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Environmental sustainability of the solar photo-Fenton process for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale

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Abstract

The environmental sustainability of a semi-industrial solar photo-Fenton reactor, treating real effluents emanating from a pharmaceutical laboratory, is assessed herein. The life cycle assessment/analysis (LCA) methodology was employed and real life cycle inventory (LCI) data was collected from a ferrioxalate-assisted homogeneous solar photo-Fenton wastewater treatment plant (WWTP), at Ciudad Real, Spain. Electricity was provided by photovoltaic (PV) panels in tandem with a battery bank, making the plant autonomous from the local grid. The effective treatment of 1 m^3 of secondary-treated pharmaceutical wastewater, containing antipyrine, was used as a functional unit. The main environmental hotspot was identified to be the chemical reagents used to enhance treatment efficiency, mainly hydrogen peroxide (H_2O_2) and to a smaller degree oxalic acid. On the other hand, land use, PV panels, battery units, compound parabolic collectors (CPC), tanks, pipes and pumps, as materials, had a low contribution, ranging from as little as 0.06% up to about 2% on the total CO_{2eq} emissions. Overall, the solar photo-Fenton process was found to be a sustainable technology for treating wastewater containing micropollutants at semi-industrial level, since the total environmental footprint was found to be 2.71 kg CO_2 m^{-3} or 272 mPt m^{-3}, using IPCC 2013 and ReCiPe impact assessment methods, respectively. A sensitivity analysis revealed that if the excess of solar power is fed back into the grid then the total environmental footprint is reduced. Depending on the amount of solar power fed back into the grid the process could have a near zero total environmental footprint.

Keywords: solar photocatalysis, solar energy, sustainability, renewable energy, LCA, endocrine disruptors

1. Introduction

Nowadays, the presence of persistent contaminants of the order of the μg/L or ng/L, i.e. micropollutans, in natural water bodies constitutes a grave environmental problem of emerging concern (Grandclément et al., 2017). Micropollutants are non-regulated contaminants with unique characteristics and behaviour in the wastewater, which even at miniscule concentrations of ng/L can cause detrimental effects to the environment and human health (Virkutyte et al., 2010). Diseases, such as endocrine-related cancers, reproductive disorders, behavioural and learning problems, asthma, and even obesity and diabetes, are linked to exposure to EDCs (WHO, 2013; Rochester, 2013). Adverse effects are also observed in natural ecosystems, with the most common of all being the feminization of male and altered oogenesis in female fish populations, which is already observed in natural water bodies downstream from WWTPs (WHO, 2013; Kidd et al., 2007). They derive from a vast and expanding array of sources, including pharmaceuticals, surfactants, personal care products, hormones, industrial chemicals, pesticides and many other emerging compounds (Luo et al., 2014; Virkutyte et al., 2010). Micropollutants usually end up to the sewer system and are transporting along with the sewage to wastewater treatment plants (WWTPs). The main problem lies to the fact that conventional physicochemical and biological WWTPs have not been designed to cope with micropollutants (Luo et al., 2014), since their main function is to deal with bulk substances that arrive regularly and in large quantities, primarily organic matter and nutrients such as nitrogen and phosphorus (Virkutyte et al., 2010). As a result, WWTPs constitute a major pathway for micropollutants introduction and diffusion to surface water.

Hence, the introduction of advanced treatment technologies, such as advanced oxidation processes (AOPs), able to cope with micropollutants is essential to safeguard human health and the environment. Light-driven AOPs are promising for removing both organic compounds and micropollutants from wastewater matrices (Davididou et al., 2017; Prieto-Rodríguez et al.,

2013). Among the different light-driven AOPs, solar-powered processes, such as the solar photo-Fenton, is believed to be one of the most environmentally friendly and cost-effective process. This is attributed to the fact that natural solar light is used, instead of artificial irradiation, to generate hydroxyl radicals, which drive the treatment process (Expósito et al., 2016). Homogeneous photo-Fenton process (system Fe(II)/H_2O_2) photogenerates hydroxyl radicals through the following reaction (1) (Monteagudo et al., 2009):

$$Fe^{3+} + h\nu + H_2O \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \quad (1)$$

However, light-driven AOPs are energy intensive and require chemical inputs, which strongly affects their environmental sustainability (Chatzisymeon et al., 2013; Giménez et al., 2015). Since, solar driven AOPs perform best at areas with abundant sunlight, solar energy harvesting to produce electricity could provide a clean energy source for AOPs operation. Therefore, in areas with high solar irradiance photovoltaic (PV) panels could provide the electricity required for the process, while with battery storage solutions autonomous AOPs treatment plants could be established. Such autonomous pilot-scale solar photocatalytic reactors have been previously used for the treatment of various azo dyes (Garcia-Segura and Brillas, 2016; Garcia-Segura and Brillas, 2014). This choice is very important for remote areas with no grid access, especially for developing countries, where abundant sunlight is available. Moreover, using solely renewable energy sources (RES), such as solar energy, can help moving towards zero or even negative total environmental footprint WWTPs.

Till now, the degradation efficiency of pharmaceuticals in wastewater using the photo-Fenton process is well established at laboratory and pilot scale and to a smaller degree at industrial scale (Expósito et al., 2016). Moreover, research has been mainly focused on the techno-economical feasibility of the solar photo-Fenton process, while only a few works have focused on its environmental performance, but mainly at laboratory (Giménez et al., 2015) or

pilot scale (Ioannou-Ttofa et al., 2017). Nonetheless, solar photo-Fenton's environmental sustainability at industrial level, where economies of scales exist, remains largely unknown. Moreover, to the best of our knowledge there is no work dealing with the environmental sustainability of an autonomous solar photo-Fenton plant, at semi-industrial scale, treating real pharmaceutical effluent that contains micropollutants.

To this end, this work examines the environmental sustainability of a semi-industrial autonomous solar compound parabolic collector (CPC) plant, based on solar photo-Fenton process assisted with ferrioxalate. The CPC plant operates under Mediterranean climatic conditions, in Ciudad Real, Spain. Real life cycle inventory (LCI) data was collected for the construction, operation and end-of-life of the CPC plant and the life cycle assessment (LCA) methodology was employed.

Results were analysed using both IPCC 2013 and ReCiPe life cycle impact assessment (LCIA) methods. The first is a single issue environmental impact assessment method based on CO_2 equivalent (CO_{2eq}) emissions and thus it is easier understood by decision and policy makers and the general public (Ioannou-Ttofa et al., 2016; Chatzisymeon et al., 2016). The latter is a state of the art method that is harmonised in terms of modelling principles and choices and offers results at both the midpoint and endpoint level (Goedkoop et al., 2009). It is the most recent and harmonized indicator approach in LCIA, which transforms the long list of LCI results into eighteen midpoint and three endpoint indicators, to express the relative severity on an environmental impact category (PRé Consultants 2017).

2. Material and methods

2.1 Description of the solar CPC autonomous unit

A semi-industrial solar compound parabolic collector (CPC reactor) treatment unit is examined herein. It is installed on the premises of the University Castilla-La Mancha in Ciudad Real, Spain. The CPC plant operates under the Mediterranean climatic conditions, where abundant sunlight is available (mean solar intensity 30 W/m^2) and is able to treat 0.7 m^3/h of aqueous effluent, operating under a continuous mode. It consists of borosilicate glass tubes (total volume 350 L), a continuously stirred reservoir tank (1500 L), a centrifugal pump and connecting tubes and valves. The CPC unit is equipped with 277 W mono-crystalline PV panels, mounted on a fixed south-facing (tilted to 39º) platform, while solar power storage is accomplished by means of a battery bank, as to provide a constant stream of electricity. Among others, the CPC plant can efficiently treat pharmaceutical wastewater at semi-industrial level, by means of the ferrioxalate-assisted solar photo-Fenton process. A description of the semi-industrial autonomous CPC plant can be found in (Expósito et al., 2016). It has to be noted that the CPC plant comprise part of a larger system that includes a 132 litre artificial ultraviolet (UV-C and UV-A) reactor, which can be used in tandem with the CPC or independently. The above system has been design to operate at standalone mode, i.e. without the need of electricity inputs from the local electrical grid, using ten 277 W PV panels and twelve 1.92 kWh battery units.

2.2 Materials

Industrial wastewater, which originated from a nearby pharmaceutical laboratory, was treated in the CPC reactor. The effluent's initial conditions were COD = 3,875mg/L, TOC = 1,914 mg/L, pH = 6.57, and turbidity=26.3 NTU. The wastewater also contained micropollutants, i.e. antipyrine=389 mg/L. The detailed physicochemical characteristics can be found in Exposito et al. (2016). It is generally accepted that a process train comprising

aerobic/anaerobic biological secondary treatment and AOPs for tertiary treatment is a viable option to effectively treat industrial wastewaters (Chatzisymeon et al., 2013; Ioannou-Ttofa et al., 2017). As such, light-driven AOPs perform better for tertiary treatment applications and therefore should be used after the secondary treatment is achieved. Hence, the pharmaceutical wastewater that was examined in this work was first diluted with tap water to reduce its initial TOC content to 400 mg/L, in order to simulate a secondary-treated effluent. The chemical reagents required for the treatment process were Merck's analytical grade ferrous sulfate ($FeSO_4.7H_2O$), oxalic acid $(COOH)_2.2H_2O$ and 30% w/v hydrogen peroxide (H_2O_2). Also, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used to adjust the pH to desirable levels, i.e. keep it constant at 2.7, as required.

3. Environmental sustainability analysis

In order to assess the environmental performance of the semi-industrial autonomous CPC plant, the life cycle assessment (LCA) methodology, as set in ISO 14040 (ISO, 2006a) and 14044 (ISO, 2006b) was employed. The LCA's geographical coverage refer Spain, the Mediterranean basin and areas with similar climate conditions (in all experiments the mean solar intensity was ~30 W/m^2). Where required background data (e.g. raw materials, fuel, electricity etc.) for Spain were used, while if they were not available European or, in their absence, global data were used as proxies. Finally, average technology was assumed.

3.2 Functional unit

The environmental performance of the ferrioxalate assisted homogeneous solar photo-Fenton process, to treat both the organic content and target pharmaceuticals, was examined. For this reason, the removal of the total organic carbon (TOC) as well as antipyrine, a typical pharmaceutical that acts as a micropollutant in wastewater matrices, was monitored. Therefore,

161 the functional unit that better corresponds to the goal and scope of this work is the effective
162 treatment of 1 m^3 of secondary-treated, in this case diluted, real industrial wastewater,
163 containing pharmaceuticals. Effective treatment corresponds to CPC plant optimal operation
164 conditions, i.e. total removal of antipyrine and at least 79% of effluent TOC or mineralization
165 of 81.3 mg/L of antipyrine and removal of 316 mg/L of TOC. This can be achieved after 120
166 min of treatment in the presence of 2,500 mg/L H_2O_2 and 20 mg/L Fe.

167 **3.3 System boundaries**

168 Figure 1 shows the LCA system boundaries, i.e. the smallest elements (unit processes)
169 considered in LCI analysis for which input and output data were quantified (ISO, 2006b). As
170 shown in Figure 1, all main materials for CPC plant construction, land use, energy usage and
171 other important inputs (e.g. chemical reagents) and outputs (e.g. waterborne emissions), as well
172 as the disposal/recycling after the end of the plant's life cycle, are included in this work.
173 Disposal/recycling was taken into account by assuming the recycling of plant's main
174 parts/materials (e.g. glass, aluminium, plastics etc.) and the disposal of the non-recycled parts
175 (e.g. pH meter, flowmeter etc.), as inert waste, at a sanitary landfill. Moreover, the
176 transportation of the main construction materials and of the chemical reagents was taken into
177 account, while the transport and the pre-treatment (i.e. dilution) of the real industrial
178 wastewater is beyond of the scope of this work and therefore is external to system boundaries.
179 Finally, since various routes for the final disposal/reuse of the treated effluent exist, e.g.
180 disposal at natural waterbodies, reuse for irrigation purposes, etc., each with its own
181 environmental impact/benefit, the discharge route of the treated effluent is beyond the scope of
182 this work and therefore is not included in the system boundaries, i.e. a cradle-to-gate
183 (treatment) approach is used.

184

Figure 1

3.4 Assumptions and limitations

The following assumptions and limitations were taken into account. It is assumed that the life span of the pilot plant is 20 years, with a 10 h daily operation all year round. The useful operating life of the solar PV units is estimated at 20-25 years, while the lifespan of the battery bank is assumed to be 15 years (i.e. it will be replaced once during the pilot plant's life span). Since, pumps were not identified in proprietary LCI databases or in the literature its main material, i.e. its motor, was taken into account, having a useful operating life of 15 years, when operating 5,000 hours annually (AAB, 2002); hence the pump will be replaced once during the CPC plant's life span. Replacement of the pipping was not considered, since according to (Ioannou-Ttofa et al., 2017) they exhibit a very high lifespan, i.e. 50 years. Moreover, it was assumed that the useful life span of the CPC photoreactors is 10 years and therefore they will be replaced once. Moreover, a mean transportation distance of 200 km, i.e. from Spain's capital Madrid to Ciudad Real, was ascribed to all materials/equipment/chemical reagents, by means of a lorry truck. Recycling was taken into account by assuming a 70% of the recyclable materials to be recycled (e.g. metals, glass etc.) and the remaining content to end up in a sanitary landfill. As mentioned above the CPC plant comprises part of a larger system and as such the solar PVs and battery bank have been design to meet the needs of the whole system. Since, the CPC plant requires only a fraction of the installed solar power and battery bank capacity, it was assumed that two 277 W PV panels and two 1.92 kWh battery units can meet the CPC plant electricity needs (Table 1). Finally, extraordinary conditions, such as natural disasters and weather extremes, are external to system boundaries.

3.5 Life cycle inventory of CPC plant

As mentioned above, the cradle-to-gate (effluent treatment) life cycle inventory (LCI) of the CPC pilot plant was built using real data from its construction, operation and end of life phase. The LCI was then simulated using the software program SimaPro to estimate the environmental sustainability of the CPC plant. Most unit processes were taken directly from SimaPro's proprietary LCI database (e.g. ecoinvent), while in cases where unit processes were not identified in proprietary databases their LCI was taken from the literature. Specifically, since LCI data for the lead-acid rechargeable battery (Sonnenschein A600 Solar Battery, A602-960S (8 OPzV 960)) was not identified in SimaPro's LCI databases, its LCI was built following (Jülch et al., 2015). For PV panels (Atersa A-277P) data from SimaPro LCI databases was used, assuming that single-Si panels were installed. The LCIs of flowmeter and pH meter were built using data for their main materials, according to our previous publication (Ioannou-Ttofa et al., 2017). The LCI of the CPC photoreactors was created using ecoinvent's LCI data for borosilicate glass tubes. The LCI of polypropylene (PP) pipping system was built following the methodology described in Ono et al. (2015) (Ono et al., 2015), while for the case of PP tank LCI data from SimaPro databases referring to its main material, i.e. PP, was used. LCI data for the pump under study was not identified. Therefore, LCI data for its main part, i.e. motor, was taken from the literature (AAB, 2002) and re-scaled to fit the rated output of the pump under study. The LCI of the chemical reagents was either taken from proprietary databases or from the literature. Specifically, ferrous sulfate was taken from SimaPro's proprietary LCI databases, in the form of iron sulphate ($FeSO_4$).After treatment theferrous and ferric ion waterborne emissions were taken from SimaPro's proprietary LCI databases, in the form of iron. Hydrogen peroxide, sulfuric acid and sodium hydroxide were also taken by proprietary LCI databases, but no waterborne emissions were taken into account, since H_2O_2 is fully consumed during the photo-Fenton reaction. Oxalic acid was not identified in existing LCI

234 databases and therefore it was built using LCI data from the literature (Raibeck, 2008).
235 Similarly, waterborne emissions were not taken into account, since oxalic acid is also fully
236 consumed during the photo-Fenton reaction. Table 1 summarizes the LCI of the solar driven
237 autonomous CPC plant, including its waterborne emissions.

238

239 Table 1

240 **3.6 Life cycle impact assessment**

241 The life cycle impact assessment (LCIA) is one of the most important stages in the
242 LCA, since in this stage the collected inventory data are associated with specific environmental
243 impacts/damages and also these impacts/damages are analysed and assessed. According to ISO
244 14040:2006 and ISO 14044:2006, LCIA consists of the following (a) mandatory elements: (i)
245 selection of impact categories, category indicators and characterization models; (ii)
246 classification, i.e. assigning inventory data to selected impact categories; and (iii)
247 characterization, i.e. modelling the inventory data within impact categories; and (b) optional
248 elements: (iv) normalisation, i.e calculate the magnitude of category indicator results relatively
249 to reference information; (v) grouping, i.e. impact categories sorting/ranking; (vi) weighting,
250 i.e. converting/aggregating indicator results across impact categories; and (vii) data quality
251 analysis, i.e. better understanding the reliability of the collection of indicator results (e.g.
252 sensitivity analysis) (ISO, 2006a; ISO, 2006b). Here, both mandatory and optional LCIA
253 elements were considered.

254 Moreover, results can be expressed at: (a) midpoint level (problem-oriented approach),
255 where environmental impacts are examined earlier in the cause-effect chain and are translated
256 into environmental themes, such as climate change and human toxicity and (b) endpoint level
257 (damage-oriented approach), where impacts are examined at the end of the cause-effect chain,

after midpoint is reached, thus translating environmental impacts into issues of concern, such as damage to human health and to ecosystem quality (Goedkoop et al., 2009). Due to data gaps and assumptions stacking up along the cause-effect chain, the endpoint approach is associated with higher levels of statistical uncertainty, but is easier to comprehend by policy- and decision-makers (Chatzisymeon et al., 2016). Therefore, in order to obtain a comprehensive overview and in-depth understanding results were analysed both at mid- and end-point level using ReCiPe impact assessment method, the successor of Eco-indicator 99 and CML-IA method (PRé Consultants 2017). ReCiPe comprises 18 midpoint impact categories, i.e. climate change (CC), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF), terrestrial ecotoxicity (TET), freshwater ecotoxicity (FET), marine ecotoxicity (MET), ionising radiation (IR), agricultural land occupation (ALO), urban land occupation (ULO), natural land transformation (NLT), water depletion (WD), mineral resource depletion (MRD), fossil fuel depletion (FD). At the endpoint level, most of these midpoint impact categories are further converted and aggregated into three endpoint categories, i.e. damage to human health (HH), damage to ecosystem diversity (ED) and damage to resource availability (RA) (Goedkoop et al., 2009).

The Hierarchist (H) perspective, which is a consensus model based on the most common policy principles, with regard to time frame and other issues, was used (Foteinis & Chatzisymeon, 2016; Goedkoop et al., 2009). Moreover, the attributional LCA (ALCA) approach was selected over the consequential LCA (CLCA), since it provides a description of resource flows and emissions attributed to the functional unit (Foteinis & Chatzisymeon, 2016), which corresponds to the goal and scope of this work. Finally, a single issue impact assessment method, namely IPCC 2013 for a timeframe of 100 years, was used. It compares processes based on CO_2 equivalent (CO_{2eq}) emissions, i.e. greenhouse gas (GHG) emission, used to

283 measure Global Warming Potential (GWP), which is a standard indicator of environmental
284 relevance (Chatzisymeon et al., 2013). This is also included in ReCiPe's midpoint impact
285 category "Climate Change", but using a single issue method allows a more simple and direct
286 results dissemination to the general public.

287

288 ## 4. Results and discussion

289 ### 4.1 Carbon footprint using IPCC 2013 impact assessment method

290 The carbon footprint of the ferrioxalate assisted homogeneous solar photo-Fenton process,
291 carried out in the CPC plant, was first estimated using the IPCC 2013 impact assessment
292 method, with a 100 years timeframe. Figure 2 shows IPCC 2013 results and the contribution
293 of each process (e.g. battery bank, PV panel, CPCs, chemical reagents etc.) to the total GHG
294 emissions. Specifically, it was found that the total GHG emissions per functional unit, i.e. for
295 treating 1 m^3 of industrial wastewater containing pharmaceuticals, was 2.71 kg CO_{2eq} m^{-3}.

296

297 Figure 2

298

299 As shown in Figure 2, the main contributor to the total CO_{2eq} emissions per functional unit,
300 i.e. the treatment of 1m^3 of pharmaceutical industry wastewater, is the use of chemical reagents
301 (92.4% or 2.5 kg CO_{2eq} m^{-3}). This large contribution and is mainly attributed to H_2O_2 (62.3%
302 or 2.5 kg CO_{2eq} m^{-3}) consumption, followed by oxalic acid (14.6% or 0.395 kg CO_{2eq} m^{-3}) use.
303 Sulfuric acid (H_2SO_4) has a much smaller contribution on the total GHG emissions (2.25 %),
304 whilst sodium hydroxide (NaOH) contribution is negligible. It should be noted that the H_2O_2
305 and the oxalic acid are assumed to be totally consumed in the solar Fenton reaction, thus no

306 waterborne emissions are produced. Moreover H_2SO_4 and NaOH are used for pH adjustment
307 during the solar Fenton process, with the latter being used only at miniscule quantities and only
308 when the pH drops below 3, thus having negligible CO_{2eq} emissions. Moreover, small
309 quantities of $FeSO_4.7H_2O$ are used, which is a non-toxic or mutagenic metal, and therefore its
310 contribution to the total CO_{2eq} emissions is miniscule. Finally, the chemical reagents
311 transportation has an overall high contribution, about 13.15%, to the total carbon footprint.
312 This is mainly attributed to the overall high quantities of H_2O_2 and oxalic acid per functional
313 unit and that their transportation distance was assumed to be 200 km.

314 The PV panels and battery bank, which provide a constant stream of electricity, contributes
315 1.03% and 1.07 % on the total carbon footprint, respectively. This small contribution is mainly
316 attributed to the low energy inputs per functional unit, compared to the large quantities of
317 chemicals used. As far as the remaining processes are concerned the foundation, the frame and
318 the CPC unit contribute, as materials, by 1.55 %, 0.988% and 2.05 % to the total CO_{2eq}
319 emissions, respectively. Moreover, the storage tank (0.29%), the pipping (0.41%), the sensors
320 (<0.06%) and the pump (0.09%) exhibit very low scores, as materials. The low contribution of
321 the above is attributed to (i) their long life span, i.e. no need or limited replacement during the
322 treatment plant's life cycle, (ii) their overall low quantity per functional unit, (iii) the fact that
323 their main materials are not associated with detrimental effects to the environment and human
324 health and (iv) that recycling was taken into account. Therefore, the main environmental
325 hotspot of the CPC plant, operating at semi-industrial level and using real pharmaceutical
326 effluent, is grossly traced back to the chemical reagents required to enhance the treatment
327 efficiency and specifically to H_2O_2 and to a smaller degree to oxalic acid.

328

329 **4.2 ReCiPe impact assessment method**

330 ReCiPe is a robust multi-issue impact assessment method and therefore it can provide a
331 more holistic overview of the environmental sustainability of the solar photo-Fenton process.
332 First, ReCiPe characterisation model (midpoint-oriented indicators) is used to calculate the
333 contribution of each parameter to each of the 18 midpoint impact categories. As shown in
334 Figure 3, the main contributor to most impact categories is, by far, the chemical reagents used,
335 which is consistent with the IPPC 2013 LCIA method. The PV modules have a generally low
336 contribution to most impact categories, apart from the ecotoxicity related impact categories,
337 i.e. TET, FET and MET, where it yields a high score. The battery bank has a similar
338 contribution to the PV modules in most impact categories, but it does not yield a very high
339 score on the ecotoxicity related impact categories. The CPC units contribute to all impact
340 categories, but with a small score in all of them. This is also the case for the foundations, the
341 frame and the pump, which exhibit an overall low contribution to most impact categories. Land
342 use is the major contributor to the impact category Urban Land Occupation (ULO), which is
343 the only impact category affected by land use. This is attributed to the fact that CPC plant
344 occupies urban area for at least 20 years according to its life span (Figure 3).

345

346 Figure 3

347

348 After characterization, midpoint results were normalized, using Europe's reference
349 inventories, and results are shown in Figure 4. The normalized midpoint impact categories that
350 yielded, by far, the highest scores are marine ecotoxicity (MET) closely followed by freshwater
351 ecotoxicity (FET). The main contributor to these categories is the chemical reagents used
352 (mainly H_2O_2), followed by the PV panels and to a smaller degree the battery bank. The
353 reagents are also mainly responsible for the large normalized scores in the impact categories,

354 from higher to lower score, natural land transformation (NLT), freshwater eutrophication (FE),
355 human toxicity (HT), fossil fuel depletion (FD), terrestrial acidification (TA), mineral resource
356 depletion (MRD), particulate matter formation (PMF), climate change (CC) and photochemical
357 oxidant formation (POF). The remaining impact categories exhibit a low to negligible
358 normalized score (Figure 4). The high normalized scores that derive from the use of chemicals
359 can be mainly attributed to the large quantities of H_2O_2 and to a smaller degree to oxalic acid.
360 H_2O_2 is a strong oxidising agent that is widely used as a bleaching agent. At industrial level it
361 is produced by reducing alkyl anthraquinones with hydrogen, in the presence of a catalyst to
362 the hydroquinone, while crude H_2O_2 is extracted from the oxidised working solution by treating
363 with water. Large quantities of energy (mainly fossil fuels) and resources (e.g. water, bauxite,
364 sulphur, etc) are consumed for the production of pure H_2O_2, while also airborne (e.g. dust, CO_2,
365 SO_x, etc), waterborne (e.g. COD, suspended solids, Cl^-, etc) emissions and solid waste (e.g.
366 mineral, slags/ash, inert chemical, etc) are produced (Boustead & Fawer, 1996). This is also
367 the case for oxalic acid production, where large quantities of energy (mainly fossil fuels) and
368 resources (mainly water) are required and also air, water and soil emissions (mainly airborne)
369 are generated. Apart from the direct pressure from raw material consumption and air, water
370 and soil emissions from their production process, a large part of their environmental impact is
371 traced back to energy use, i.e. fossil fuel. For example, airborne emissions (e.g. nitrogen oxides)
372 attributed to power generation from fossil fuel combustion have a negative impact on human
373 health, while phosphate waterborne emissions from fossil fuel extraction negatively affect
374 freshwater ecosystems (Ioannou-Ttofa et al., 2017). Moreover, large areas of natural land are
375 transformed for the extraction, transportation, storage and burning of fossil fuels to produce
376 electricity, thus affecting the impact category NLT, while the fossil fuel burning contribute to
377 their depletion (impact category FD). Also, fossil fuels are consumed for the transportation of
378 the chemical reagents from the place of production to the CPC plant. Therefore, the large

quantities of H_2O_2 and to a smaller extent oxalic acid that are consumed during the solar photo-Fenton process yield the high normalized scores on the aforementioned impact categories.

Moreover, the high normalized scores of the PV modules and to a smaller degree of the battery bank on MET and FET (Figure 4) are attributed to their manufacturing processes, which are responsible for metal emissions (e.g. copper) to the environment. Freshwater and marine ecosystems are very sensitive to metal waterborne emissions, since metals can cause major changes on these ecosystems (Ioannou-Ttofa et al., 2017).

Figure 4

Figure 5 shows the ReCiPe weighted results at endpoint level, using the damage categories human health (HH), ecosystem diversity (ED) and resource availability (RA). Results were expressed using the Hierarchist version, with European normalization and average weighting, which is ReCiPes' default endpoint method. Weighting is an optional step in the LCIA, after normalisation, where the normalised results are multiplied by weighting factors corresponding to each impact category. Weighted results are expressed in Eco-Indicator points (Pt), where 1000 Pt is the yearly environmental load of an average European citizen. As shown in Figure 5 the total environmental footprint of the ferrioxalate assisted homogeneous solar photo-Fenton process is 286.55 mPt per treatment of 1 m^3 of pharmaceutical industry wastewater. Specifically, the damage category HH exhibits the highest score (122.36 mPt), followed by RA (110.09 mPt), while ED has the lowest score (54.10 mPt). Similarly to midpoint level, the main contributor to all damage categories is traced to the reagents (91.66%) required to enhance treatment efficiency, with H_2O_2 being the main contributor (59.2%), owing to the high quantities required per functional unit, followed by oxalic acid (14.1%). As mentioned above

403 the resources and energy required for reagents manufacturing, as well as direct emissions from
404 their manufacturing process strongly affect the environmental sustainability of the CPC plant,
405 since large quantities of H_2O_2 and oxalic acid are required per functional unit. H_2SO_4
406 contributed 6.05% on the total environmental footprint, while $FeSO_4.7H_2O$ and NaOH had a
407 very low and a miniscule contribution, respectively. Chemical reagents transportation
408 contributed about 12% on the total environmental footprint. Moreover, in all damage categories
409 the CPCs, as materials, exhibited a small contribution (1.99%), followed by the foundations
410 (1.24%) and the frame (1%). The land use (0.5%) contributes to the damage category ED, due
411 to the industrial land occupied by the plant during its life span. The score of the foundations
412 and frame to all damage categories is associated with emissions from the extraction and
413 processing, as well as the energy required for the production of cement, steel and aluminium.
414 The pump, tank, sensors and pipping have an overall low contribution to all damage categories,
415 due to their high life span, non toxic, non mutagenic and non carcinogenic nature of their main
416 materials, and the small input per functional unit.

417

418 Figure 5

419

420 The results of this work are in agreement with the study of Rodríguez et al. (2016) where
421 the environmental sustainability of the homogenous Fenton processes for the treatment of
422 pharmaceutical wastewater was examined. It was observed that apart from the metal ion-
423 containing sludge generated during the treatment, which is not generated here, the next
424 environmental hotspot was the use of chemicals, with the contribution of the H_2O_2 being clearly
425 higher than the other chemicals (Rodríguez et al., 2016). Nonetheless, at bench and pilot scale
426 results vary. Giménez et al. (2015) studied, among others, the environmental sustainability of

427 the photo-Fenton process at laboratory scale, using as a functional unit the removal of 30−50%
428 TOC from 1 L of 50 mg·L−1 metropolol aqueous solution. Since, this study was based on
429 laboratory scale results an average value of 6 g/L Fe^{2+} and an average value of 90 g/L of H_2O_2
430 was taken into account. It was found that the strongest environmental impacts were always
431 associated with energy consumption, while the impact of producing and delivering the
432 chemicals was more than 2 orders of magnitude lower than that of energy consumption
433 (Giménez et al., 2015).

434 Moreover, Ttofa et al. (2017) examined the environmental sustainability of solar photo-
435 Fenton oxidation at pilot scale, using as functional unit the treatment of $1m^3$ of secondary-
436 treated urban wastewater (initial concentrations: COD 25-27 mg L^{-1}, trimethoprim (TMP) 100
437 μg L^{-1} and ofloxacin (OFX) 100 μg L^{-1}), and the complete removal of OFX and TMP and 50
438 % of the COD. In this work also the main environmental hotspot was found to be electricity
439 consumption, while chemical use had an overall low contribution on the total environmental
440 footprint (Ioannou-Ttofa et al., 2017).

441 The underlying reason for electricity usage being the main hotspot in the lab or pilot scale
442 is mainly attributed to the fact that in these experimental set-ups the effluent that is treated is
443 usually clean water spiked with targeted pharmaceuticals or high quality treated effluent,
444 containing very low concentration of organics. Hence, in these cases very low reagent amounts
445 are required, compared to real effluent which are rich in organic matter.

446 The large contributions of the reagents, i.e. H_2O_2 and oxalic acid, to the total environmental
447 footprint observed herein is twofold. First, and more importantly, the treatment of real effluent
448 was examined here and therefore its initial organic and micropollutant load was high, thus
449 requiring high amounts of chemical reagents for its effective treatment. In general, the higher
450 the initial organic load the higher the amounts of oxidation reagents, i.e. H_2O_2 and oxalic acid,

451 are required. Therefore, when a secondary treated effluent with low organic load, such in the
452 case of existing work at bench and pilot scale, is assessed, then only a fraction of chemicals is
453 required. Moreover, in this work electricity was provided directly by a renewable energy
454 source, i.e. solar energy, which is more environmentally friendly from energy mixes based on
455 fossil fuels, such as in the case of Ioannou-Ttofa et al. (2017), which minimized electricity
456 contribution to the total environmental footprint.

457

458 **4.3 Sensitivity analyses**

459 A sensitivity analysis was carried out to examine the effect of the chemical reagents
460 concentration on the total environmental footprint and how results will be affected if the excess
461 of solar power was fed into the grid. First, the H_2O_2 concentration was kept constant at optimal
462 conditions (2,500 mgL^{-1}) and the ferrous concentration was changed. Four indicative
463 alternative peroxide/ferrous ratios were examined, in addition to the initial scenario
464 (H_2O_2/Fe=125). The examined ratios along with their treatment efficiencies are as follows: (i)
465 H_2O_2/Fe=150, TOC removal 74%; (ii) H_2O_2/Fe=90, TOC removal 65%; (iii) H_2O_2/Fe= 60,
466 TOC removal 51%, and (iv) H_2O_2/Fe=30, TOC removal 42%. The 125 H_2O_2 to iron (mg/mg)
467 ratio, which was the initial scenario that yielded a 79% TOC removal, was found to have the
468 optimal treatment efficiency. When higher or lower H_2O_2/Fe ratios are examined, then the total
469 environmental footprint is not affected, compared to the treatment efficiency which suffers
470 significant losses.

471 Another sensitivity analysis was carried out to examine how the total environmental footprint
472 would be affected if the excess of solar power was fed back into the grid. In this case, where
473 two 277 W PV modules are used, it is estimated that about 2.5 kWh/day could be fed back into
474 the local grid while the battery bank will also not be required, thus bringing down the total

environmental footprint of the solar photo-Fenton process to 275.30 mPt, or reducing it by 3.93% reduction compared to the initial scenario, where the CPC plant operates in an autonomous mode. Nonetheless, it should be mentioned that in this case the CPC plant is not as versatile and adaptable and it would not be able to be installed in remote areas. Moreover, if additional PV modules were added in the system, as to solely produce and supply electricity to the grid, then depending on the amount of solar power fed back into the grid the process could have a near zero total environmental footprint. This would not mean that the system would not produce an impact to the environment, but rather that be a trade-off between wastewater treatment and renewable energy generation would be achieved. Therefore, incorporating renewable energy sources (RES), such as solar, in photo-Fenton and in wastewater treatment in general, is a strategy that can minimize environmental impacts and lead towards sustainable and low carbon wastewater treatment.

5. Conclusions

In this work the environmental sustainability of a semi-industrial autonomous solar compound parabolic collector (CPC) plant, based on solar photo-Fenton process assisted with ferrioxalate was assessed. The CPC plant treats effluents emanating from a pharmaceutical laboratory and it operates under Mediterranean climatic conditions, in Ciudad Real, Spain. The environmental sustainability was estimated by means of the life cycle assessment (LCA) methodology. It was found that the chemical reagents used (i.e. mainly hydrogen peroxide (H_2O_2) and to a lesser degree oxalic acid) were the main contributors to almost all impact categories, with marine and freshwater ecotoxicity categories being mostly affected. Therefore, future research should focus on investigating the effect of the effluent's initial organic loading on the environmental impacts of the process. To be more specific, the higher the initial organic content, the more the

amount of chemical reagents will be required to effectively treat the effluent. As a consequence, the environmental sustainability of the process will be decreased. All in all, results of this work may be a useful tool for researchers, the industry, decision and policy makers, since the effective treatment of pharmaceuticals from real wastewater matrices is a major problem and insight on the environmental sustainability of solar AOPs could help mitigate this problem.

Acknowledgements

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List of Tables

601 Table 1.

CPC WWTP configuration			Life span
Land use	Industrial area	40 m^2	20 years
Foundations	Concrete	2 m^3	20 years
	Reinforced steel	120 kg	
Frame	Aluminium	100 kg	20 years
Hourly energy needs	Electricity	0.277 Kwh	-
Photovoltaic panel	Atersa A-277P (277W)	2 units	20 years
Battery	Sonnenschein OPzV 960 Ah (1.92 kWh)	2 units	10-15 years
pump	Pan World NH-30PI-Z-D (50W)	1 unit	15 years
Flowmeter	Yokogawa ADMAG AXF0259	1 unit	20 years
PH-meter	CRISON Multimeter 44	1 unit	20 years
Storage tank	Polypropylene (PP)	48.13 kg	20 years
Pipping system	Polypropylene (PP)	55.52 kg	20 years
Compound Parabolic Collectors (CPC)	Borosilicate glass tubes; Aluminum reflector	189.16 kg 50 kg	10 years 10 years
Reagent	**Chemical nomenclature**	**Mass concentration (mg/L)**	
Hydrogen peroxide	H_2O_2	2,500	
Ferrous sulfate	$FeSO_4.7H_2O$	20	
Oxalic acid	$(COOH)_2.2H_2O$	120	
Sulfuric acid	H_2SO_4	1,100	
Sodium hydroxide	NaOH	~10^{-3} (scarcely used, only if pH drops below 3)	
Waterborne emissions	**Chemical nomenclature**	**Mass concentration (mg/L)**	
Ferrous ion	Fe^{2+}	2	
Ferric ion	Fe^{3+}	18	

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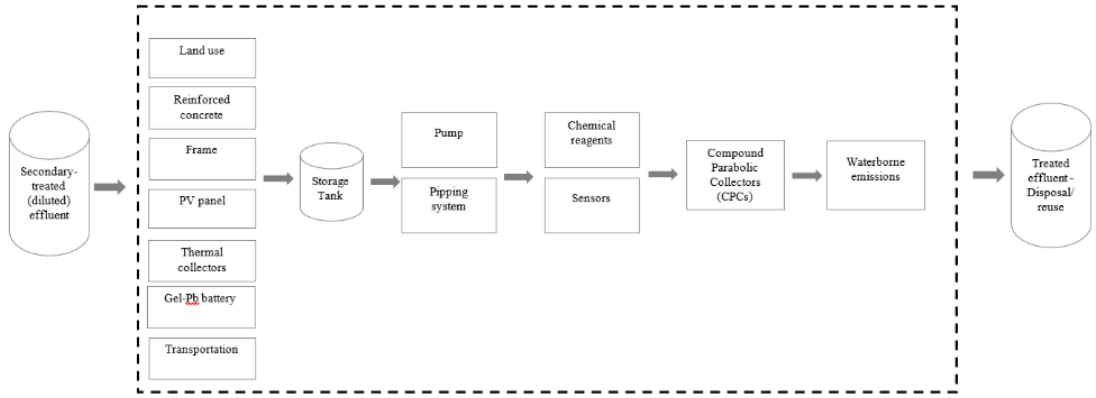
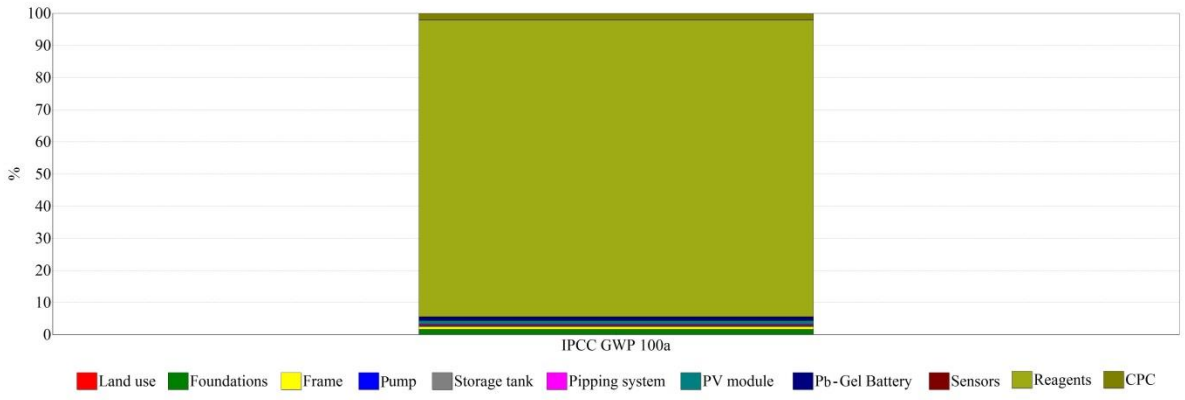


Figure 1.



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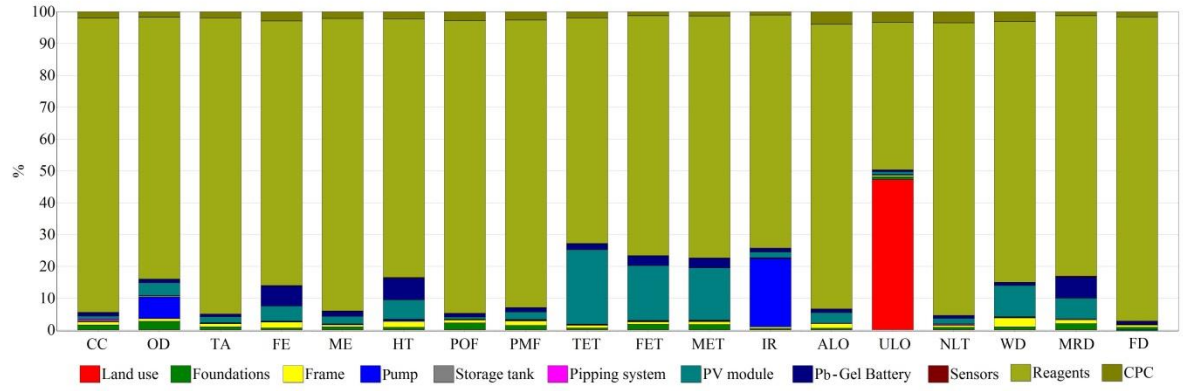

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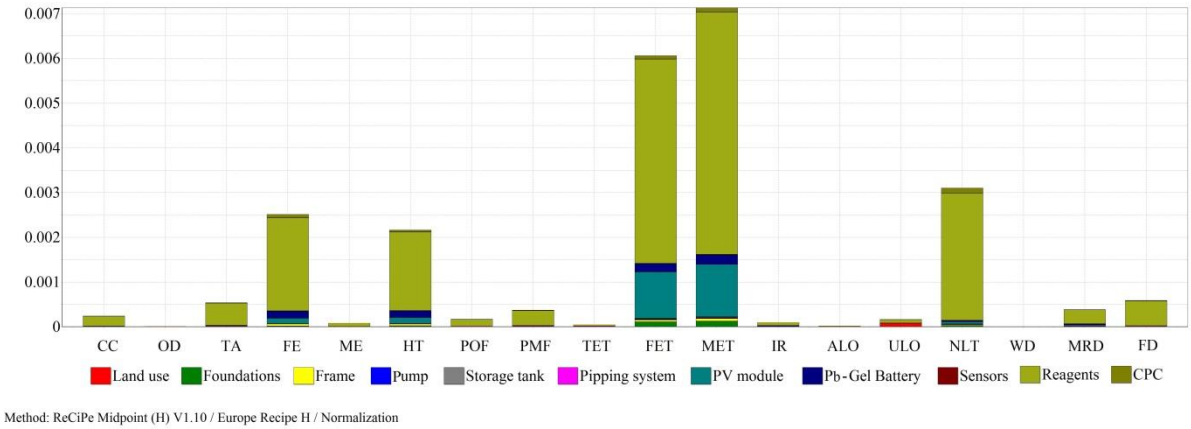

Figure 4.

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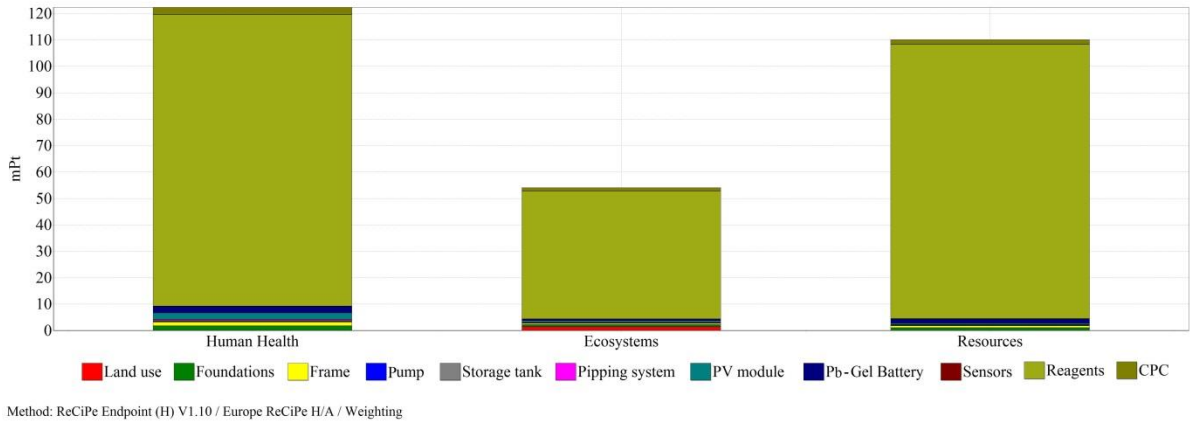

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645 Figure 5.

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