per m^3 of
249 contaminated water. E_{EO} (kWh/m^3/order), for a batch-operated reactor, is calculated
250 from the following equation:

251 $$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_i/C_f)} \quad (1)$$

252 where P is the electrical power of the irradiation source (kW), t is the irradiation time
253 (min), V is the volume of the treated effluent (L), and C_i and C_f are the initial and the
254 final pollutant concentrations (mg/L), respectively.

255

256 **4 Results and discussion**

257 To render the analysis both comprehensive and straightforward to follow, the results
258 for the solar and UV irradiation light sources are considered separately. Then, a
259 comparative analysis of all processes follows in order to identify the most promising
260 result in terms of environmental sustainability. Finally, a sensitivity analysis is carried
261 out using scenarios to investigate the effect of the main environmental hotspots and to
262 propose "greener" alternatives by which to improve sustainability.

4.1 Environmental sustainability of solar-driven AOPs and effects of Fe^{2+} and H_2O_2

Results provided by ReCiPe for natural and simulated solar-driven photolysis/photocatalysis at endpoint level (Figure 1) show that simulated (artificial light) and natural solar photolysis yielded by far the highest environmental footprints of ~11 mPt and ~2 mPt per functional unit, respectively. The environmental footprint due to photolysis was ~ 23 times larger than that of simulated/natural solar/Fe, using low reagent concentration (5 mg/L Fe^{2+}), with scores of 0.477 mPt (artificial light) and 0.089 mPt (natural light). For photolysis, as well as all other AOPs, the main environmental hotspot was electricity use derived from Greece's fossil fuel-dependent electricity mix. At the time of writing, electricity systems worldwide use fossil fuels for bulk power generation (Berill et al., 2016) and so the foregoing results are presently valid for Greece, Europe and beyond. Indirect impacts of the use of electricity from fossil fuels can be traced mainly to the "Human Health" damage category, followed by "Resources", and less so the "Ecosystem" (Chatzisymeon et al., 2016). "Human Health" damage is affected by fossil-fuel mining and combustion, which release toxic materials including metals, sulphur, and polycyclic aromatic hydrocarbons (PAHs) to the environment (Chatzisymeon et al., 2016). Fossil-fuel extraction and burning contribute to climate change. Natural gas extraction also releases SO_2. Impacts from coal arise from tailpipe emissions after combustion and emissions during blasting at coal mines (Berill et al., 2016). "Resources" damage is primarily caused by depletion of fossil fuels for electricity generation and of mineral resources used to construct equipment required for resource extraction, processing and consumption, and to a lesser degree by equipment related to AOPs (i.e. the stirrer and photoreactor). Turning to "Ecosystem" damage, phosphate leachate from coal mining spoil landfill sites and the

emission of nitrogen oxides from combustion of fossil-fuel directly impact on acidification and eutrophication. Waterborne metal emissions from coal power plants, natural gas extraction (particularly of bromine) and from disposed coal mine spoil (nickel and magnesium) affect ecotoxicity (Berill et al., 2016; Ioannou-Ttofa et al., 2017).

Use of simulated irradiation raised the environmental impact because the total environmental footprint of simulated solar photolysis and photocatalysis is about a factor of 5 higher than natural solar light. This is attributed to electricity consumption by the lamp (~ 81.3% of total environmental footprint), and to a much lower degree to the lamp material (~ 0.05% of total environmental footprint). In terms of material, the stirrer (i.e. motor) contributed 12.4% and 2.3% to the total environmental footprints for natural and simulated solar photolysis. Finally, the photoreactor material (glass) made a very low contribution to the total environmental footprint, 0.257% and 0.0494% for natural and simulated solar photolysis, respectively, mainly because of the long lifespan of glass whose recycling was included in the system boundaries. The relatively high environmental footprint of solar photolysis is due to its low treatment efficiency as it consumes energy during the stirring process while EE2 is removed from wastewater.

Figure 1.

To study the environmental impacts of the more environmentally friendly natural solar-driven AOPs, a separate comparison was undertaken, neglecting photolysis and simulated solar irridiation. Figure 2 shows that the amount of oxidation reagents used strongly affected the environmental sustainability of solar-driven AOPs,

312 with high reagent concentration improving the overall environmental sustainability of
313 solar AOPs. At low concentration of iron ions (5 mg/L Fe^{2+}) the total evironmental
314 footprint of natural solar/Fe was estimated to be 0.089 mPt, whereas when the
315 concentration was increased to 15 mg/L the total environmental footprint reduced by
316 about half to 0.047 mPt per functional unit (Figure 2). When H_2O_2 was also added as a
317 reagent, the environmental sustainability of the process was further enhanced. More
318 specifically, when keeping the iron ion concentration constant at 5 mg/L and adding 10
319 mg/L H_2O_2 the total environmental footprint of the process was ~0.01 mPt per
320 functional unit, and by increasing the H_2O_2 concentration to 17.2 mg/L the
321 environmental footprint of the process achieved a minumum of ~ 0.356×10^{-3} mPt per
322 functional unit.

323 This large reduction is attributed to: (a) increased degradation efficiency at
324 higher H_2O_2 concentration (Table 1); (b) lower treatment time (15 min for 10 mg/L
325 H_2O_2, and 1 min for 17.2 mg/L H_2O_2) and hence reduced energy consumption; and (c)
326 use of low amounts of H_2O_2, a non-toxic chemical without elevated environmental
327 impact. As mentioned before, the environmental impacts of solar/Fe can be traced back
328 to Greece's fossil fuel-dependent electricity mix used to drive the stirrer. The
329 contributions of electricity consumption to the total environmental footprint of natural
330 solar/Fe (5 mg/L and 15 mg/L), natural solar/Fe/H_2O_2 (10 mg/L) and natural
331 solar/Fe/H_2O_2 (17.2 mg/L) were 87.4%, 87.3% and 86.5%. The photoreactor and the
332 stirrer-drive motor made material contributions of 0.256 ± 0.02 % and 12.35 ± 0.05 %.
333 As a non-hazardous reagent when in small concentrations, Fe^{2+} had a negligible effect
334 in all cases (its biggest score was 0.058% in natural solar/Fe/H_2O_2 (17.2 mg/L)).
335 Similarly, the addition of miniscule amounts of H_2SO_4 in concentrations of about 50
336 μL/L led to it also making a negligible contribution. For natural solar/Fe/H_2O_2, addition

of hydrogen peroxide at concentrations of 10 mg/L and 17.2 mg/L contributed ~0.037% and 0.943% to total environmental footprint. The latter, higher percentage contribution is related to the overall low environmental footprint of the process (0.356×10^{-3} mPt) and the higher quantity of hydrogen peroxide used (and the knock-on increased energy and materials required for its synthesis). It should be noted that no H_2O_2 emissions (e.g. airborne, waterborne) or harmful by-products were assumed to be generated during treatment.

Figure 2.

4.2 Environmental sustainability of UV-A and UV-C photocatalysis

Figure 3 presents the environmental footprints of UV-A and UV-C photolysis/photocatalysis in terms of "Human Health", "Resources" and "Ecosystems" endpoint damage categories. UV-A photolysis yields a higher environmental footprint (0.309 mPt), whereas that of UV-C is about a factor of three smaller (0.117 mPt). This is expected because UV-C treatment has a much higher treatment efficiency due to the higher energy (Frontistis et al., 2015), compared to UV-A treatment. In both cases the lamp materials hardly contributed to the total environmental footprint, whereas the UV-C lamp required about 20% higher power but also had significantly higher treatment efficiency (see Table 1). As a result, UV-C removed 1 μg/L of EE2 at a much faster rate than UV-A treatment, requiring less energy and contributing less environmental footprint per functional unit.

When reagents were added, the environmental footprint of both UV-A and UV-C treatment was substantially reduced. Figure 3 shows that addition of titania (10 mg/L

TiO_2) drastically reduced the total environmental footprint of UV-A treatment, from ~309 μPt for UV-A photolysis to ~9.2 μPt for UV-A/TiO_2 heterogenous photocatalysis. As far as UV-C treatment is concerned, the addition of H_2O_2 (10 mg/L) also had a profound effect, with the environmental footprint of UV-C photolysis reducing from ~117 μPt for UV-C to ~13.8 μPt for UV-C/H_2O_2. These large reductions (~97% for UV-A/TiO_2 and ~88% for UV-C/H_2O_2) are due to a combination of improved treatment efficiency and reduced treatment time (Table 1).

As with solar-driven AOPs, the environmental sustainability of UV-driven AOPs is enhanced by addition of small amounts of the non-hazardous reagents, TiO_2 and H_2O_2, leading to significant improvement in degradation efficiency and reduction in treatment time, especially for UV-A treatment.

Electricity consumption makes the largest contribution to most damage categories, reflected by its contribution to the total environmental footpint of UV-driven AOPs of 88.3 ± 0.1 %. This score is dominated by electricity consumption by the stirrer motor and, to a lesser degree, to the lamp(s). The stirrer motor as a material was the next most important environmental hotspot with scores ranging from 9.15% to 9.63% of the total environmental footpint. The lamp as a material contributed from 1.79% for UV-A to 2.35% for UV-C. The photoreactor as a material (glass) contributed from 0.19% for UV-C to 0.29% for UV-A. The reagents TiO_2 and H_2O_2 contributed very low percentages, 0.236% for UV-A/TiO_2 and 0.0273% for UV-C/H_2O_2, of the total environmental footprint. Even though TiO_2 had a higher impact than H_2O_2, UV-C/H_2O_2 exhibited a slightly higher total environmental footprint than UV-A/TiO_2, mainly due to the reduced treatment time of the latter (Table 1).

385 Figure 3.

386

387 **4.3 Environmental sustainability of solar versus UV-A and UV-C photocatalysis**

388 Given that photolysis invariably exhibited the highest overall environmental footprint,
389 the most promising photocatalytic processes were determined in terms of
390 environmental sustainability. Figure 4 presents a comparative analysis, using ReCiPe
391 impact assessment method, of natural solar/Fe, natural solar/Fe/H_2O_2, UV-A/TiO_2 and
392 UV-C/H_2O_2 photocatalysis. Natural solar/Fe/H_2O_2, at high reagent concentrations (Fe^{2+}
393 = 5 mg/L and H_2O_2 = 17.2 mg/L) yielded the lowest score (0.356 μPt per functional
394 unit) amongst all processes. For simulated solar irradiation, the total environmental
395 footprint of solar/Fe/H_2O_2 rose to 1.869 μPt, but nevertheless remains substantially
396 lower than all the other light-driven AOPs considered. Again, the presence of iron and
397 hydrogen peroxide oxidants, the reduced treatment time and enhanced EE2 removal
398 efficiency caused the energy demand per functional unit to be minimized, lowering the
399 environmental footprint. The next most environmentally friendly AOPs were UV-
400 A/TiO_2 (~9.2 μPt or ~96% higher than natural solar/Fe/H_2O_2) and UV-C/H_2O_2 (~13.8
401 μPt). Both exhibited relatively high treatment efficiency, with UV-A/TiO_2 requiring
402 less treatment time to achieve EE2 removal (Table 1), which meant less energy input
403 and a lower environmental footprint than UV-C/H_2O_2. Also, the lamp required higher
404 energy to drive the UV-C/H_2O_2 process (11W) than UV-A/TiO_2 (9 W). The lamps,
405 photoreactor, and stirrer made low contributions as materials to the total environmental
406 footprints of the UV-C/H_2O_2 and UV-A/TiO_2 processes. The contribution by the
407 reagents, TiO_2 and H_2O_2, was miniscule compared to electricity consumption. Finally,
408 natural solar/Fe exhibited a high overall environmental footprint, especially at low

409 reagent concentration (5 mg/L Fe^{2+}) where the value was 0.089 mPt. For a high iron
410 concentration (i.e. 15 mg/L), the total environmental footprint was halved, to 0.047 mPt
411 per functional unit (Figures 2 and 4).

412 In short, all the light-driven AOPs considered in this work were limited by the
413 same environmental hotspot, namely electricity consumption from Greece's fossil fuel-
414 dependent energy mix, which dominated the contributions to ReCiPe's damage
415 categories "Human Health" and "Resources". Similar findings were obtained by
416 (Chatzisymeon et al., 2013) who compared the environmental sustainability of UV-
417 A/TiO_2 with electrochemical and wet air oxidation processes for treatment of agro-
418 industrial wastewater.

419

420 Figure 4.

421

422 The present comparison is based on bench-scale experimental data. It is expected that
423 further benefits can be achieved for all AOPs examined, in terms of lowering the
424 environmental footprint per functional unit when the processes are scaled up. For
425 example, in prototype applications, the stirring processes, which required large energy
426 inputs at bench scale, will be replaced by pumping which is more energy efficient.
427 Given that it also consumes electricity, pumping is likely to be a prime environmental
428 hotspot (as also suggested by Foteinis et al. (2018) in a study of pilot-scale Fenton
429 processes for pharmaceutical wastewater treatment).

430 Energy consumption to degrade 90% of EE2 was also estimated in order to undertake
431 a more comprehensive comparative analysis of artificial light-driven oxidation
432 processes. The corresponding treatment time was estimated either using experimental

values from photocatalytic tests carried out by Frontistis et al. (2015), Frontistis et al. (2012) and Frontistis et al. (2011) or by extrapolating the experimental values to achieve 90% removal of EE2. The results are shown in Table 2, where it is observed that UVA/TiO_2 process has the lowest energy demands followed by UVC/H_2O_2, solar/Fe(5mg/L)/H_2O_2, UVC, UVA, solar/Fe(15mg/L), solar/Fe(5mg/L) and simulated solar process. In principle, these results are consistent with those obtained from LCA (Figure 4) confirming the high dependence of AOPs on electricity consumption.

Table 2.

4.5 Sensitivity analysis

The main environmental barrier to light-driven AOPs under study is electricity consumption from the Greek energy mix dominated by fossil fuels. Power systems based largely on renewable energy sources (RES) perform much better regarding climate change and other impact categories than systems based on fossil fuels (Berrill et al., 2016). A sensitivity analysis was carried out involving three energy mix scenarios solely based on RES, i.e. solar, wind, and hydropower, all naturally abundant in Greece, Europe and beyond. Energy storage, curtailment, and grid extension were neglected because the aim of scenario analysis is purely to illustrate possible pathways and futures, rather than make forecasts or predictions (Kouloumpis et al., 2015). Moreover, the extra impacts caused by energy storage and grid extension are likely to be of such relatively small magnitude that the environmental benefits of switching to renewables would not be undermined (Berrill et al., 2016). The use of RES to meet the electricity needs of light-driven AOPs is expected to lead to substantial improvement in their

environmental sustainability. For example, use of an electricity mix solely based on photovoltaic (PV) systems (i.e. 3 kWp single-Si panels mounted on slanted roofs) decreases the total environmental footprint of solar AOPs by about 85% and UV-driven AOPs by 87%. On the other hand, use of an electricity mix solely based on wind energy (onshore wind turbines, capacity in the range from 1 to 3 MW) further improves the environmental sustainability of light-driven AOPs because energy from wind turbines usually has a lower environmental impact than solar PVs (Chatzisymeon et al., 2016). In this case, the total environmental footprint of solar AOPs and UV-driven AOPs is decreased by about 81% compared to the initial scenario. Finally, use of an electricity mix solely based on hydropower leads to the largest decrease in total environmental footprint of light-driven AOPs by 86% (solar) and 87% (UV) because hydropower is the most environmentally friendly RES option (Ioannou-Ttofa et al., 2017).

In all cases, the highest reduction in environmental footprint occurred for the most energy intensive AOPs (i.e. simulated solar, UV-A, and UV-C, ordered from higher to lower reduction), whereas the smallest reduction occurred for the most energy efficient AOPs (i.e. solar/Fe/H_2O_2, solar/Fe, UV-A/TiO_2, and UV-C/H_2O_2, ordered from lower to higher reduction). The order of light-driven processes in terms of environmental sustainability remained the same for all scenarios; from higher to lower score: natural or simulated solar > UV-A > UV-C > natural or simulated solar/Fe > UV-A/TiO_2 > UV-C/H_2O_2 > natural or simulated solar/Fe/H_2O_2. Even so, it should be noted that UV-A/TiO_2 and UV-C/H_2O_2 exhibited similar environmental footprints when using RES.

5. Conclusions

481 This paper has investigated the environmental performance of light-driven AOPs at
482 removing an endocrine disruptor, EE2, from wastewater using actual life cycle
483 inventory (LCI) data. It was found that the environmental sustainability of light-driven
484 AOPs was directly proportional to treatment efficiency (which was expected given that
485 the chosen functional unit was the removal of 1 μg EE2 per liter of wastewater), and
486 was also inversely proportional to treatment time. Moreover, electricity consumption
487 from the fossil fuel-dependent Greek energy mix was the main environmental hotspot
488 for all examined AOPs. The Fe^{2+}, H_2O_2, and H_2SO_4 reagents used in light-driven AOPs
489 were associated with low environmental impacts because the chemicals did not
490 detrimentally affect health or the eco-system, no harmful by-products were generated,
491 and only low dosages were used. Use of RES to meet the electricity needs of light-
492 driven AOPs substantially improved their environmental sustainability, by up to 87%
493 for solar- and 88% for UV-driven AOPs.

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590 **List of Tables**

Table 1.

Light-driven processes	Irradiation power, W	[TiO_2], mg/L	Power for water stirring, W	[Fe^{2+}], mg/L	H_2O_2, mg/L	Treatment time, min	EE2 removal, µg/L	Reference
Solar	150	-	30	-	-	60	2	(Frontistis et al., 2015)
Solar/Fe	150	-	30	5	-	60	46	(Frontistis et al., 2015)
	150	-	30	15	-	60	86	(Frontistis et al., 2015)
Solar/Fe/H_2O_2	150	-	30	5	10	15	98	(Frontistis et al., 2015)
	150	-	30	5	17.2	1	196	(Frontistis et al., 2011)
UVA	9	-	30	-	-	60	17	(Frontistis et al., 2015)
UVA/TiO_2	9	750	30	-	-	10	95	(Frontistis et al., 2012)
UVC	11	-	30	-	-	60	47	(Frontistis et al., 2015)
UVC/H_2O_2	11	-	30	-	10	15	100	(Frontistis et al., 2015)

Table 2.

Light-driven processes	Irradiation power, kW	Volume, L	Treatment time to remove 90% of EE2, min	E_{EO}, kWh/m^3/order	Reference
Solar	0.150	0.3	2251	18758	(Frontistis et al., 2015)
Solar/Fe(5mg/L)	0.150	0.3	115	958	(Frontistis et al., 2015)
Solar/Fe(15mg/L)	0.150	0.3	70	583	(Frontistis et al., 2015)
Solar/Fe(5mg/L)/H_2O_2	0.150	0.3	2	17	(Frontistis et al., 2015)
UVA	0.009	0.3	312	156	(Frontistis et al., 2015)
UVA/TiO_2	0.009	0.3	7	4	(Frontistis et al., 2012)
UVC	0.011	0.3	113	69	(Frontistis et al., 2015)
UVC/H_2O_2	0.011	0.3	10	6	(Frontistis et al., 2015)

600 **List of Figures**

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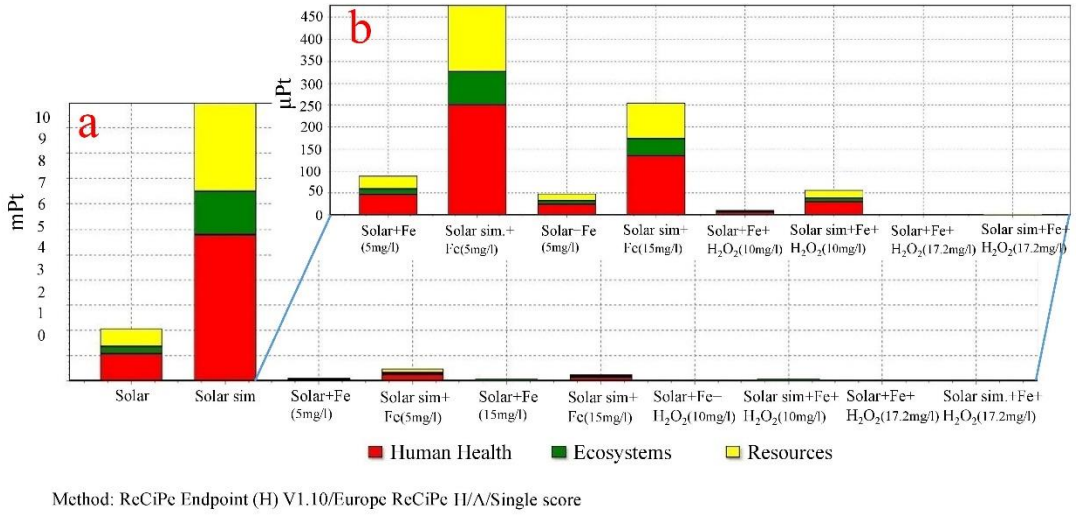

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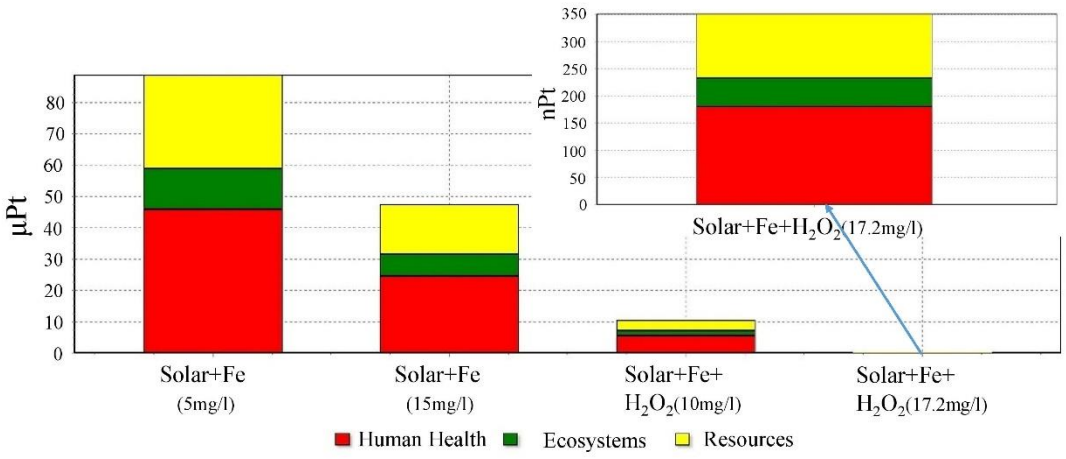

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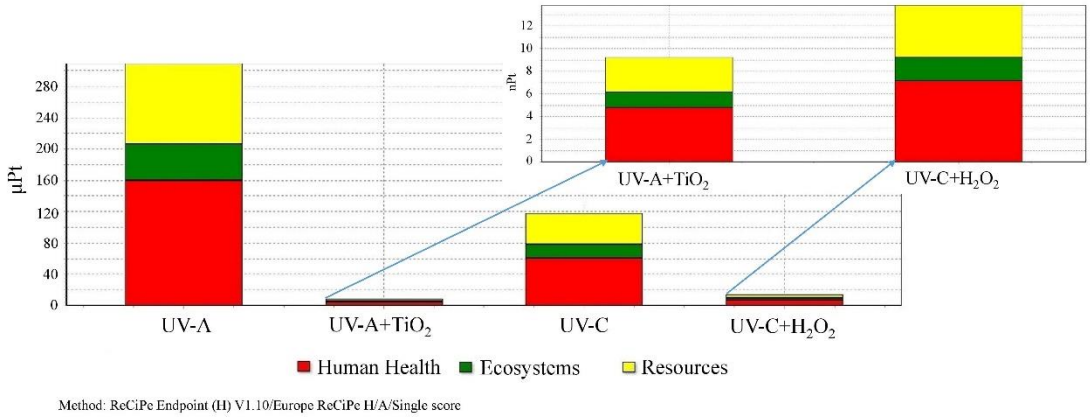

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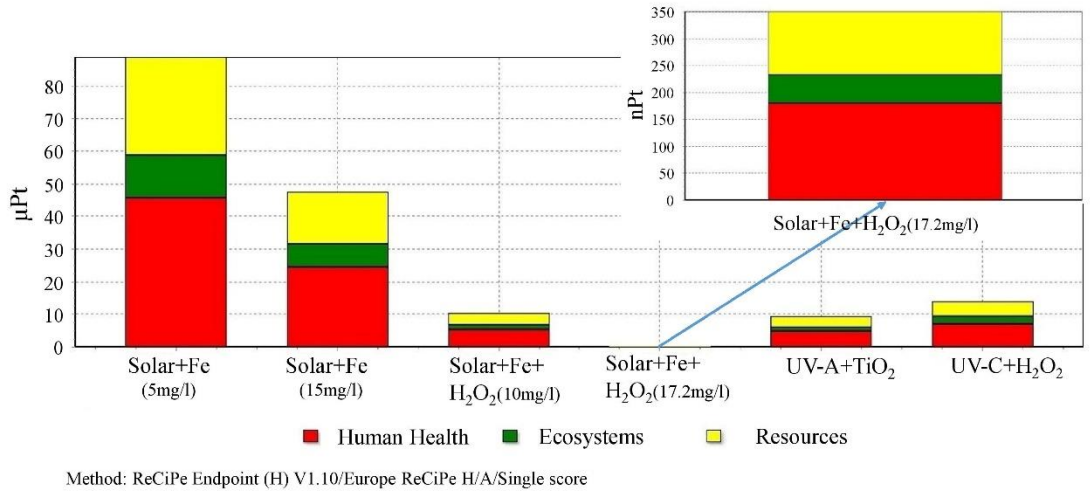

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627 Figure 4.

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