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

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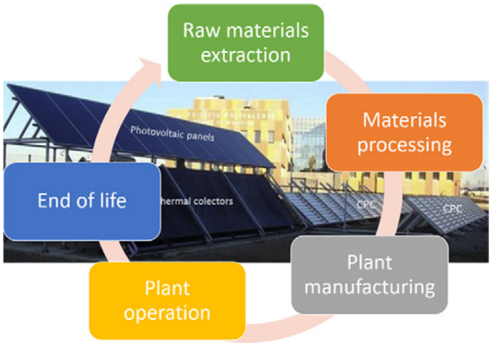
HIGHLIGHTS

- Environmental impacts of a CPC plant treating pharmaceuticals effluent were studied.
- A ferrioxalate-assisted homogeneous solar photo-Fenton treatment process was used.
- The main hotspot in all cases was the use of chemical reagents, mainly H_2O_2.
- The initial organic content (TOC) of the effluent can affect process sustainability.

GRAPHICAL ABSTRACT



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ABSTRACT

The environmental sustainability of a semi-industrial solar photo-Fenton reactor, treating real effluents emanating from a pharmaceutical laboratory, is assessed herein. The life cycle assessment/analysis (LCA) methodology was employed and real life cycle inventory (LCI) data was collected from a ferrioxalate-assisted homogeneous solar photo-Fenton wastewater treatment plant (WWTP), at Ciudad Real, Spain. Electricity was provided by photovoltaic (PV) panels in tandem with a battery bank, making the plant autonomous from the local grid. The effective treatment of 1 m^3 of secondary-treated pharmaceutical wastewater, containing antipyrine, was used as a functional unit. The main environmental hotspot was identified to be the chemical reagents used to enhance treatment efficiency, mainly hydrogen peroxide (H_2O_2) and to a smaller degree oxalic acid. On the other hand, land use, PV panels, battery units, compound parabolic collectors (CPC), tanks, pipes and pumps, as materials, had a low contribution, ranging from as little as 0.06% up to about 2% on the total CO_{2eq} emissions. Overall, the solar photo-Fenton process was found to be a sustainable technology for treating wastewater containing micropollutants at semi-industrial level, since the total environmental footprint was found to be 2.71 $kgCO_2\ m^{-3}$ or 272 mPt m^{-3}, using IPCC 2013 and ReCiPe impact assessment methods, respectively. A sensitivity analysis revealed that if the excess of solar power is fed back into the grid then the total environmental footprint is reduced. Depending on the amount of solar power fed back into the grid the process could have a near zero total environmental footprint.

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1. Introduction

Nowadays, the presence of persistent contaminants of the order of the μg L^{-1} or ng/L, i.e. micropollutans, in natural water bodies constitutes a grave environmental problem of emerging concern (Grandclement et al., 2017). Micropollutants are non-regulated contaminants with unique characteristics and behaviour in the wastewater, which even at miniscule concentrations of ng/L can cause detrimental effects to the environment and human health (Virkutyte et al., 2010). Diseases, such as endocrine-related cancers, reproductive disorders, behavioural and learning problems, asthma, and even obesity and diabetes, are linked to exposure to EDCs (WHO, 2013; Rochester, 2013). Adverse effects are also observed in natural ecosystems, with the most common of all being the feminization of male and altered oogenesis in female fish populations, which is already observed in natural water bodies downstream from WWTPs (WHO, 2013; Kidd et al., 2007). They derive from a vast and expanding array of sources, including pharmaceuticals, surfactants, personal care products, hormones, industrial chemicals, pesticides and many other emerging compounds (Luo et al., 2014; Virkutyte et al., 2010). Micropollutants usually end up to the sewer system and are transporting along with the sewage to wastewater treatment plants (WWTPs). The main problem lies to the fact that conventional physicochemical and biological WWTPs have not been designed to cope with micropollutants (Luo et al., 2014), since their main function is to deal with bulk substances that arrive regularly and in large quantities, primarily organic matter and nutrients such as nitrogen and phosphorus (Virkutyte et al., 2010). As a result, WWTPs constitute a major pathway for micropollutants introduction and diffusion to surface water.

Hence, the introduction of advanced treatment technologies, such as advanced oxidation processes (AOPs), able to cope with micropollutants is essential to safeguard human health and the environment. Light-driven AOPs are promising for removing both organic compounds and micropollutants from wastewater matrices (Davididou et al., 2017; Prieto-Rodríguez et al., 2013). Among the different light-driven AOPs, solar-powered processes, such as the solar photo-Fenton, is believed to be one of the most environmentally friendly and cost-effective process. This is attributed to the fact that natural solar light is used, instead of artificial irradiation, to generate hydroxyl radicals, which drive the treatment process (Expósito et al., 2016). Homogeneous photo-Fenton process (system $Fe(II)/H_2O_2$) photogenerates hydroxyl radicals through the following reaction (1) (Monteagudo et al., 2009):

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

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

Till now, the degradation efficiency of pharmaceuticals in wastewater using the photo-Fenton process is well established at laboratory and pilot scale and to a smaller degree at industrial scale (Expósito et al., 2016). Moreover, research has been mainly focused on the techno-economical feasibility of the solar photo-Fenton process, while only a few works have focused on its environmental performance, but mainly at laboratory (Giménez et al., 2015) or pilot scale (Ioannou-Ttofa et al., 2017). Nonetheless, solar photo-Fenton's environmental sustainability at industrial level, where economies of scales exist, remains largely unknown. Moreover, to the best of our knowledge there is no work dealing with the environmental sustainability of an autonomous solar photo-Fenton plant, at semi-industrial scale, treating real pharmaceutical effluent that contains micropollutants.

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

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

2. Material and methods

2.1. Description of the solar CPC autonomous unit

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

2.2. Materials

Industrial wastewater, which originated from a nearby pharmaceutical laboratory, was treated in the CPC reactor. The effluent's initial conditions were COD = 3875 mg/L, TOC = 1914 mg/L, pH = 6.57, and turbidity = 26.3 NTU. The wastewater also contained micropollutants, i.e. antipyrine = 389 mg/L. The detailed physicochemical characteristics can be found in Expósito et al. (2016). It is generally accepted that a process train comprising aerobic/anaerobic biological secondary treatment and AOPs for tertiary treatment is a viable option to effectively treat industrial wastewaters (Chatzisymeon et al., 2013; Ioannou-Ttofa et al.,