Environmental sustainability of light-driven processes for wastewater treatment applications

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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 1 μg 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%.

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

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

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

This paper describes a comparative life cycle assessment (LCA)

of seven well-established light-driven AOPs, namely: solar, solar/Fe, solar/Fe/H_2O_2, UVA, UVA/TiO_2, UVC, and UVC/H_2O_2. The aim is to identify the strengths and weaknesses of AOPs from an environmental sustainability perspective, thus enabling process scale up. LCA methodology is employed, in accordance with ISO 14040 and ISO 14044 (ISO, 2006a; b), using SimaPro 8. The assessment was made using life cycle inventory (LCI) data collected from bench-scale experiments, rather than extracted from a database. The results should provide researchers, decision- and policy-makers, and the water treatment industry with a better understanding of the environmental sustainability of light-driven AOPs, which in turn should help advance the technology so that it becomes ready for industrial-scale application. To the best of the authors' knowledge this is the first study to date dealing with LCA of several light-driven oxidation processes. Many publications focus on comparing several irradiation sources in terms of ability to decontaminate/disinfect water and wastewater. Assessment of environmental sustainability of such processes, including both solar and UV-irradiated techniques, is presently missing from the literature.

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

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 $25 \pm 2\,°C$. 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 96,000, 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, 9 W/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

Table 1
Experimental data, taken from Frontistis et al. (2011, 2012, 2015), used to build the LCI of light-driven AOPs.

Light-driven processes	Irradiation power, W	[TiO$_2$], mg/ L	Power for water stirring, W	[Fe^{2+}], mg/ L	H$_2$O$_2$, 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$_2$O$_2$	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$_2$O$_2$	11	–	30	–	10	15	100	(Frontistis et al., 2015)

14,044 (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 inventory data were collected for laboratory-scale experiments, while, for the background system, data were used regarding the most recent average technology (e.g. for electricity the average technology mix in Greece was imported from the ecoinvent database).

3.1. Functional unit

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

3.2. System boundaries and life cycle inventory (LCI)

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

For the AOPs photoreactor, LCI data could not be identified and so their primary materials, i.e. glass, lamps, and the stirrer, were taken into account. It was assumed that solar and UV photoreactors have similar dimensions and materials, and that all experiments were carried out at the same ambient temperature. Two different scenarios were examined for the solar AOPs. The first scenario comprised the photoreactor and lamp (i.e. simulated solar irradiation), whereas the second scenario did not include the lamp (i.e. natural solar irradiation). The latter scenario is closer to actual operating conditions of solar AOPs. Following Ioannou-Ttofa et al. (2017), the photoreactor glass was assigned a useful lifespan of five years (10 h/d operation, all year round). Recycling was also incorporated. Photoreactor lamps are not included in SimaPro's proprietary life cycle inventory (LCI) databases, and so the LCI data

were obtained from relevant literature (Garrett and Collins, 2009; OSRAM, 2016). The data were re-scaled according to the power requirements of each process and input to SimaPro in order to simulate the environmental impact of each lamp under study. Data on the stirrer used to mix effluent were not available in SimaPro's proprietary LCI databases, and so were substituted by relevant data concerning the LCI of a low-power motor (AAB, 2002), re-scaled to fit the rated output of the stirrer under study, and used as input to SimaPro.

Information on the Fe^{2+} ion as iron sulphate was supplied from the SimaPro LCI databases. Residual Fe^{2+} in the treated wastewater was also taken into account as waterborne emission. Data on H$_2$O$_2$ and H$_2$SO$_4$ reagents were obtained from proprietary LCI databases. Energy used to drive each process was supplied as electricity from the Greek energy grid, which is fossil fuel-dependent and comprises 54% lignite, 11% crude oil, 17% natural gas, and 18% renewable energy (Ioannou-Ttofa et al., 2017). To carry out the comparative analysis, from an environmental perspective, of light-driven AOPs, the final use and disposal route of treated effluent was taken to be external to system boundaries. In other words, cradle-to-gate (treated effluent) was used.

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; Giménez et al., 2015). Light-driven AOPs comprise a nascent technology for wastewater treatment, and so comparative environmental studies based on similar operating conditions and similar initial organic loads are needed; however, information on these important parameters is scarce.

3.4. Energy consumption

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

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

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

4. Results and discussion

To render the analysis both comprehensive and straightforward to follow, the results for the solar and UV irradiation light sources are considered separately. Then, a comparative analysis of all processes follows in order to identify the most promising result in terms of environmental sustainability. Finally, a sensitivity analysis is carried out using scenarios to investigate the effect of the main environmental hotspots and to 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 (Fig. 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
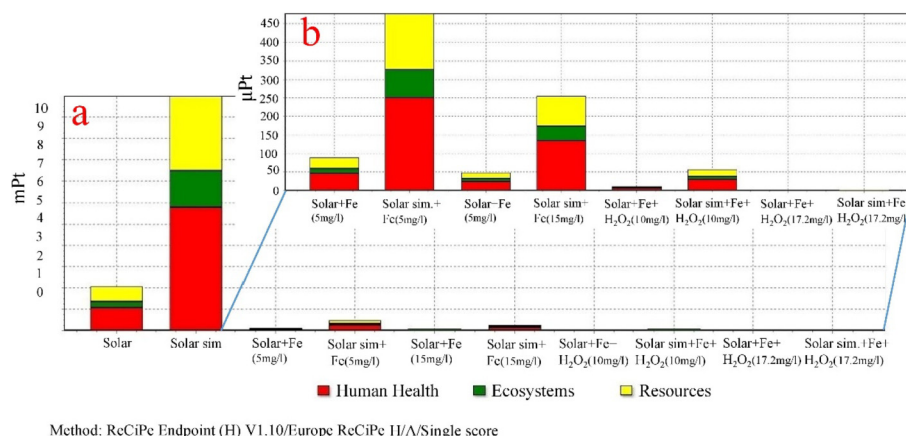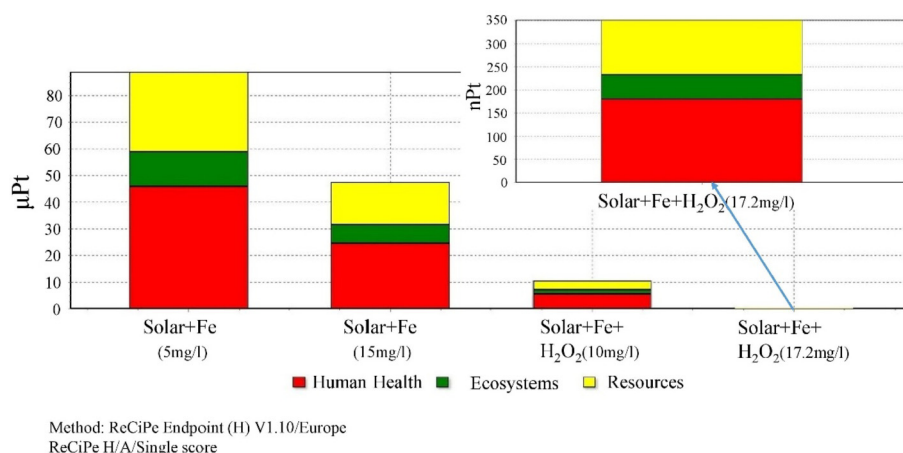

Fig. 1. Environmental footprint of natural and simulated solar (a) photolysis and (b) photocatalysis per functional unit, i.e. removal of 1 μg EE2 per liter of wastewater.

Fig. 2. Environmental footprint of natural solar photocatalysis for removal of 1 μg EE2 per liter of wastewater. Inset: environmental footprint of natural solar/Fe/H2O2 (17.2 mg/L).

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.

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. Fig. 2 shows that the amount of oxidation reagents used strongly affected the environmental sustainability of solar-driven AOPs, with high reagent concentration improving the overall environmental sustainability of solar AOPs. At low concentration of iron ions (5 mg/L Fe^{2+}) the total environmental footprint of natural solar/Fe was estimated to be 0.089 mPt, whereas when the concentration was increased to 15 mg/L the total environmental footprint reduced by about half to 0.047 mPt per functional unit (Fig. 2). When H_2O_2 was also added as a reagent, the environmental sustainability of the process was further enhanced. More specifically, when keeping the iron ion concentration constant at 5 mg/L and adding 10 mg/L H_2O_2 the total environmental footprint of the process was ~0.01 mPt per functional unit, and by increasing the H_2O_2 concentration to 17.2 mg/L the environmental footprint of the process achieved a minimum of ~0.356×10^{-3} mPt per functional unit.

This large reduction is attributed to: (a) increased degradation efficiency at higher H_2O_2 concentration (Table 1); (b) lower treatment time (15 min for 10 mg/L H_2O_2, and 1 min for 17.2 mg/L H_2O_2) and hence reduced energy consumption; and (c) use of low amounts of H_2O_2, a non-toxic chemical without elevated environmental impact. As mentioned before, the environmental impacts of

solar/Fe can be traced back to Greece's fossil fuel-dependent electricity mix used to drive the stirrer. The contributions of electricity consumption to the total environmental footprint of natural solar/Fe (5 mg/L and 15 mg/L), natural solar/Fe/H_2O_2 (10 mg/L) and natural solar/Fe/H_2O_2 (17.2 mg/L) were 87.4%, 87.3% and 86.5%. The photoreactor and the stirrer-drive motor made material contributions of $0.256 \pm 0.02\%$ and $12.35 \pm 0.05\%$. As a non-hazardous reagent when in small concentrations, Fe^{2+} had a negligible effect in all cases (its biggest score was 0.058% in natural solar/Fe/H_2O_2 (17.2 mg/L)). Similarly, the addition of miniscule amounts of H_2SO_4 in concentrations of about 50 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.

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

Fig. 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).
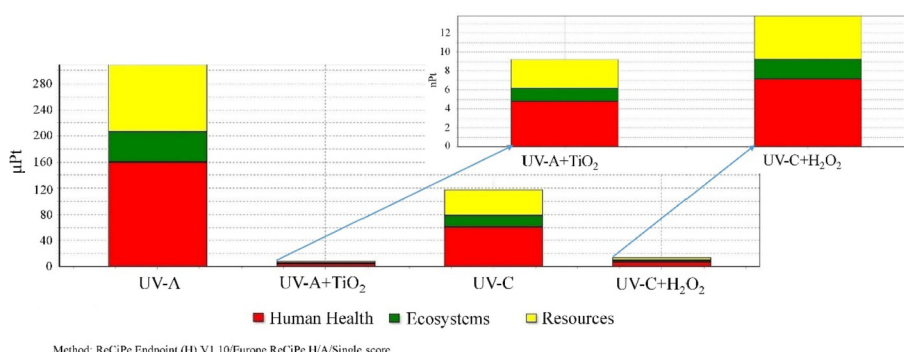
Fig. 3. Environmental footprint of UV-A and UV-C AOPs per functional unit (removal of 1 μg EE2 per liter of wastewater).

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. Fig. 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 footprint of UV-driven AOPs of $88.3 \pm 0.1\%$. 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).

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

Given that photolysis invariably exhibited the highest overall environmental footprint, the most promising photocatalytic processes were determined in terms of environmental sustainability. Fig. 4 presents a comparative analysis, using ReCiPe impact assessment method, of natural solar/Fe, natural solar/Fe/H_2O_2, UV-A/TiO_2 and UV-C/H_2O_2 photocatalysis. Natural solar/Fe/H_2O_2, at high reagent concentrations (Fe^{2+} = 5 mg/L and H_2O_2 = 17.2 mg/L) yielded the lowest score (0.356 μPt per functional unit) amongst all processes. For simulated solar irradiation, the total environmental footprint of solar/Fe/H_2O_2 rose to 1.869 μPt, but nevertheless remains substantially lower than all the other light-driven AOPs considered. Again, the presence of iron and hydrogen peroxide oxidants, the reduced treatment time and enhanced EE2 removal efficiency caused the energy demand per functional unit to be minimized, lowering the environmental footprint. The next most environmentally friendly AOPs were UV-A/TiO_2 (~9.2 μPt or ~96% higher than natural solar/Fe/H_2O_2) and UV-C/H_2O_2 (~13.8 μPt). Both exhibited relatively high treatment efficiency, with UV-A/TiO_2 requiring less treatment time to achieve EE2 removal (Table 1), which meant less energy input and a lower environmental footprint than UV-C/H_2O_2. Also, the lamp required higher energy to drive the UV-C/H_2O_2 process (11 W) than UV-A/TiO_2 (9 W). The lamps, photoreactor, and stirrer made low contributions as materials to the total environmental footprints of the UV-C/H_2O_2 and UV-A/TiO_2 processes. The contribution by the reagents, TiO_2 and H_2O_2, was miniscule compared to electricity consumption. Finally, natural solar/Fe exhibited a high overall environmental footprint, especially at low reagent concentration (5 mg/L Fe^{2+}) where the value was 0.089 mPt. For a high iron concentration (i.e. 15 mg/L), the total environmental footprint was halved, to 0.047 mPt per functional unit (Figs. 2 and 4).

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

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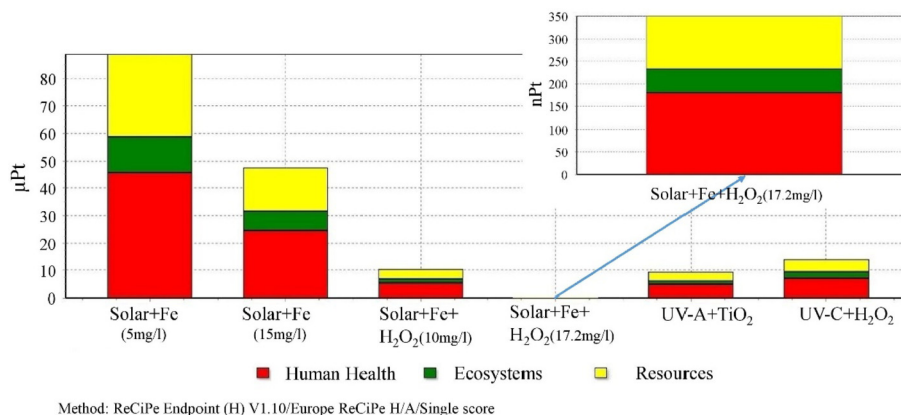

Fig. 4. Environmental footprint of natural solar, UV-A and UV-C photocatalysis for removal of 1 μg EE2 per liter of wastewater.

Table 2
Electrical energy (E_{EO}) consumed by several light-driven oxidation processes.

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	18,758	(Frontistis et al., 2015)
Solar/Fe(5 mg/L)	0.150	0.3	115	958	(Frontistis et al., 2015)
Solar/Fe(15 mg/L)	0.150	0.3	70	583	(Frontistis et al., 2015)
Solar/Fe(5 mg/L)/H$_2$O$_2$	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$_2$O$_2$	0.011	0.3	10	6	(Frontistis et al., 2015)

processes for pharmaceutical wastewater treatment).

Energy consumption to degrade 90% of EE2 was also estimated in order to undertake a more comprehensive comparative analysis of artificial light-driven oxidation processes. The corresponding treatment time was estimated either using experimental values from photocatalytic tests carried out by Frontistis et al. (2015, 2012, 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$_2$O$_2$, solar/Fe (5 mg/L)/H$_2$O$_2$, UVC, UVA, solar/Fe (15 mg/L), solar/Fe (5 mg/L) and simulated solar process. In principle, these results are consistent with those obtained from LCA (Fig. 4) confirming the high dependence of AOPs on electricity consumption.

4.4. 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$_2$O$_2$, solar/Fe, UV-A/TiO$_2$, and UV-C/H$_2$O$_2$, 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$_2$O$_2$ > natural or simulated solar/Fe/H$_2$O$_2$. Even so, it should be noted that UV-A/TiO$_2$ and UV-C/H$_2$O$_2$ exhibited similar environmental footprints when using RES.

5. Conclusions

This paper has investigated the environmental performance of light-driven AOPs at removing an endocrine disruptor, EE2, from wastewater using actual life cycle inventory (LCI) data. It was found that the environmental sustainability of light-driven AOPs was directly proportional to treatment efficiency (which was expected given that the chosen functional unit was the removal of 1 μg EE2 per liter of wastewater), and was also inversely proportional to treatment time. Moreover, electricity consumption from the fossil fuel-dependent Greek energy mix was the main environmental hotspot for all examined AOPs. The Fe^{2+}, H$_2$O$_2$, and H$_2$SO$_4$ reagents used in light-driven AOPs were associated with low environmental impacts because the chemicals did not detrimentally affect health or the eco-system, no harmful by-products were generated, and only low dosages were used. Use of RES to meet the electricity needs of light-driven AOPs substantially improved their environmental sustainability, by up to 87% for solar- and 88% for UV-driven AOPs.

References

AAB, 2002. Environmental Product Declaration for Electric Motor Type 90S 4 Pole (3GAA092001-ASC). ABB Motors A/S, Petersmindevej 1, DK-5000 Odense C.

Birnbaum, L.S., 2013. State of the science of endocrine disruptors. Environ. Health Perspect. 121, a107.

Bolton, J.R., Bircher, K.G., Tumas, W., Tolman, C.A., 2001. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems. Pure Appl. Chem. 73, 627–637.

Chatzisymeon, E., Foteinis, S., Borthwick, A.G.L., 2016. Life cycle assessment of the environmental performance of conventional and organic methods of open field pepper cultivation system. Int. J. Life Cycle Assess. 1–13.

Chatzisymeon, E., Foteinis, S., Mantzavinos, D., Tsoutsos, T., 2013. Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment. J. Clean. Prod. 54, 229–234.

Clarizia, L., Russo, D., Di Somma, I., Marotta, R., Andreozzi, R., 2017. Homogeneous photo-Fenton processes at near neutral pH: a review. Appl. Catal. B Environ. 209, 358–371.

Foteinis, S., Kouloumpis, V., Tsoutsos, T., 2011. Life cycle analysis for bioethanol production from sugar beet crops in Greece. Energy Policy 39, 4834–4841.

Foteinis, S., Monteagudo, J.M., Durán, A., Chatzisymeon, E., 2018. Environmental sustainability of the solar photo-Fenton process for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale. Sci. Total Environ. 612, 605–612.

Frontistis, Z., Daskalaki, V.M., Hapeshi, E., Drosou, C., Fatta-Kassinos, D., Xekoukoulotakis, N.P., Mantzavinos, D., 2012. Photocatalytic (UV-A/TiO2) degradation of 17α-ethynylestradiol in environmental matrices: experimental studies and artificial neural network modeling. J. Photochem. Photobiol. A

Chem. 240, 33—41.

Frontistis, Z., Kouramanos, M., Moraitis, S., Chatzisymeon, E., Hapeshi, E., Fatta-Kassinos, D., Xekoukoulotakis, N.P., Mantzavinos, D., 2015. UV and simulated solar photodegradation of 17α-ethynylestradiol in secondary-treated waste-water by hydrogen peroxide or iron addition. Catal. Today 252, 84—92.

Frontistis, Z., Xekoukoulotakis, N.P., Hapeshi, E., Venieri, D., Fatta-Kassinos, D., Mantzavinos, D., 2011. Fast degradation of estrogen hormones in environmental matrices by photo-Fenton oxidation under simulated solar radiation. Chem. Eng. J. 178, 175—182.

Garrett, P., Collins, M., 2009. Life Cycle Assessment of Product Stewardship Options for Mercury Containing Lamps in New Zealand. Final Report. Environmental Resources Management (ERM), Ministry for the Environment, New Zealand.

Giménez, J., Bayarri, B., González, O., Malato, S., Peral, J., Esplugas, S., 2015. Advanced oxidation processes at laboratory scale: environmental and economic impacts. ACS Sustain. Chem. Eng. 3 (12), 3188—3196.

Hermann, B.G., Kroeze, C., Jawjit, W., 2007. Assessing environmental performance by combining life cycle assessment, multi-criteria analysis and environmental performance indicators. J. Clean. Prod. 15, 1787—1796.

Ioannou-Ttofa, L., Foteinis, S., Chatzisymeon, E., Michael-Kordatou, I., Fatta-Kassinos, D., 2017. Life cycle assessment of solar-driven oxidation as a polishing step of secondary-treated urban effluents. J. Chem. Technol. Biotechnol. 92 (6), 1315—1327.

ISO, 2006a. ISO 14040:2006—Environmental Management — Life Cycle Assessment — Principles and Framework. International Organization for Standardization, Geneva, Switzerland.

ISO, 2006b. ISO 14044:2006—Environmental Management — Life Cycle Assessment — Requirements and Guidelines. International Organization for Standardization, Geneva, Switzerland.

Kouloumpis, V., Stamford, L., Azapagic, A., 2015. Decarbonising electricity supply: is climate change mitigation going to be carried out at the expense of other environmental impacts? Sustain. Prod. Consum. 1, 1—21.

Koutantou, V., Kostadima, M., Chatzisymeon, E., Frontistis, Z., Binas, V., Venieri, D.,

Mantzavinos, D., 2013. Solar photocatalytic decomposition of estrogens over immobilized zinc oxide. Catal. Today 209, 66—73.

Lee, C.M., Palaniandy, P., Dahlan, I., 2017. Pharmaceutical residues in aquatic environment and water remediation by TiO2 heterogeneous photocatalysis: a review. Environ Earth Sci. 76, 611.

Madsen, H.T., Søgaard, E.G., 2012. Case study of treatment of waste water for 17α-ethinylestradiol and microorganisms with UV and photocatalysis in an on-going process of introducing AOP techniques in the Danish water sector. Water Pract. Technol. 7 (4).

Marinho, B.A., de Liz, M.V., Lopes Tiburtius, E.R., Nagata, N., Peralta-Zamora, P., 2013. TiO2 and ZnO mediated photocatalytic degradation of E2 and EE2 estrogens. Photochem. Photobiological Sci. 12 (4), 678—683.

Mohagheghian, A., Nabizadeh, R., Mesdghinia, A., Rastkari, N., Mahvi, A.H., Alimohammadi, M., Yunesian, M., Ahmadkhaniha, R., Nazmara, S., 2014. Distribution of estrogenic steroids in municipal wastewater treatment plants in Tehran, Iran. J. Environ. Health Sci. Eng. 12, 97.

OSRAM, 2016. Life cycle analysis of OSRAM products. OSRAM GmbH, Hellabrunner Straße 1, D-81543 München, Deutschland.

Rochester, J.R., 2013. Bisphenol A and human health: a review of the literature. Reprod. Toxicol. 42, 132—155.

Rodríguez, R., Espada, J.J., Pariente, M.I., Melero, J.A., Martínez, F., Molina, R., 2016. Comparative life cycle assessment (LCA) study of heterogeneous and homogenous Fenton processes for the treatment of pharmaceutical wastewater. J. Clean. Prod. 124, 21—29.

Tiedeken, E.J., Tahar, A., McHugh, B., Rowan, N.J., 2017. Monitoring, sources, receptors, and control measures for three European Union watch list substances of emerging concern in receiving waters — a 20 year systematic review. Sci. Total Environ. 574, 1140—1163.

Zhang, Z., Ren, N., Kannan, K., Nan, J., Liu, L., Ma, W., Qi, H., Li, Y., 2014. Occurrence of endocrine-disrupting phenols and estrogens in water and sediment of the Songhua river, Northeastern China. Archives Environ. Contam. Toxicol. 66, 361—369.