Environmental assessment of solar photo-Fenton processes in combination with nanofiltration for the removal of micro-contaminants from real wastewaters

DOI: 10.1016/j.scitotenv.2018.09.361

Citation for published version (APA):
Gallego Schmid, A., Tarpani, R., Miralles-Cuevas, S., Cabrera-Reina, A., Malato, S., & Azapagic, A. (2019). Environmental assessment of solar photo-Fenton processes in combination with nanofiltration for the removal of micro-contaminants from real wastewaters. *Science of the Total Environment, 650*, 2210-2220. https://doi.org/10.1016/j.scitotenv.2018.09.361

Published in:  
*Science of the Total Environment*

Citing this paper
Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights
Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy
If you believe that this document breaches copyright please refer to the University of Manchester’s Takedown Procedures [http://man.ac.uk/04Y6Bo] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.
Environmental assessment of solar photo-Fenton processes in combination with nanofiltration for the removal of micro-contaminants from real wastewaters

Alejandro Gallego-Schmid, Raphael Ricardo Zepon Tarpani, Sara Miralles-Cuevas, Alejandro Cabrera-Reina, Sixto Malato, Adisa Azapagic

Sustainable Industrial Systems, School of Chemical Engineering and Analytical Science, The University of Manchester, The Mill, Sackville Street, Manchester M13 9PL, UK
Tyndall Centre for Climate Change Research, School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Pariser Building, Sackville Street, Manchester M13 9PL, UK
Solar Energy Research Centre (CIESOL), Ctra. de Sacramento s/n, Almería, Spain
Escuela Universitaria de Ingeniería Mecánica (EUDIM), Universidad de Tarapacá, Av. General Velásquez 1775, Arica, Chile
Laboratorio de Investigaciones Medioambientales de Zonas Áridas (LIMZA), Universidad de Tarapacá, Av. General Velásquez 1775, Arica, Chile
Plataforma Solar de Almería-CIEMAT, Ctra Senés km 4, 04200, Tabernas, Almería, Spain

HIGHLIGHTS
• First LCA of acidic/neutral solar photo-Fenton (SPF) with/without nanofiltration
• Coupling SPF with nanofiltration (NF) reduces environmental impacts by 24%–67%.
• Acidic SPF treatment is environmentally more sustainable than the neutral version.
• GWG of neutral SPF without NF is 3 times higher than that of the acidic version with NF.

GRAPHICAL ABSTRACT

ABSTRACT
Scarcity of water and concerns about the ecotoxicity of micro-contaminants are driving an interest in the use of advanced tertiary processes in wastewater treatment plants. However, the life cycle environmental implications of these treatments remain uncertain. To address this knowledge gap, this study evaluates through life cycle assessment the following four advanced process options for removal of micro-contaminants from real effluents: i) solar photo-Fenton (SPF) operating at acidic pH; ii) acidic SPF coupled with nanofiltration (NF); iii) SPF operating at neutral pH; and iv) neutral SPF coupled with NF. The results show that acidic SPF coupled with NF is the best option for all 15 impacts considered. For example, its climate change potential is almost three times lower than that of the neutral SPF process (311 vs 928 kg CO₂ eq./1000 m³ of treated effluent). The latter is the worst option for 12 impact categories. For the remaining three impacts (acidification, depletion of metals and particulate matter formation), acidic SPF without NF is the least sustainable; it is also the second worst option for seven other impacts. Neutral SPF with NF is the second worst technology for climate change, ozone and fossil fuel depletion as well as marine eutrophication. In summary, both types of SPF perform better environmentally with than without NF and the acidic SPF treatment is more sustainable than the neutral version. Thus, the results of...
1. Introduction

Water quality and availability are of an increasing concern in many regions worldwide, calling for a better management of water resources (FAO, 2007; OECD, 2012). An emerging but important concern is also related to the presence in surface, ground and even drinking water of micro-contaminants (also referred to as micro-pollutants) from pharmaceuticals, pesticides, hormones, personal care products and industrial additives (Geissen et al., 2015). As a result, these have recently been considered for monitoring in Europe (European Parliament, 2013). The main secondary sources of these substances in the environment are effluents from municipal wastewater treatment plants (MWTPs) (Luo et al., 2014).

Regulation related to the presence of micro-contaminants in water is in its infancy internationally, with the focus being mainly on drinking water rather than on wastewater discharge or reuse (Bui et al., 2016). An exception is Switzerland, which has set an 80% reduction target for the release of micro-contaminants from MWTPs (including primary, secondary and tertiary treatment) with any of the following characteristics (Eggen et al., 2014): i) serving capacity >80,000 people; ii) serving capacity >24,000 people and discharging into sensitive waters or drinking reservoirs; or iii) serving capacity >8000 people and a contribution >10% of the dry-weather flow in the receiving waters. This is expected to affect 123 MWTPs nationally and reduce the total load of micro-contaminants discharged to the environment by 50% (Mulder et al., 2015). However, apart from this isolated example, international regulation of micro-contaminants is unlikely to be introduced soon due to their widespread use and human health benefits. Thus, there is a need for more scientific evidence on the impacts that these substances may cause in water bodies, as well as for systematic monitoring of some of the compounds (Taylor and Senac, 2014; NRMMC, 2015).

For example, some of the regions in southern Spain have the highest water scarcity in Europe (Sabater and Barceló, 2010). Over the past years, various efforts have been undertaken in these regions to provide steady and good quality water supply for urban and agricultural uses, including through wastewater reuse (Barceló and Petrovic, 2011). Spain is particularly well placed with respect to the latter as it has the highest water reuse potential in Europe – its capacity is estimated at 1200 Mm3/yr of reclaimed water by 2025 (TVPSA, 2013). Spanish legislation (Ministerio de la Presidencia, 2007) allows water reuse for urban, agricultural, industrial, recreational and environmental uses, establishing both microbiological (e.g. Legionella sp., Salmonella sp.) and physico-chemical (e.g. metals, turbidity) limits but not for micro-contaminants. However, the presence of micro-contaminants in Spanish ground, fresh and drinking water (López-Serna et al., 2013; Camacho-Muñoz et al., 2010; Carmona et al., 2014) is a concern and could reduce the reuse potential of treated water due to bio-accumulation. Furthermore, the variability in the flow rate of Spanish rivers due to droughts and seasonal variations could increase the environmental risk from micro-contaminants since many of these compounds are released to the environment at fairly constant rates (Barceló and Petrovic, 2011; Baker and Kasprzyk-Hordern, 2013).

Therefore, challenges in the improvement of water quality and reuse potential in Spain are noteworthy among Mediterranean countries and future adoption of advanced wastewater treatment methods may be required in order to cope with the above-mentioned issues. Technical evaluations of some options for the removal of micro-contaminants, such as activated carbon and advanced oxidation processes (AOPs), have been tackled in literature, often showing promising results (Rivera-Utrilla et al., 2013). Evaluations of the economic viability of AOPs and nanofiltration (NF) have also been published (Miralles-Cuevas et al., 2016; Miralles-Cuevas et al., 2017a). Among these, integration of solar photo-Fenton (SPF) and NF has been identified as a suitable solution for reducing micro-contaminants loads from MWTP effluents (Ganiyu et al., 2015). In the case of SPF, technology developments are focused on enabling its operation at neutral pH instead of conventional acidic SPF, to avoid the need for acidification and subsequent neutralisation. Recent studies have demonstrated that this can be achieved using new iron complexing agents, such as ethylenediamine-N,N′-disuccinic acid (EDDS) (Nogueira et al., 2017; Clarizia et al., 2017). Some other challenges for this treatment include reducing the consumption of reagents and implementation of automated control systems (Romero et al., 2016; Barona et al., 2015; Miralles-Cuevas et al., 2013). Furthermore, Ganiyu et al. (2015) highlighted the need for studies on the environmental implications of these treatment methods.

Although the life cycle impacts of some tertiary methods have already been evaluated in literature, in most cases they have been based on laboratory-scale experiments (Chatzisymeon et al., 2013; Meneses et al., 2010; Muñoz et al., 2005; Muñoz et al., 2009). Muñoz (2006) assessed the environmental sustainability of SPF based on laboratory results but considering the infrastructure needed for a pilot-scaled plant. A couple of studies also considered the impacts of SPF at a pilot plant scale (Foteinis et al., 2018; Ioannou-Trofa et al., 2017). More recently, Zepon Tarpani and Azapagic (2018) compared the environmental sustainability of SPF and NF as stand-alone treatments at an industrial scale. However, no previous studies explored the potential for coupling advanced treatment options to increase the overall removal efficiency and, potentially, their environmental sustainability. Furthermore, all existing studies evaluated only the conventional SPF process operating at acidic pH.

Thus, this study goes beyond the state-of-the art in environmental evaluations of advanced treatment options to determine the life cycle impacts of SPF and NF, considering the following process options:

- i) stand-alone SPF operating at acidic pH (conventional process);
- ii) acidic SPF coupled with NF;
- iii) stand-alone SPF operating at neutral pH, mediated by EDDS as an iron complexing agent (new process currently under development); and
- iv) neutral SPF coupled with NF.

These techniques have been chosen for evaluation as the two most promising options for removal of micro-contaminants from MWTPs, as mentioned earlier (Ganiyu et al., 2015). The study is based on the data from pilot-scale plants using a real MWTP effluent. The systems considered and the related data are described in the next section.

2. Methods

The environmental impacts have been estimated through attributional life cycle assessment (LCA), following the ISO 14040/44 guidelines (ISO, 2006a, 2006b).
Fig. 1. System boundaries for the four options considered for the removal of micro-contaminants from secondary effluent. (Influent represents the effluent from secondary treatment in a municipal wastewater treatment plant. *Includes construction and decommissioning of the plant as well as electricity in the operation stage; for details see Table 1. SPF: solar photo-Fenton. NF: nanofiltration. EDDS: ethylenediamine-N,N′-disuccinic acid. EDTA: Ethylenediaminetetraacetic acid. T: transport).
2.1. Goal and scope definition

The goal of the study is to assess the life cycle impacts of using the above-mentioned options to treat secondary effluents from MWTPs containing micro-contaminants. These options are outlined in Fig. 1.

As can be seen, acidic SPF treatment involves first stripping the carbonates (HCO$_3^-$/CO$_3^{2-}$) from the secondary effluent (Fig. 1a) as they are scavengers of hydroxyl radicals and would inhibit the treatment (Pignatello et al., 2006). This is followed by acidification to a pH of 2.7–2.9, usually by sulphuric acid. The effluent is then pumped into the photo-reactor, where the low pH is needed to maintain the added iron (photo-catalyst) in solution, as it would otherwise precipitate (Pignatello et al., 2006). Hydrogen peroxide is also added to the reactor, which decomposes in the presence of iron. This reaction mechanism yields mainly hydroxyl radicals that are highly reactive and capable of oxidising nearly all micro-contaminants (Gogate and Pandit, 2004). The effluent then has to be neutralised, usually by adding sodium hydroxide. The photo-catalyst is regenerated using solar radiation and recirculated in the reactor. The latter consists of compound parabolic collectors (CPC), which allow even distribution of solar irradiation on the surface of the tube through which water is recirculated, thus achieving higher reaction rates and conversions than other photo-reactors (Malato et al., 2002).

As mentioned earlier, SPF can be operated at neutral pH by using iron complexing agents, which avoids the need for the acidification and neutralisation steps (Nogueira et al., 2017; Clarizia et al., 2017). In this work, the complexing agent considered is EDDS. As can be seen in Fig. 1c, the neutral SPF process is similar to the acidic, except that acidification and neutralisation are no longer needed due to the addition of EDDS.

The efficiency of both the acidic and neutral SPF can be enhanced by coupling them with NF, which operates with highly-pressurised water influent (1 MPa). Thereafter, the influent is passed through membranes with pore sizes of 0.1–1.0 nm, producing the permeate (treated effluent) and the concentrate with the removed micro-contaminants (Lee et al., 2009). The latter are removed primarily through physical sieving, whereby the substances with molecular weights above the membrane cut-off point (200 Da) are retained. This is followed by adsorption, electrostatic repulsion and hydrophobic interaction between the membrane and the compounds dissolved in the treated water solute (Bellona et al., 2004). The membranes have to be cleaned periodically, using sulphuric acid, sodium hydroxide, ethylenediaminetetraacetic acid (EDTA) and chlorine.

Where NF is coupled with SPF (Fig. 1bd), the effluent is first treated by NF so that a high quality permeate is obtained and discharged, and the concentrate is treated by SPF. NF also reduces the volume to be treated by SPF thus reducing the overall costs of the treatment (Miralles-Cuevas et al., 2016; Miralles-Cuevas et al., 2017a). The concentration factor of four is considered in this work.

To enable comparison of the four systems, the functional unit is defined as the ‘treatment of 1,000 m$^3$ of secondary effluent per day’. The scope of the study is from cradle to grave, encompassing construction, operation and decommissioning of the treatment plant (Fig. 1). The inventory data are detailed in the following section.

2.2. Inventory analysis

The inventory data for the four treatment options are summarised in Table 1. The primary data for the concentrations of micro-contaminants in the influent into and the effluent from the advanced treatment plants, as well as for the construction and operation of the latter, have been obtained from the pilot-plant experiments detailed in Miralles-Cuevas et al. (2017a). The pilot plant comprises a 1000 L tank, a 3-meter CPC used for SPF and two FILMTEC NF90-2540 membranes (5.2 m$^2$) used for NF; for further details on the pilot plant, see Malato et al. (2003) and Miralles-Cuevas et al. (2013). The influent into the pilot plant is the secondary effluent from the activated sludge treatment, collected from a MWTP in El Ejido in the province of Almería in Andalucía, Spain. The main physicochemical characteristics of the secondary effluent can be found in Miralles-Cuevas et al. (2017b). The MWTP serves 62,300 inhabitants and has a treatment capacity of 100,000 population equivalent (PE) with an average inlet flow of 12,500 m$^3$/day. The secondary effluent from the MWTP contains 35 micro-contaminants; for details, see Table S1 in the Supporting Information (SI). Their removal rate in the tertiary treatment plants ranges from 70%–90% (Miralles-Cuevas et al., 2017a), so the average rate of 80% has been assumed in the base case. This removal level is also a requirement in Switzerland, as mentioned in the introduction. The effect of the full range of the removal rates is considered in a sensitivity analysis.

The background data have been sourced from the EcoInvent database v2.2 database (EcoInvent Centre, 2010). The following data

| Life cycle stages | SPF acidic | SPF neutral | SPF acidic + NF | SPF neutral + NF |
|-------------------|-----------|------------|----------------|----------------|
| Construction      | Steel, reinforcing (kg) | 9.6 | 3.1 | 6.5 | 1.7 |
|                    | Steel, stainless (kg)  | 2.4 | 0.7 | 1.6 | 0.4 |
|                    | Steel, galvanized (kg) | 0.05 | 0.02 | 0.04 | 0.01 |
|                    | Steel, low-alloyed (kg) | – | 0.006 | – | 0.006 |
|                    | Aluminium, anodised (kg) | 1.5 | 0.5 | 1.0 | 0.2 |
|                    | Concrete (kg) | 247.2 | 76.7 | 163.6 | 40.4 |
|                    | Polypropylene (kg) | 0.4 | 0.1 | 0.3 | 0.07 |
|                    | Polyvinyl chloride (kg) | – | 0.1 | – | 0.1 |
|                    | Borosilicate glass (kg) | 1.0 | 0.3 | 0.7 | 0.2 |
|                    | Glass fibre (kg) | – | 0.02 | – | 0.02 |
| Operation         | Consumables | Fe$_2$(SO$_4$)$_3$ (kg) | – | – | 20.0 | 10.4 |
|                    |                        | FeSO$_4$ (kg) | 27.8 | 6.9 | – | – |
|                    |                        | Ethylenediamine-N$N$-disuccinic acid (EDDS) (kg) | – | – | 110.0 | 55.7 |
|                    |                        | H$_2$SO$_4$ (kg) | 450.0 | 112.5 | 111.3 | 65.0 |
|                    |                        | NaOH (kg) | 72.0 | 19.0 | – | – |
|                    |                        | H$_2$O$_2$ (kg) | 32.4 | 9.1 | 50.7 | 24.2 |
|                    | Cleaning               | NaOH (kg) | – | 0.25 | – | 0.25 |
|                    |                        | H$_2$SO$_4$ (kg) | – | 36.0 | – | 36.0 |
|                    |                        | Ethylenediaminetetraacetic acid (EDTA) | – | 0.25 | – | 0.25 |
|                    | Chlorine (kg) | – | 0.6 | – | 0.6 |
|                    | Tap water (L) | 1192.6 | 304.0 | 1052.3 | 257.2 |
| Membrane           | Polyester resin | – | – | 0.14 | – | 0.14 |
|                    | Acrylonitrile/formamide | – | – | 0.12 | – | 0.12 |
|                    | Polypropylene sulphide | – | – | 0.0014 | – | 0.0014 |
|                    | Polyvinyl chloride | – | – | 0.05 | – | 0.05 |
|                    | Epoxy resin | – | – | 0.03 | – | 0.03 |
|                    | Isopropanol | – | – | 0.017 | – | 0.017 |
| Energy             | Electricity (kWh) | 280 | 350 | 280 | 350 |
| Decommission       | Landfilling (metals) | 0.7 | 0.2 | 0.5 | 0.1 |
|                    | Landfilling (plastics) | 0.2 | 0.1 | 0.1 | 0.1 |
|                    | Landfilling (concrete) | 247.2 | 76.7 | 163.6 | 40.4 |
|                    | Landfilling (glass) | 1.0 | 0.3 | 0.7 | 0.2 |
|                    | Landfilling (sludge) | 10.7 | 2.7 | 10.7 | 5.6 |
|                    | Recycling (metals) | 12.4 | 3.9 | 8.3 | 2.0 |
|                    | Recycling (plastics) | 0.1 | 0.09 | 0.1 | 0.06 |
|                    | Incineration (plastics) | 0.07 | 0.04 | 0.05 | 0.04 |
| Transport          | Construction truck 16–32 t (tkm) | 52.4 | 16.3 | 34.7 | 8.5 |
|                    | Operation truck 16–32 t (tkm) | 144.0 | 44.5 | 120.3 | 69.1 |
|                    | Decommission truck 16–32 t (tkm) | 13.6 | 4.9 | 9.2 | 2.5 |

* a All data expressed per functional unit (treatment of 1000 m$^3$/day of secondary effluent).
  b Removal rate: 80% SPF; solar photo-Fenton; NF: nanofiltration.
  c Metals: 95% recycled and 5% landfilled; plastics: 50% landfilled, 34% recycled and 16% incinerated with energy recovery; concrete: 100% landfilled; glass: 100% landfilled; sludge: 100% landfilled (Monier et al., 2011; Plastics Europe, 2015; Villoria, 2014).
adaptations and assumptions have been made with reference to the data in Table 1:

- The pilot-plant data have been scaled up for a treatment capacity of 1000 m³/day as described in Miralles-Cuevas et al. (2016, 2017a).
- The treatment plant is assumed to be based in Andalucía, Spain. To reflect this, the Ecoinvent data for electricity mix in Spain have been adapted using the 2015 electricity mix in Andalucía (REE, 2017); for details, see Table S2 in the SI.
- The lifespan of the whole plant is 20 years (Bonton et al., 2012; Muñoz, 2006). The lifespan of the membranes and other NF components is 10 years (Bonton et al., 2012) while the SPF parts (CPC and glass tubes) are assumed to be replaced after 15 years (Muñoz, 2006).
- Data for the production of EDDS have been obtained from the patent of Kezerian and Ramsey (1964).
- Due to a lack of specific data, the amounts of cleaning agents and infrastructure materials for NF are based on a facility treating 2000 m³/day (Bonton et al., 2012).
- The infrastructure materials for SPF correspond to a pilot plant treating 7 m³/day (Muñoz, 2006). To scale the data to 1000 m³/day, the "economy of scale" relationship, used for scaling up the costs of process plants (Coulson et al., 1993), has been adapted as follows:

\[ C_2 = C_1 \left( \frac{C_2}{C_1} \right)^{0.6} \]

where \( C_1 \) and \( C_2 \) are the amounts of infrastructure materials for smaller and larger scale plants, respectively; \( C_1 \) and \( C_2 \) are the respective treatment capacities and 0.6 the "economy of scale" factor.

For SPF, the illuminated surface, occupied surface and the number of CPC modules needed have been calculated (see Tables S3 and S4 and Fig. S1 in the SI) as follows (Malato et al., 2003):

\[ Q_{\text{UVG,n+1}} = Q_{\text{UVG,n}} + \Delta t_n \frac{\Delta \lambda}{V_T} A_I = t_{n+1} - t_n \]

where \( Q_{\text{UVG,n+1}} \) and \( Q_{\text{UVG,n}} \) (kJ/L) represent the cumulative global UV energy per unit of volume needed to reach a particular degradation level of contaminants for the sampling times \( t_{n+1} \) and \( t_n \) respectively; \( \Delta \lambda \) is the average solar UV radiation (λ < 400 nm) between the sampling times \( t_{n+1} \) and \( t_n \); \( A_I \) (3 m²) is the irradiated surface; \( V_T \) is the total volume of the photo-reactor (35 L); and \( n \) is the sample number.

- The construction materials and consumables are assumed to be transported for 200 km by a 16–32 t Euro5 truck. Waste is transported to final disposal for 50 km, also by a 16–32 t Euro 5 truck.
- As the end of their useful lifetime, the treatment plant is decommissioned and the waste disposed based on current waste management practices in Spain for recycling, incineration with energy recovery and landfiling of construction materials (Monier et al., 2011; Plastics Europe, 2015; Villoria, 2014). The sludge from the pilot-plant is landfilled.

### 2.3. Sensitivity analysis

The influence on the environmental impacts of the following two parameters has been explored as part of the sensitivity analysis:

- variation in the removal rates of micro-contaminants; and
- different electricity mixes in different countries.

These are discussed in more detail below.

#### 2.3.1. Removal rate

As mentioned earlier, the removal rates in the treatment plants range from 70%–90% (Miralles-Cuevas et al., 2017a) and hence this range is considered in the sensitivity analysis. As the removal rate affects the sizing of the CPC modules and glass tubes, the amount of materials needed for their construction has been scaled from the base case (see Table S5 in the SI). The transport and end-of-life data have also been modified accordingly.

#### 2.3.2. Electricity mix

The electricity mix is region-dependent and can influence the overall impacts. As the location of SPF is suitable mainly in areas with abundant solar insolation, the following countries in the Mediterranean region have been selected as good candidates for the location of the treatment plant: Spain (as opposed to Andalucía considered in the base case), Italy, France, Greece, Turkey, Morocco, Algeria, Egypt, Tunisia and Israel. Their electricity mixes can be found in Table S2 in the SI. They are also relevant for analysis as the most populous countries in the Mediterranean region as well as being main agricultural producers (Eurostat, 2016; IEE, 2017; World Bank, 2017), suggesting higher generation of micro-contaminants and thus greater water-treatment needs. To simplify the analysis, only the electricity mixes which are significantly different have been assessed individually, as follows:

- Spain: the mix comprises coal (16%), natural gas (17%), nuclear (20%), hydro (15%), wind (19%) and other sources (12%). The mix considered for Andalucía (base case), is quite different, with 53% of fossil fuels (34% coal), 45% renewables (18% wind) and 2% nuclear (Table S2 in the SI). The profile for Italy is similar to that in Spain, with the main difference being a higher contribution from natural gas (33%) due to the absence of nuclear power. Hence, only the Spanish electricity mix is considered in the analysis of individual electricity mixes.
- France: the mix is mainly nuclear (78%).
- Morocco: electricity is generated largely from fossil fuels (86%), with a high contribution of coal (54%). This profile is similar in Greece (75% fossil fuels, 51% coal) and Israel (98% fossil fuel, 50% coal). Thus, the mix in Morocco is considered as representative for these three countries.
- Algeria: electricity is supplied almost exclusively by fossil fuels (99%), with the large majority being from natural gas (98%). The other Mediterranean countries have a similar electricity mix: Tunisia (96% fossil fuels, 94% natural gas), Egypt (91% fossil fuels, 79% gas) and Turkey (79% fossil fuels, 48% gas). Therefore, the Algerian mix is considered in the analysis.

#### 2.4. Impact assessment

Gabi 8.0 (Thinkstep, 2017) has been used for LCA modelling and environmental impacts have been estimated according to the ReCiPe 2008 method (Goedkoop et al., 2009). A total of 15 impact categories have been considered: climate change potential (CCP), depletion potential of fossil fuels (RDPf) and metals (RDPm), ozone depletion potential (ODP), freshwater and marine eutrophication potential (FEP and MEP), terrestrial acidification potential (TAP), freshwater, marine and terrestrial ecotoxicity potential (FAETP, MAETP and TETP), human toxicity potential (HTP), photochemical oxidants formation potential (POFP), water depletion potential (WDP), ionising radiation potential (IRP) and particulate matter formation potential (PMFP). Land use is not considered because the majority is due to the rest of the MWTP (Zang et al., 2015).

The ReCiPe 2008 method does not include characterisation factors for human and ecotoxicity related to micro-contaminants. Instead, USES-LCA 2.0 characterisation factors have been used, but they are available for only four of the micro-contaminants considered here: carbamazepine, naproxen, sulfamethoxazole and trimethoprim (Alfonsín...
| Construction | Operation: EDDS | Operation: Electricity | Operation: H2SO4 | Operation: NaOH |
|-------------|-----------------|-----------------------|-----------------|----------------|
| CCP (kg CO2 eq.) | RDPf (kg oil eq.) | RDPm x 0.1 (kg Fe eq.) | ODP x 0.1 (mg CFC-11 eq.) | FEP (g P eq.) |
| TAP x 0.01 (kg SO2 eq.) | MEP x 0.01 (kg N eq.) | FAETP x 0.01 (kg 1,4-DB eq.) | MAETP x 0.01 (kg 1,4-DB eq.) | TETP (g 1,4-DB eq.) |
| HTP (kg 1,4-DB eq.) | POFP x 0.01 (kg NMVOC eq.) | WDP x 10 (m3) | IRP (kg U235 eq.) | PMFP x 0.01 (kg PM10 eq.) |

Fig. 2. Life cycle environmental impacts of four treatment options for the removal of micro-contaminants. (All impacts expressed per functional unit (treatment of 1000 m³/day of secondary effluent). The values shown represent the total impact after the recycling credits and should be multiplied by the factor for relevant impacts to obtain the original values. The human and ecotoxities of the micro-contaminants in the treated effluent released to freshwaters include only four micro-contaminants (carbamazepine, naproxen, sulfamethoxazole and trimethoprim) as the characterisation factors for the others are not available. SFFa: acidic solar photo-Fenton, NF: nanofiltration, SFPn: neutral solar photo-Fenton, CCP: climate change potential, RDPf: fossil fuels, RDPm: resource depletion potential of metals, ODP: ozone depletion potential, MEP: marine eutrophication potential, TAP: terrestrial acidification potential, TETP: terrestrial ecotoxicity potential, HTP: human toxicity potential, POFP: photochemical oxidants formation potential, IRP: ionising radiation potential; PMFP: particulate matter formation potential, DB: dichlorobenzene, NMVOC: Non-methane volatile organic compounds).
et al., 2014). Hence, the results for these impacts should be interpreted with this in mind.

3. Results and discussion

3.1. Environmental impacts

The environmental impacts of the four treatment options considered and the contributions of different life cycle stages are presented in Fig. 2. As can be seen, neutral SPF is the worst option for 12 of the 15 impact categories, while acidic SPF coupled with NF is the best alternative for all the impacts. For the remaining two options, the picture is mixed. Neutral SPF with NF is the second worst technology for four categories (CCP, RDPf, ODP and MEP), while acidic SPF is the worst option for three (RDPm, TAP and PMFP) and the second worst for the other seven impacts (FEP, FAETP, MAETP, HTP, POP, WP and IRP); both options have similar TETP. Overall, acidic SPF is more environmentally sustainable than its neutral equivalent. Furthermore, both types of SPF have lower impacts if they are coupled with NF than if they are stand-alone. As also indicated in Fig. 2, operation of the plant is the major contributor (>70%) to most of the impacts across the options considered. Specifically, EDDS used in neutral SPF and electricity, sodium hydroxide and sulphuric acid required for acidic SPF, are the most relevant contributors to 14 impacts. The only impact category less influenced by the operation stage is RDPm, for which the construction of the plant is the most significant contributor (15%–48%). Transport is only relevant for ODP in acidic SPF (14%), with contributions below 10% to the rest of the impacts across the treatment alternatives. Finally, the decommission stage reduces most impacts due to the credits for the recycling of materials. However, these reductions are generally low (<4%), except for RDPm (3%–10%). These results are discussed further for each impact category in the following sections.

3.1.1. Climate change potential (CCP)

As indicated in Fig. 2, neutral SPF has the highest CCP, estimated at 928 kg CO2 eq./1000 m³. This is 62% higher than for its equivalent with NF (573 kg CO2 eq.) and almost three times greater than the value for the best option, acidic SPF with NF (311 kg CO2 eq.). Assuming the treatment of 1000 m³/day and the 20-year life expectancy, the total difference in CO2 eq. between the best and worst options (aceticid SPF with NF and neutral SPF, respectively) would be 4500 t CO2 eq. over the lifetime. This is equivalent to the annual greenhouse gases emitted by 2300 households (EEA, 2014) or 4000 light-duty vehicles (Winkler et al., 2014).

The EDDS and electricity consumption contribute respectively 60% and 16% to the total CCP of neutral SPF. The CO2 emissions from the burning of fossil fuels to generate the electricity consumed directly in the treatment processes and indirectly in the production of the main chemical precursors of EDDS (ethylenediamine, sodium hydroxide and maleic anhydride) are the main contributors. For neutral SPF with NF, the consumption of electricity is higher due to NF (350 vs 280 kWh/1000 m³) but the consumption of EDDS is much lower (56 vs 110 kg/1000 m³). This is the main reason for an overall reduction in the CCP compared to the option without NF. Acidic SPF has slightly lower impact than neutral SPF with NF. The benefits related to the avoidance of EDDS in acidic SPF are counteracted mainly by the higher consumption of electricity in the production of sodium hydroxide and, to a lesser extent, by the heat used in the production of sulphuric acid, as well as the material requirements for the construction of plants. For the acidic SPF with NF option, the electricity consumed for the operation of the plant is the main contributor (60%).

3.1.2. Resource depletion of fossil fuels and metals (RDP and RDPm)

The ranking of options for RDP, is the same as for the CCP, with neutral SPF being the worst alternative (338 kg oil eq./1000 m³) and acidic SPF with NF the best (89 kg oil eq./1000 m³). The reasons for that mirror those for the CPP as do the contribution trends.

The addition of NF has a positive effect on RDPm due to the reduction of the treatment volume (by a factor of four) and the corresponding reduction in the size of the SPF plant. The best option is again acidic SPF with NF (24.6 kg Fe eq./1000 m³), followed by neutral SPF with NF (33.8 kg Fe eq.). For the alternatives without NF, the worst option is acidic SPF (75.5 kg Fe eq.), mainly because it needs more CPC modules (see Table S4 in the SI) and consumes more sulphuric acid and sodium hydroxide. The impact from neutral SPF is slightly better (74.8 kg Fe eq.). The recycling of construction materials, especially metals, reduces the depletion of metals by 3%–10%.

3.1.3. Ozone layer depletion potential (ODP)

Acidic SPF with NF is the best option for this impact with 19.4 mg CFC-11 eq./1000 m³, followed by its equivalent without the NF at 41.1 mg CFC-11 eq./1000 m³. Neutral SPF is by far the worst alternative with 135.8 mg CFC-11 eq./1000 m³, mainly due to the production of EDDS (79%). Finally, neutral SPF with NF is the second worst option with 72.7 mg CFC-11 eq./1000 m³.

3.1.4. Freshwater and marine eutrophication potential (FEP and MEEP)

The high consumption of EDDS in the neutral SPF process makes it the least desirable option for FEP, with a total impact of 447 g P eq./1000 m³. This is specifically related to the life cycle of electricity (phosphate emissions to water during coal mining) used in the production of EDDS precursors. The avoidance of EDDS and lower consumption of sodium hydroxide result in acidic SPF with NF being the best alternative, with a three times lower impact (136 g P eq./1000 m³). Acidic SPF is a slightly worse alternative (301 g P eq./1000 m³) than neutral SPF with NF (263 g). The main contributor to the former is sodium hydroxide (50%) and to the latter EDDS (61%).

For MEEP, the high consumption of EDDS makes neutral SPF again environmentally the least sustainable option, with the impact estimated at 484 g N eq. This is followed by neutral SPF with 292 g N eq./1000 m³. The lowest value of 97 g N eq./1000 m³ is found for acidic SPF with NF. Finally, the same option but without NF has a 30% higher impact (139 g N eq.). For the neutral SPF options, the production of EDDS is again the main contributor, followed by the consumption of electricity in the treatment process. The most significant burdens are ammonia and nitrates emitted in the production of ethylenediamine (precursor of EDDS) and NOx from the combustion of fossil fuels during electricity generation.

3.1.5. Terrestrial acidification potential (TAP)

Acidic SPF is the worst option for TAP (8.3 g SO2 eq./1000 m³), mainly because of its high consumption of sulphuric acid. Neutral SPF has the second highest impact (5.2 g SO2 eq./1000 m³), due to EDDS and sulphuric acid. The remaining two options with NF have similar values (3.7 and 4.0 g SO2 eq./1000 m³, respectively) with the acidic SPF being slightly better. The production of sulphuric acid, mainly due to the emissions of SO2, is the main contributor to this impact for the acid treatment options (41%–71%). For the neutral treatments, electricity used in the production of EDDS is the main contributor (26%–40%).

3.1.6. Ecotoxicity (FAETP, MAETP and TETP)

Acidic SPF with NF has the lowest FAETP and MAETP (4.6 kg and 4.3 kg 1,4 DB eq./1000 m³, respectively), mainly associated with the electricity consumed in the treatment process (28% for both impacts). Neutral SPF with NF has the second best values for these two categories, but still significantly higher than for the acidic SPF version (8.7 kg and 8.1 kg 1,4 DB eq./1000 m³). The main contributor here is EDDS (58% for both impacts). The highest impacts are again found for neutral SPF (16.6 kg and 15.3 kg 1,4 DB eq./1000 m³) due to the high consumption of EDDS and hydrogen peroxide. For acidic SPF, the two impacts (12.3 kg and 11.4 kg 1,4 DB eq./1000 m³) are due to the electricity consumption
to produce sodium hydroxide and to the emissions of chromium from the manufacture of stainless steel used for the construction of the plant.

The ranking of the best and worst options for TET follows the same trend: acidic SPF with NF is the best (115 g 1.4 DB eq./1000 m³) and neutral SPF the worst (394 g 1.4 DB eq./1000 m³). The remaining two options have similar impact (229 g and 233 g 1.4 DB eq./1000 m³), with the acidic SPF process being slightly better. The main contributors are emissions of metals to soil associated with the generation of electricity used in the production of EDDS and sodium hydroxide, as well as in the treatment process.

### 3.1.7. Human toxicity (HTP)

Acidic SPF with NF is also the preferred alternative for this impact, estimated at 138 kg 1.4 DB eq./1000 m³. Neutral SPF with NF is the second best alternative (263 kg 1.4 DB eq./1000 m³), followed by acidic SPF (324 kg 1.4 DB eq./1000 m³). As for most other impacts, neutral SPF is the least sustainable with 460 kg 1.4 DB eq./1000 m³. The emission of manganese to water from the mining of coal used for electricity generation is the main contributor to HTP. Therefore, the electricity consumption in the production of EDDS, sodium hydroxide and in the operation stage is the main contributor to this impact category.

### 3.1.8. Photochemical oxidants formation potential (POPF)

Emissions of NOx from fossil fuels during electricity generation are the main contributors to POPF. Therefore, the options with the highest consumption of EDDS (neutral SPF) and sodium hydroxide (acidic SPF) have the highest impact (2.6 kg and 2.3 kg NMVOC eq./1000 m³, respectively). The alternatives with NF consume less of these chemicals and, consequently, have a lower impact. The acidic SPF version is again the best option (1.3 kg NMVOC eq.), followed closely by its neutral equivalent (1.8 kg NMVOC eq.).

### 3.1.9. Water depletion potential (WDP)

The lowest water consumption is found for acidic SPF with NF at 1165 m³/1000 m³. Neutral SPF with NF is the second best option, but with a 75% higher water consumption (2036 m³/1000 m³). Finally, both treatments without NF have more than two times (2826 m³ for acidic SPF) and three times (3626 m³ for neutral) higher water depletion than SPF with NF. Therefore, for all the four treatment options, more water is consumed along the life cycle than it is treated. This is largely due to the water consumption during electricity generation, and the production of EDDS and sodium hydroxide.

### 3.1.10. Ionising radiation potential (IRP)

Acidic SPF with NF has the lowest IRP (58 kg U²³⁵ eq./1000 m³), which is the worst option for this impact. Neutral SPF with NF is the second best treatment, (149 kg U²³⁵ eq.), followed by acidic SPF (178 kg U²³⁵ eq.). For all the technologies, the main source of ionising radiation is nuclear power present in the electricity mix.

### 3.1.11. Particulate matter formation potential (PMFP)

The treatments with NF are the best alternatives, with a similar impact of ~1 kg PM₁₀ eq./1000 m³. Neutral and acidic SPF without NF have a 50% and 100% higher impact (1.5 and 2.1 kg PM₁₀ eq./1000 m³, respectively). This impact is mainly associated with the production of sulphuric acid (15%–55%), specifically due to the emission of SO₂, which contributes to the formation of particulates. The other significant contributor is the electricity consumed in the operation (16%–43%) of the plants and in the production of EDDS for neutral treatments (29%–41%), again due to the SO₂ emissions but also due to NOx, which also contribute to the particulate formation.

### Table 2

| Impacts | SPF<sub>acidic</sub> | SPF<sub>acidic + NF</sub> | SPF<sub>neutral</sub> | SPF<sub>neutral + NF</sub> |
|---------|----------------|----------------|----------------|----------------|
|         | 80%   | 70%   | 90%  | 80%  | 70%  | 90%  | 80% | 70%  | 90% |
| CCP (kg CO₂ eq.) | 553.8 | 529.1 | 590.1 | 311.4 | 296.4 | 340.3 | 927.7 | 878.9 | 1003.9 | 572.9 | 556.7 | 604.4 |
| RDP<sub>p</sub> (kg oil) | 159.1 | 152.9 | 168.6 | 89.3 | 85.0 | 99.1 | 338.0 | 322.9 | 361.0 | 200.9 | 195.3 | 210.5 |
| RDP<sub>mf</sub> (kg Fe eq.) | 75.5 | 66.1 | 88.5 | 24.6 | 20.2 | 38.8 | 74.8 | 63.0 | 94.5 | 33.8 | 31.5 | 41.1 |
| ODP (mg SF<sub>111</sub> eq.) | 41.1 | 39.0 | 44.3 | 19.4 | 18.3 | 21.7 | 135.8 | 131.0 | 143.3 | 72.7 | 71.3 | 74.7 |
| FEP (g P eq.) | 300.6 | 293.4 | 311.6 | 136.0 | 131.3 | 146.8 | 446.9 | 430.3 | 472.4 | 262.8 | 256.8 | 273.5 |
| MEP (g N eq.) | 139.4 | 135.6 | 145.1 | 97.1 | 94.6 | 103.2 | 484.3 | 476.1 | 496.9 | 292.3 | 289.5 | 297.6 |
| TAP (kg SO₂ eq.) | 8.3 | 8.2 | 8.4 | 3.7 | 3.6 | 3.8 | 5.2 | 5.0 | 5.4 | 4.0 | 3.9 | 4.1 |
| FAETP (kg 1.4 DB eq.) | 12.3 | 12.4 | 13.5 | 4.6 | 4.1 | 5.8 | 16.6 | 15.2 | 18.8 | 8.7 | 8.2 | 9.6 |
| MAETP (kg 1.4 DB eq.) | 11.4 | 10.7 | 12.5 | 4.3 | 3.8 | 5.4 | 15.3 | 14.0 | 17.4 | 8.1 | 7.7 | 8.9 |
| TETP (kg 1.4 DB eq.) | 229.4 | 218.7 | 244.6 | 115.0 | 109.3 | 131.7 | 393.6 | 377.1 | 420.2 | 232.8 | 228.3 | 243.2 |
| HTP (kg 1.4 DB eq.) | 324.4 | 312.9 | 341.0 | 138.0 | 131.4 | 155.4 | 460.3 | 439.1 | 491.6 | 262.8 | 256.2 | 276.4 |
| POFP (kg NMVOC) | 2.3 | 2.3 | 2.4 | 1.3 | 1.2 | 1.4 | 2.6 | 2.5 | 2.8 | 1.8 | 1.7 | 1.9 |
| WDP (m³) | 2825.8 | 2631.5 | 3057.5 | 1165.1 | 1094.3 | 1310.0 | 3621.9 | 3382.7 | 4009.2 | 2035.7 | 1974.5 | 2184.0 |
| IRP (kg U²³⁵ eq.) | 178.5 | 173.3 | 186.4 | 58.2 | 54.2 | 65.1 | 287.4 | 275.9 | 305.2 | 149.4 | 145.3 | 156.7 |
| PMFP (g PM₁₀ eq.) | 2095.3 | 2056.3 | 2150.9 | 988.0 | 967.2 | 1046.7 | 1554.8 | 1491.8 | 1655.3 | 1143.9 | 1125.9 | 1183.4 |

---

*For the impacts nomenclature, see Fig. 2.*

*The values in brackets represents the percentage decrease or increase on the 80% removal rates (base case).*
3.2. Sensitivity analysis

3.2.1. Effect of removal rates

Table 2 shows the effect on the impacts if the removal efficiency of the treatment is varied between 70% and 90%. As can be seen, the most significant changes are found for RDPm, which, depending on the treatment option, decreases on the base case by 7%–18% for a 70% removal and increases by 17%–58% for a 90% removal. These variations are related to the required CPC surface which varies with the removal rate (see Table S5 in the SI); this in turn results in different amounts of materials required for the construction of CPC modules. These findings are congruent with the results presented in the previous section, showing that this impact is mostly influenced by the construction stage (Fig. 2).

The next most influenced impacts are MAETP and FAETP, which decrease by 5%–10% for the 70% removal rate and increase by 9%–27% for the removal of 90%. HTP and TETP are less affected (2%–5% decrease for 70% and 4%–13% increase for 90%). These findings may appear contrary to what could be expected as the toxicity values decrease for a lower removal rate. This is due to two effects: the lower requirements for the plant construction materials and consumables (mainly H2O2) and considerations of the impacts of only four micro-contaminants in the treated effluent released into the environment (as explained in Section 2.4). The reduction or increase of the removal efficiency implies, respectively, a reduction or increase in the amount of construction materials and consumables (see Table S5 in the SI), which affects directly MAETP, FAETP, HTP and TETP. In all the scenarios, virtually all of the variation in the toxicity-related impacts is associated with these changes. At the same time, the increase or decrease in the removal efficiency also affects those impacts, as the amount of micro-contaminants in the final effluent varies. However, the total effect of the reduction or increase in the concentration of micro-contaminants in the final effluent cannot be fully addressed due to the lack of toxicity characterisation factors for all micro-contaminants. Therefore, the conclusions on the variations in these four impact categories should be considered carefully bearing these limitations in mind.

For the remaining categories, the decrease in the impacts is <6% for the 70% removal and the increase is <12% for 90%.

However, the ranking of the alternatives remains the same across the removal rates considered. The only exception is RDPm where neutral SPF is a better option than acidic SPF for a 90% removal, but only by <6% (94.5 kg vs 88.5 kg Fe eq./1000 m³).

3.2.2. Effect of electricity mix

The effect of different electricity mixes is discussed here for climate change only (Fig. 3) as this is the impact category most affected by electricity consumption in the operation stage (Fig. 2). The effect on the other impacts can be seen in Tables S6–S9 in the SI.

As expected, situating the plants in France would lead to a significant reduction in CCP (15%–57%) on the base case (Andalucía), due to the substitution of fossil fuels by nuclear energy (Fig. 3). Operating the plants in countries with a high percentage of fossil fuels, and particularly coal, such as Algeria and Morocco, would increase the CCP by 3%–12% and 9%–33%, respectively. In the regions with more varied electricity sources and lower contribution of fossil fuels, like Spain, the reductions in the CCP range from 7% to 24%.

Overall, the different electricity mixes do not change the relative ranking of the options for any of the impacts.

3.3. Comparison of results with literature

Comparison with other LCA studies is not possible for the neutral SPF and the options combining SPF and NF as they are not available. Direct comparison of acidic SPF studies is difficult either because of the differences in the goal and scope, impact assessment methods, scale of the plant or geographical location. However, an attempt is made to compare the results for CCP with the studies found in the literature. These results are shown in Fig. 4.

Recent studies by Ioannou-Ttofa et al. (2017) and Fotelinis et al. (2018) have reported a much higher CCP than found in the present work: 8700 and 2710 kg CO2 eq./1000 m³, respectively, compared with the 554 kg CO2 eq./1000 m³ here. The difference with the study former is due to the extremely high consumption of electricity (9000 kWh/1000 m³) assumed by Ioannou-Ttofa et al., which is generated largely from coal (92.5%). The second study considered high consumption of hydrogen peroxide and sulphuric acid, about 77 and 2.4 times higher than in the present work.

On the other hand, the estimate by Zepon Tarpini and Azapagic (2018) for an acidic SPF plant in the UK is around half of the value found here (249 kg CO2 eq./1000 m³). This can be attributed to a lower consumption of sulphuric acid (3.5 times) and construction materials as well as the exclusion of electricity in the operation stage due to a lack of data. A similar difference is noticed for the other impact categories which are 1.7–3.3 higher in the present study, also attributed to the aforementioned differences in the inventory data. The only exception is terrestrial ecotoxicity which is slightly lower in the present study (233 versus 290 g 1,4 DB eq./1000 m³), due to the shorter transport distances considered.

4. Conclusions

This study has analysed for the first time the life cycle environmental performance of acidic and neutral SPF treatments coupled with NF for
the removal of micro-contaminants from real wastewaters. The results reveal that acidic SPF with NF is the best alternative for all 15 impacts considered while neutral SPF (without NF) is the worst option for 12 categories. The ranking of the alternatives is not sensitive to the variation in micro-contaminant removal rates or electricity mix. Thus, these findings demonstrate that current efforts on developing neutral SPF should instead be focused on further improvements of its acidic equivalent coupled with NF. Specifically, the consumption of electricity, sodium hydroxide, and sulphuric acid should be reduced as these are the main environmental hotspots.

For neutral SPF, the main hotspot is the complexing agent, in this case EDDS. Therefore, using different agents (e.g. oxalic acid, citric acid or nitritolacetic acid) could help reduce the impacts from neutral SPF. However, as there are no environmental studies for other complexing agents, it is not possible to corroborate this supposition at present. This could form part of future work.

Furthermore, this work has highlighted the limitations related to the lack of toxicity characterisation factors for micro-contaminants. Out of the 35 species present in the wastewater considered in the study, the characterisation factors were available for only four. This means that the toxicity impacts of the effluents released into the environment are underestimated. Therefore, future research should focus on the development of characterisation factors to enable a better understanding of the role of different micro-contaminants in human and ecotoxicity. The factors should consider in particular the toxicity effects of bioaccumulation in fish and plants and the formation of transformation products by natural hydrolysis and photolysis with higher toxicity levels than their parent compounds. This would also help to inform future development of policy on micro-contaminants and their treatment, which is currently in its infancy.

Acknowledgments

This research has been funded by the UK Engineering and Physical Sciences Research Council, United Kingdom (EPSRC; Gr. no. EP/F007132/1). Sara Miralles-Cuevas wishes to thank MINECO, Spain for the Juan de la Cierva-formación grant (No. FJCI-2016-28965). Alejandro Cabrera is grateful to FONDECYT, Chile (No. 11160680) and the Solar Sciences Research Council, United Kingdom (EPSRC; Gr. no. EP/P00686X/1).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.09.361.

Fig. 4. Comparison with the literature of change potential (CCP) for acidic solar photo-Fenton.

References

Alfonso, C., Hospido, A., Orni, F., Moreira, M.T., Feijoo, G., 2014. PPCPs in wastewater - update and calculation of characterization factors for their inclusion in LCA studies. J. Clean. Prod. 83, 245–255.

Baker, D.R., Kagrzyck-Hordern, B., 2013. Spatial and temporal occurrence of pharmaceuticals and illicit drugs in the aqueous environment and during wastewater treatment: new developments. Sci. Total Environ. 454–455, 442–456.

Barona, J.F., Morales, D.F., González-Bahamón, L.F., Pulgarín, C., Benítez, L.N., 2015. Shift from heterogeneous to homogeneous catalysis during resorcinol degradation using the solar photo-Fenton process initiated at circumneutral pH. Appl. Catal. B Environ. 165, 620–627.

Barecki, D., Petrovic, M., 2011. Waste Water Treatment and Reuse in the Mediterranean Region. Springer, London (UK), p. 306.

Bellona, C., Drewes, J.E., Xu, P., Amy, G., 2004. Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review. Water Res. 38, 2795–2809.

Bonton, A., Bouchard, C., Barbeau, B., Jedrzejak, S., 2012. Comparative life cycle assessment of water treatment plants. Desalination 284, 42–54.

Bui, X.T., Vo, T.P.T., Ngo, H.H., Guo, W.S., Nguyen, T.T., 2016. Multicriteria assessment of advanced treatment technologies for micro-contaminants removal at large-scale applications. Sci. Total Environ. 563–564, 1050–1067.

Camacho-Muñoz, D., Martín, J., Santos, J.L., Aparicio, I., Alonso, E., 2010. Occurrence, temporal evolution and risk assessment of pharmaceutically active compounds in Doñana Park (Spain). J. Hazard. Mater. 183 (1–3), 602–608.

Carmona, E., Andreu, V., Picó, Y., 2014. Occurrence of acidic pharmaceuticals and personal care products in Turia River Basin: from waste to drinking water. Sci. Total Environ. 484 (1), 53–63.

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

Clarijia, 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.

Coulson, J., Richardson, J., Sinnennt, R.K., 1993. Chemical Engineering. 2nd revised ed. Butterworth-Heinemann Ltd, Oxford (UK), p. 954.

Ecoinvent Centre, 2010. Ecoinvent v.2.2 Database. Swiss Centre for Life Cycle Inventories, Dübendorf, Switzerland.

EEA, 2014. Environmental Indicator Report 2014 – Environmental Impacts of Production-Consumption Systems in Europe. European Environment Agency (EEA), Copenhagen, Denmark. p. 95.

Eggen, R.L.I., Hollender, J., Joss, A., Schärer, M., Stamm, C., 2014. Reducing the discharge of micro-contaminants in the aquatic environment: the benefits of upgrading wastewater treatment plants. Environ. Sci. Technol. 48 (14), 7683–7689.

European Parliament, 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy Text With EEA Relevance. OJL, 226, 248.2013. pp. 1–17.

Eurostat, 2010. Agricultural production — crops. Available at:. http://ec.europa.eu/eurostat/statistics-explained/index.php/Agricultural_production_-_crops, Accessed date: 8 January 2018.

FAO, 2007. Coping with Water Scarcity: Challenge of the Twenty-First Century. Food and Agriculture Organization, Rome, Italy, p. 29.

Foteinis, S., Monteagudo, J.M., Durán, A., Chatziyiannou, 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.

Ganiyu, S.O., Van Hullebusch, E.D., Cretin, M., Esposito, G., Oturan, M.A., 2015. Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: a critical review. Sep. Purif. Technol. 156, 891–914.
2220

A. Gallego-Schmid et al. / Science of the Total Environment 650 (2019) 2210–2220

Geissen, V., Mol, H., Klump, E., Umlauf, G., Nadal, M., van der Ploeg, M., van de Zee, S.E.A.T.M., Ritsema, C.J., 2015. Emerging pollutants in the environment: a challenge for water resource management. Int. Soil Water Conserv. Res. 3 (1), 57–65.

Goeildoop, M., Heijungs, R., Huijbregts, M., De Schuyver, A., Struijs, J., Van Zelm, R., 2009. Recipe 2008. A Life Cycle Impact Assessment Method Which Comprises Harmonised Category Indicators at the Midpoint and the Endpoint Level. Ministry of Housing Spatial Planning and the Environment. The Hague. p. 132.

Gogate, P.R., Pandit, A.B., 2004. A review of comparative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Adv. Environ. Res. 8, 501–551.

IEA, 2017. Electricity and heat statistics. Available at: http://www.iea.org/statistics/statisticssearch/, Accessed date: 8 January 2018.

Ioannou-Ttofa, L., Foteinis, S., Chatzisymeon, E., Michael-Kordatou, I., Fatta-Kassinos, D., ISO, 2006a.ISO14040:2006. Environmental Management

Lee, L.Y., Ng, H.Y., Ong, S.L., Hu, J.Y., Tao, G., Kekre, K., Viswanath, B., Lay, W., Seah, H., 2009. Pharmaceuticals as emerging contaminants and their removal during wastewater treatment: Sci. Total Environ. 473–474, 619–641.

Malato, S., Blanco, J., Vidal, A., Richter, C., 2002. Photoanalysis with solar energy at a pilot-plant scale: an overview. Appl. Catal. B Environ. 37, 1–15.

Malato, S., Blanco, J., Vidal, A., Alarcón, D., Malikondo, M.I., Cáceres, J., Gernjak, W., 2003. Ozone–biological activated carbon as a pretreatment process for reverse osmosis brine treatment and recovery. Water Res. 43, 3948–3955.

López-Serna, R., Jurado, A., Vázquez-Suñé, E., Carreza, J., Petrović, M., Barceló, D., 2013. Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain. Environ. Pollut. 174, 305–315.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Total Environ. 473–474, 619–641.

Muñoz, I., Rodríguez, A., Rosal, R., Fernández-Alba, A.R., 2009. Life cycle assessment of urban wastewater reuse with ozonation as tertiary treatment. A focus on toxicity-related impacts. Sci. Total Environ. 407 (4), 1245–1256.

OECD, 2012. The OECD Environmental Outlook to 2050 - The Consequences of Inaction. OECD Publishing, Paris, France.

Pignatello, J.J., Ollivieros, E., Mackay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Environ. Sci. Technol. 36 (1), 1–84.

Plastics Europe, 2015. Plastics – The Facts 2014/2015: An Analysis of European Plastics Production, Demand and Waste Data. Plastics Europe, Brussels (Belgium). p. 34.

REE, 2017. El sistema eléctrico español. Avance 2016 [in Spanish]. Red eléctrica española, Madrid. p. 30.

Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M.A., Prados-Joya, G., Ocampo-Pérez, R., 2013. Pharmaceuticals as emerging contaminants and their removal from water. A review. Chemosphere 93 (7), 1268–1287.

Rowe, T., 2018. The Facts 2014/2015: An Analysis of European Plastics Production, Demand and Waste Data. Plastics Europe, Brussels (Belgium). p. 34.

Winkler, S.L., Wallington, T.J., Maas, H., Hass, H., 2014. Light-duty vehicle CO2 targets consistent with 450 ppm CO2 stabilization. Environ. Sci. Technol. 48 (11), 6453–6460.

World Bank, 2017, Population 2015. World development indicators database. Available at: http://worldbank.org/data/download/PDF, Accessed date: 8 January 2018.

Zang, Y., Li, Y., Wang, C., Zhang, W., Xiong, W., 2015. Towards more accurate life cycle assessment of municipal wastewater treatment plants: a review. J. Clean. Prod. 107, 676–692.

Zepon Tarpani, R.R., Azapagic, A., 2018. Life cycle environmental impacts of advanced wastewater treatment techniques for removal of pharmaceuticals and personal care products (PPCPs). J. Environ. Manag. 215, 258–272.