Improving sustainability of electrolytic wastewater treatment processes by green powering

C.M. Fernández-Marchante, F. L. Souza, M. Millán, J. Lobato, M.A. Rodrigo

Department of Chemical Engineering. University of Castilla La Mancha. Campus Universitario s/n. 13071 Ciudad Real. SPAIN

Abstract

This work focuses on the evaluation of the impact of powering electrolytic wastewater treatment processes with grid or renewable energy on the sustainability of this electrochemical remediation technology. To face this goal, it was made an inventory of three bench-scale plants with the same treatment technology but powered with a power supply connected to grid and directly by solar photovoltaic panel or a wind turbine. Results show that the powering mode can affect very importantly the results, not only in terms of electricity demand but also on the formation of intermediates, which are more important in the cases in which the intensity profile varied. A life cycle assessment (LCA) is carried out in order to quantify the environmental impacts of green powering electrolytic wastewater treatment processes. Ecoinvent 3.3 data base, AWARE, USEtox, IPPC and ReCiPe methodologies are used to quantify the environmental burden into 5 midpoint (water footprint, global warming 100a, ozone layer depletion, human toxicity, freshwater ecotoxicity) and 17 endpoint impact categories. All impact categories are higher in the case in which the supplied electricity is grid mix. For the removal of 0.1 g 2,4-dichlorophenoxyacetic acid (2,4 D) per liter (functional unit) of treated wastewater releases 0.14 kgCO$_2$ eq. If the energy is provided by a wind turbine or solar panel the processes emit 0.020 kgCO$_2$ eq and 0.019 kgCO$_2$ eq, respectively. A comparison of the impact based on the grid mix used in different countries is also made, which has pointed out the relevance of this input on the sustainability of the environmental electrochemical technologies.

Keywords

Life cycle assessment; electrolysis; wastewater; solar photovoltaic; wind turbine

Highlights

- Electrolytic treatment of 2,4-D wastes is successful regardless being applied alone or combined with UV or US
- Green powering has an important impact on sustainability of electrolytic treatment technologies
- LCA indicates that all impact categories are higher in the case in which the electricity supply is grid mix.
- The most sustainable way of powering environmental electrochemical technologies is using solar photovoltaics energy.

1. Introduction

The treatment of wastewater containing pesticides and organochlorine compounds has recently attracted a growing commitment from the scientific community and it is a topic of the major interest in order to preserve the environment, because of their high toxicity and persistent character, which can affect not only the ecosystems but also human health, because of the subsequent pollution of supply water reservoirs (Terzopoulou and Voutsa, 2017; Llanos et al., 2018). In this context, 2,4-dichlorophenoxyacetic acid (2,4-D) is chlorinated phenoxy herbicide. 2,4-D is one of the oldest and most widely available herbicides and defoliants in the world. Since this compound, the exhibit high water-solubility, lifetime and mobility, its continuous use may cause soil percolation and groundwater contamination (Kwan and Chu, 2004, Souza et al., 2016). However, in the recent years it has been highlighted that environmental worrying should not be only focused on the treatment of these wastes, but also on the development of more sustainable technologies (Bebelis et al., 2013). Humankind is now within a context of environmental emergency because of the very important impact of human activities on the health of the planet and, currently, society is becoming conscious that sometimes the search of new technologies has forgotten important sustainability concepts.

Electrolysis is a well-known electrochemical process with many important applications at high technology readiness levels (TRL8-9), being the core of many industrial processes used to manufacture commodities, like chlorine and alkali, and specialties, such as medicines. Despite the promising results shown in the literature in the last three decades, its application to environmental remediation is nowadays at a lower TRL of 6-7, because of the lack of important elements in the value chain, in particular of the existence of a market with large companies interested in manufacturing real solutions based on these technologies (Sires et al., 2014; Martinez-Huitle et al., 2015; Dewil et al., 2017). Two factors can help to explain this lack of companies with interest

- The excessively rapid transfer of technology tried to be made in the 80s and 90s, in which electrodes developed for other applications were proposed to treat organic-polluted wastes. Thus, formulations of Mixed Metal Oxides (MMO) coatings were proposed to remove organics being inefficient, not only in terms of cost, but also because of the poor mineralization reached (Rodrigo et al., 2010).
- The complex scale-up of the technology, which associated difficulties that ranges from the management of the cathodically produced hydrogen to the mechanical development of efficient stacks of cells capable to face the important mass transfer limitations that these processes undergo (Sires et al., 2014; Dewil et al., 2017).

At the turn of the century, the role of the hydroxy radicals on the electrolysis with several types of anodes was successfully demonstrated (Marselli et al., 2003), being very important to highlight the outstanding properties of the doped diamond coatings for reaching very high efficiencies in the oxidation based on the use of these radicals. From that moment on, these technologies are considered as a type of Advanced Oxidation Processes (AOPs). Comparison of costs based on exhaustive compilation of experimental results demonstrated that this electrochemical technology can compete successfully with other AOPs, both in terms of capital and operating cost (Canizares et al., 2009). Thus, operation costs in the range from 2.4- 4.0 € kg^{-1} COD removed were proposed and have been confirmed later in many papers and reports.

Nowadays, because of the previously commented environmental emergency, there is a need for a more complete comparison, not only focused on economy but also on the sustainability impact. To perform this life cycle assessment (LCA) tools based on the deep understanding of the performance of the process, are required. The application of these tools, ~~based on the deep understanding of the performance of the process,~~ allows to quantify the real impact of a process on many different factors, being key to understand and improve its sustainability, for this reason LCA is a research tool.

Recently, it has been proposed the powering of electrochemical processes with green energy sources, like solar photovoltaic or wind (Souza et al., 2015a; Souza et al., 2015b; Millan et al., 2019). Results obtained in different tests suggest that direct use of these sources, without energy accumulation, leads to important operation results, both in the treatment of liquid wastes and, more importantly, in soil remediation (Souza et al., 2016a; Souza et al., 2016b). These changes are associated to the important fluctuations undergone by the current, which have an impact on the production of oxidant and transport of species. Therefore, taking account of all these experiences acquired by this research group, three different LCA scenarios were studied.

LCA is a technique to evaluate resources and environmental impacts associated with all the stages of a product or a process (Guinèe et al, 2000; Burgess and Brennan, 2001; Demenèch et al., 2002). It is the only environmental assessment tool currently standardized by means of ISO standards (ISO 14044, 2006). In the specific case of a chemical reaction, the application of LCA requires of an inventory of reagents, auxiliary materials consumed and the energy, as well as the wastes generated and emissions (Muñoz et al., 2005). The carbon, hydric, and energy footprints are one of the most important outputs that can be obtained from its application (Fernández-Marchante et al., 2019).

In the recent years, the LCA of different advanced oxidation processes has been studied (Muñoz et al., 2005; Foteinie et al., 2018; Zepon Tarpani et al., 2018; Arzate et al., 2019). However, there are few data related to Conductive-Diamond Electrochemical Oxidation (CDEO) (Chatzisymeon et al., 2013) and, to the authors knowledge, no LCA studies of CDEO powered with green energy have been found until now. Thus, the goal of this work is to compare, using LCA tools, the sustainability of removal of 2,4-D by CDEO powered with solar panels or wind turbines or with the conventional use of grid electricity. This work is the only LCAs of removal of 2,4-D by CDEO which achieve the total removal of the pollutant and total mineralization (0.1 g L^{-1} of 2,4 D). To do this, an inventory of three lab-scale equipment and operational results reached in the treatment of the same waste have been used. AWARE, USEtox, IPPC and ReCiPe methodologies are used to quantify the environmental burden into 5 midpoint (water footprint, global warming 100a, ozone layer depletion, human toxicity, freshwater ecotoxicity) and 17 endpoint impact categories.

2. Methods and Data

2.1. Experimental setup and procedures

The degradation of an organochlorinated pesticide model was assessed using a commercial conductive diamond electrochemical oxidation (CDEO) reactor, DiaCell® 101 ~~suppied~~ supplied by Adamant Technologies (Switzerland). Boron-doped diamond electrodes, BDD (p-Si-boron-doped diamond) were used as the anode and cathode. The BDD coating has a film thickness of 2 mm, a resistivity of 100 mΩ cm, and a boron concentration of 500 ppm, and the sp^3/sp^2 ratio is 150. The cell was equipped with BDD electrodes (WaterDiam, France) of 70 cm^2 of area and the interelectrode gap is 3 mm. Figure 1 shows a scheme of a DiaCell® 101 reactor (Figure 1).

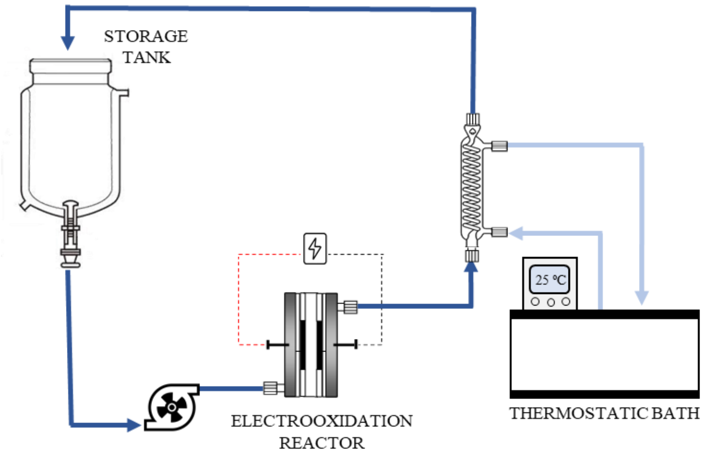


Figure 1. Electro-oxidation bench scale setup working on batch mode.

A synthetic solution of 4 dm^3 containing 100 mg dm^{-3} of 2,4-D at natural pH (3.5) and 3000 mg dm^{-3} of NaCl as supporting electrolyte was used as wastewater effluent. The cell reactor was operated in batch-operation mode and it was connected by a peristaltic pump (flow rate 26.4 dm3 h-1) to a tank though silicon tubes (Souza et al., 2015a).

All the samples extracted from electrolyzed solutions were filtered using 0.45 mm nylon filters form Whatman prior to analysis. The decay of 2,4-D was followed using reversed-phase chromatography and total organic carbon (TOC) (Souza et al., 2015b).

Electricity produced by two photovoltaic panels connected in series (each panel with an area of 1.313 m^2) can be used to power the electrochemical cell, or it can be stored in batteries. Computer software (Labview, National Instruments) was used to control the process, and durint the tests, energy was directly supplied to the electrochemical cell.

A Bornay 600 wind power turbine was provided by Bornay Aerogenerators (Alicante, Spain). The turbine is composed of two fiberglass blades (1 m long) controlled by and electronic regulator of 24 V and 30 A. the regulator acts on the turbines as an automatic overspeed-governing systems to keep the rotor from spinning out of control in very high winds. The performance of the wind speed for turn on is 3.5 m s^{-1}, for nominal power 11.0 m s^{-1}.

~~The cell reactor was operated in batch-operation mode and it was connected by a peristaltic pump (flow rate 26.4 dm^3 h^{-1}) to a tank.~~ The electrochemical cell was powered by the wind turbine, photovoltaic panels or with a conventional power supply. The photovoltaic panels and wind turbine are located in the roof of the E3L (3.59N 3.55O) in Ciudad Real (Spain). This location corresponds to a region that presents a continentalized Mediterranean climate (Peel et al., 2007).

To assess the performance of the coupled wind turbine electrolytic cell, a treatment test was planned according to the weather forecast in the area of Ciudad Real by AEMET (the official Spanish Weather Forecasting Service) for a slightly windy day, representing typical conditions, rather than a very windy day, on which the production of energy would be much higher but less representative. As can be observed, there is a random distribution of wind speeds over the testing period with an average wind velocity of 4.2 m s^{-1} (Souza et al., 2015a).

In addition previous work had been carried out at different times of the year, favourable solar conditions (February) and unfavourable conditions (September) (Souza et al., 2015b, Millán et al., 2019, García-Orozco et al., 2020 , Millán et al., 2020a. Millán et al., 2020b and Millán et al., 2020c). The most conservative scenario has been chosen in this study of LCAs of electrolytic wastewater treatment processes by solar powered (Souza et al., 2015b).

The specific energy consumption is calculated according to equation (1), where I is the exerted current intensity, E is the cell voltage and V is the treated waste volume.

$$W = I*E/V \qquad (1)$$

2.2. Functional Unit Definition

Treatment of 1.0 L of synthetic waste containing 0.1 g L^{-1} of 2,4 D was taken as the functional unit for this study and the three conductive-diamond electrochemical oxidation processes were compared, with the same electrolyzer equipment but powered directly with solar panels, wind turbines or regulated power supplies. The reaction times for obtaining mineralization in the different processes were 12 hours in Wind CDEO, 7.5 hours in solar CDEO and 4 hours in conventional CDEO.

2.3. Inventory

The inventories of the three-laboratory units are shown in Figure 2.

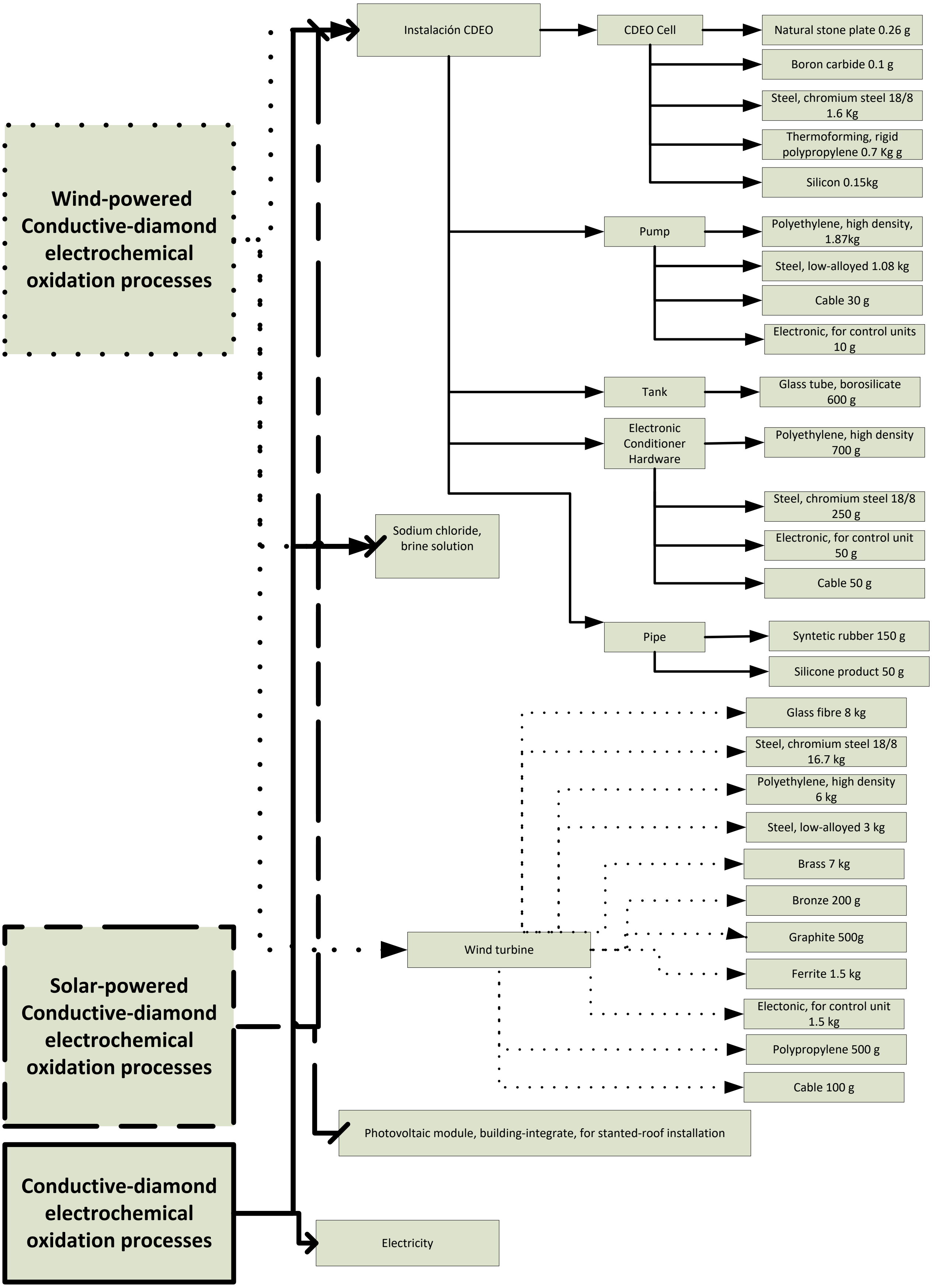


Figure 2. System boundaries and specifications of the model systems for green powered CDEO process.

CDEO inventory includes a Diacell® (type 101) single-compartment electrolytic flow-cell with a life span of 10 years. The inventory was simulated using the Econveint 3.3 database. A Bornay 600 wind power turbine has a life span of 20 years. The inventory of wind power was simulated using the Econveint 3.3 database. Photovoltaic panel has a life span of 20 years.

2.4. Methods

In this study, the LCA was carried out using the SimaPro 9.0 software. The ReCiPe, IPCC, AWARE, USEtox Mid-point and ReCiPe End-point methods were used in order to point out a large variety of impacts associated with each of the three processes presented and to determine the environmental performance as a whole. One of the main differences between the endpoint and midpoint methods is that they look at the different stages in the cause and effect chain to calculate the impact. The endpoint methods are applied to the indicator to express the current damages while the midpoint methods are applied to the characterization factor in order to measure the impact (Gorrée et al., 2002; Huijbregt, et al, 2003; Parascanu et al., 2018).

These methodologies were used to quantify the environmental burden into 23 impact categories in the three LCA of electrolytic wastewater treatment processes by conventional and green powering.

2.4.1. Climate Change

Climate change is related to emissions of greenhouse gases to atmosphere. The model used to quantify global warming was developed by Intergovernmental Panel on Climate Change (IPCC) and defines the potential global warming expressed in kilogram of carbon dioxide per kg of emission (Houghton et al., 1992; Fernández-Marchante et al., 2019).

2.4.2. Stratospheric Ozone Depletion

The model used to characterize ozone depletion was developed by the World Meteorological Organization and defines the capacity for the disappearance of the ozone layer as the kg of equivalent CFC-11 per kg of emission (Fernández-Marchante et al., 2019).

2.4.3. Water Footprint

AWARE method was used to calculate the water footprint and this method is considered suitable for the assessment of sustainable water resource management for the point of view of water availability (Ansorge et al., 2017). The water footprint recognizes the quantity of water consumed in the manufacturing process of CDEO (Boulay et al., 2017).

2.4.4. Freshwater ecotoxicity and Human Toxicity

USEtox is a model endorsed by the UNEP/SETAC Life Cycle Initiative for characterizing ecotoxicological and human impacts of chemicals. Effect factors for freshwater ecosystems expressed as an estimate of the potentially affected fraction of species (PAF) integrated over volume and time per unit emitted. The comparative toxic unit for human toxicity impacts (CTUh) indicates the estimated increase in morbidity in the human population per unit emitted (Rosenbaum et al., 2008).

3. Results and Discussion

Figure 3 shows the removal of 2,4-D (raw pollutant) and its mineralization as a function of the specific energy consumption, calculated according to equation (1).

As seen, total removal of the pollutant and total mineralization is obtained, regardless of the type of powering applied. There are important differences in terms of the energy consumed and the degradation tendency of the pollutant and the TOC. Thus, to operate at galvanostatic conditions using a power supply connected to the electricity grid, the decrease in the concentration of pollutant almost matches with the increase in the mineralization, suggesting the formation of only very low concentrations of reactions intermediates species (Souza et al., 2015a; Souza et al., 2015b). Meanwhile, differences are higher in the case of the electrolyzer powered with green energies, being especially remarkable in the case of the solar PV powering. The highly changing profile in the applied intensity modifies importantly the time-course of the production of oxidants in the treated waste favoring the accumulation of intermediates, which are finally degraded because of the action of the oxidants accumulated. Parallel experiments have been carried out and the results showed similar trends (Millán et al., 2019 and Millán et al., 2020b).

Obviously, the amount of energy required to degrade the same waste is similar, because the waste and the treatment technologies are the same. However, energy savings are obtained using grid energy instead of direct wind turbine or solar panel powering. So, to solve the nil or limited remediation at specific times of the day, energy storage systems should be used (Garcia-Orozco et al., 2020 and Millán et al., 2020c).

Initially, it can be thought that because of this required lower energy consumption, this alternative is the most sustainable from the environmental point of view, because of the higher efficiency observed in the use of electricity. However, this is not what the LCA tools state for this case, as it is going to be discussed later, in terms of the different footprints derived from the application of the remediation technology with the different types of powering.

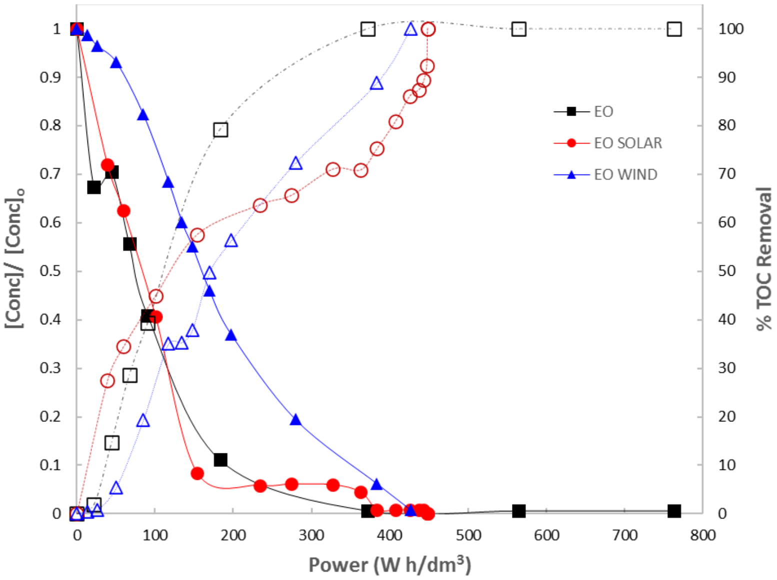


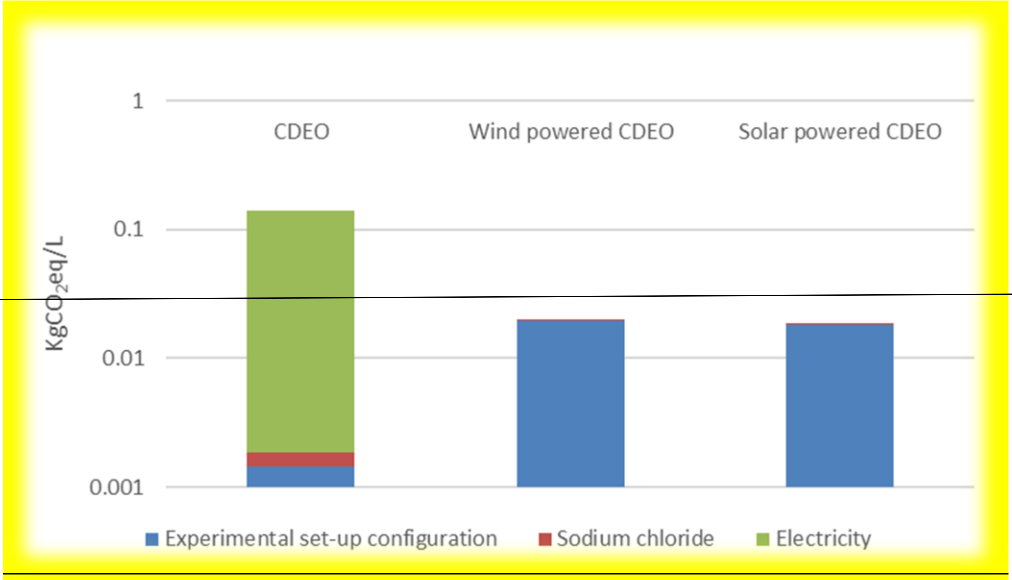
Figure 3. Influence of the powering mode on the removal of pollutant and TOC under electro-oxidation processes. Pesticide removal (full symbol) and TOC removal (empty symbols).

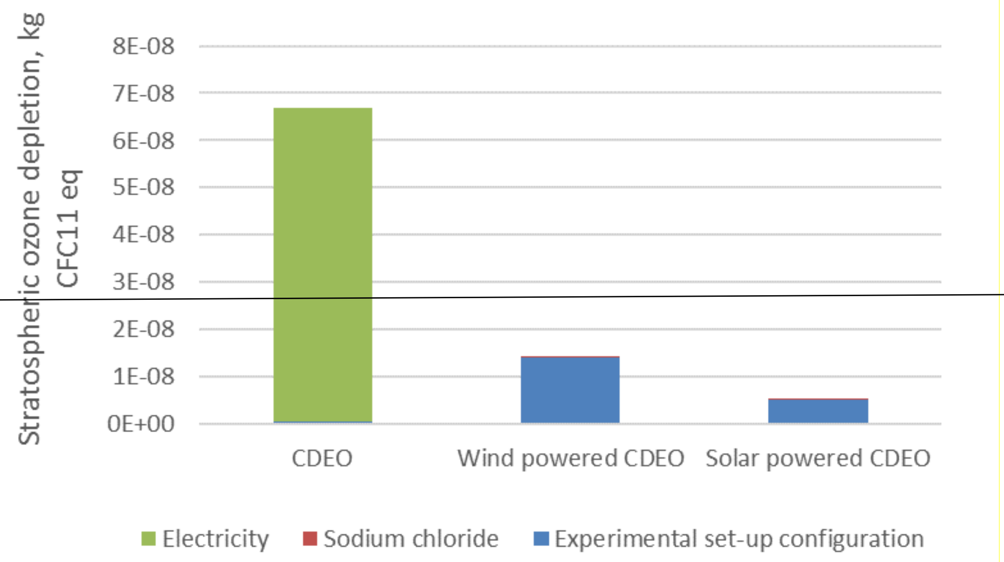
Thus, Figure 4 shows the outcomes from the IPCC GWP 100a impact category, which indicates that the equivalent emissions of carbon dioxide for a timeframe of 100 years by electrolysis powered by grid is almost one-fold over those obtained with the powering with green energies (to make the calculations the grid mix of Spain is used). In the later cases, the carbon fingerprint associated to the manufacture of the equipment is rather important but fully compensated by the much higher influence on this parameter of the non-renewable powering. Regarding values found, CDEO can be considered an environmentally friendly process: according to our results the treatment of 1L of wastewater only releases 0.14 kgCO_2 eq. This value agrees with other previously reported in the literature. Thus, Chatzisymeon et al., 2013 studied LCA of an electrochemical oxidation process for 1 g COD L^{-1} of olive mill wastewater and they obtained 0.16 kgCO_2 eq (see Table 1). If the energy is provided by a wind turbine or solar panel, the processes emit 0.020 kgCO_2 eq and 0.019 kgCO_2 eq, respectively. These emissions represent a reduction of 85.7% and 86.6% with respect to the CDEO (considered to be powered by the Spanish electricity grid), and this can be explained because the 98.7 % of emissions are released of electricity grid demand. Muñoz et al., 2005 studied the contribution of electricity in advanced oxidation processes to the global warming potential and the Grid electricity (Spanish mix) was a 93 %.

As it is shown in Table 1, the CDEO is a process less contaminant and with less impact that other advanced oxidation process (wet air oxidation, heterogeneous photocatalysis and photoFenton). The solar powering was a better choice to reduce the impacts than grid mix in the countries studied.

Figure 4 shows the contribution of powering CDEO by Spanish electricity grid, a wind turbine or a solar panel in the ozone layer depletion. These contributions are 66.8, 14.2 and 5.3 µg/L kg CFC11eq, respectively, so the impact is reduced to 79% with the use of wind turbine and 92% with solar panel. In the case of CDEO powered by electricity grid, this electricity generates the 99.1 % of emission.

The results of carbon footprint obtained in this work and reported by other studies indicated that the main contributor to the environmental footprint of all process was the electricity consumption from the energy grid.


1
0.1
0.01
0.001
KgCO$_2$eq/L
CDEO
Wind powered CDEO
Solar powered CDEO
Experimental set-up configuration
Sodium chloride
Electricity


Stratospheric ozone depletion, kg CFC11 eq
8E-08
7E-08
6E-08
5E-08
4E-08
3E-08
2E-08
1E-08
0E+00
CDEO
Wind powered CDEO
Solar powered CDEO
Electricity
Sodium chloride
Experimental set-up configuration

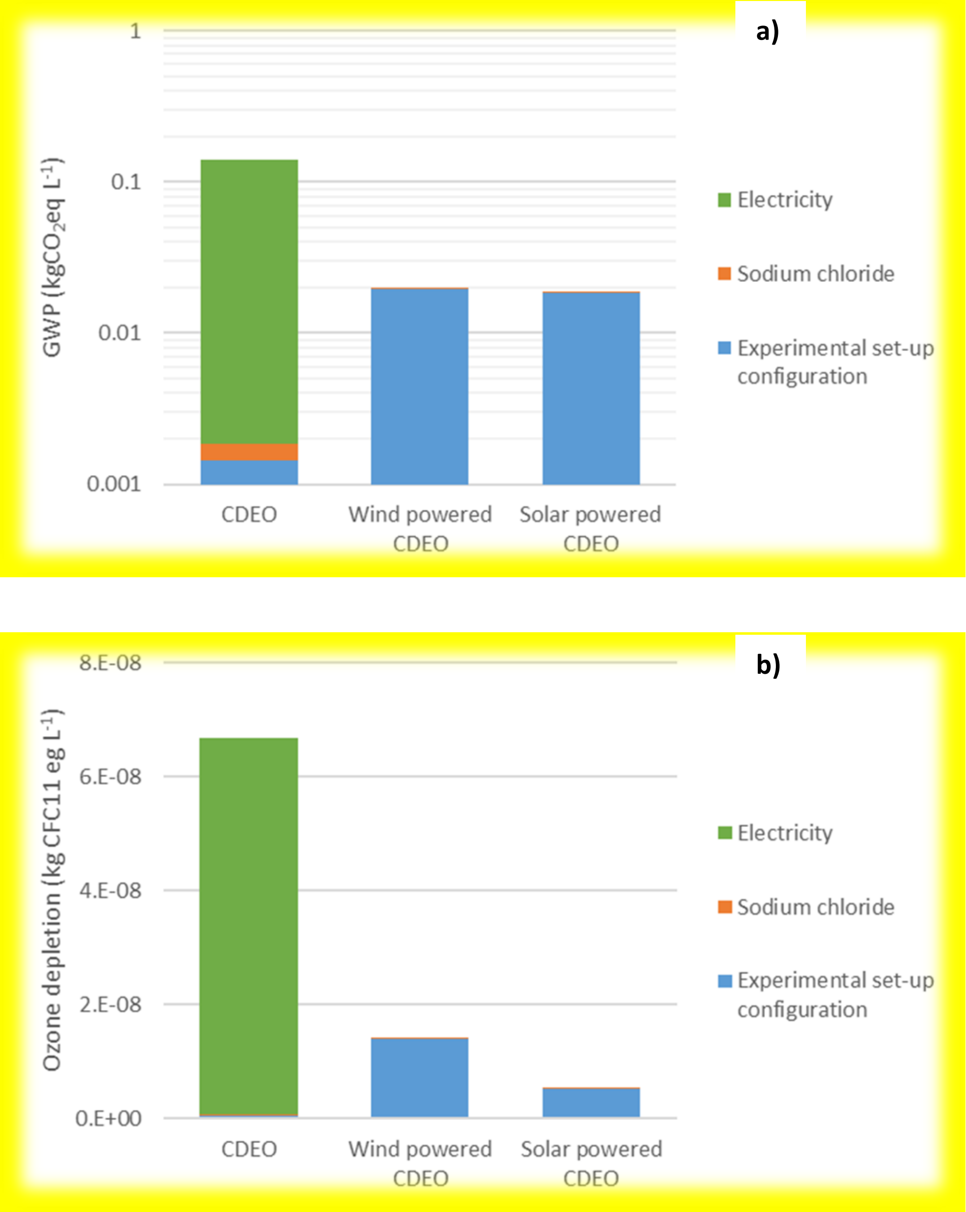
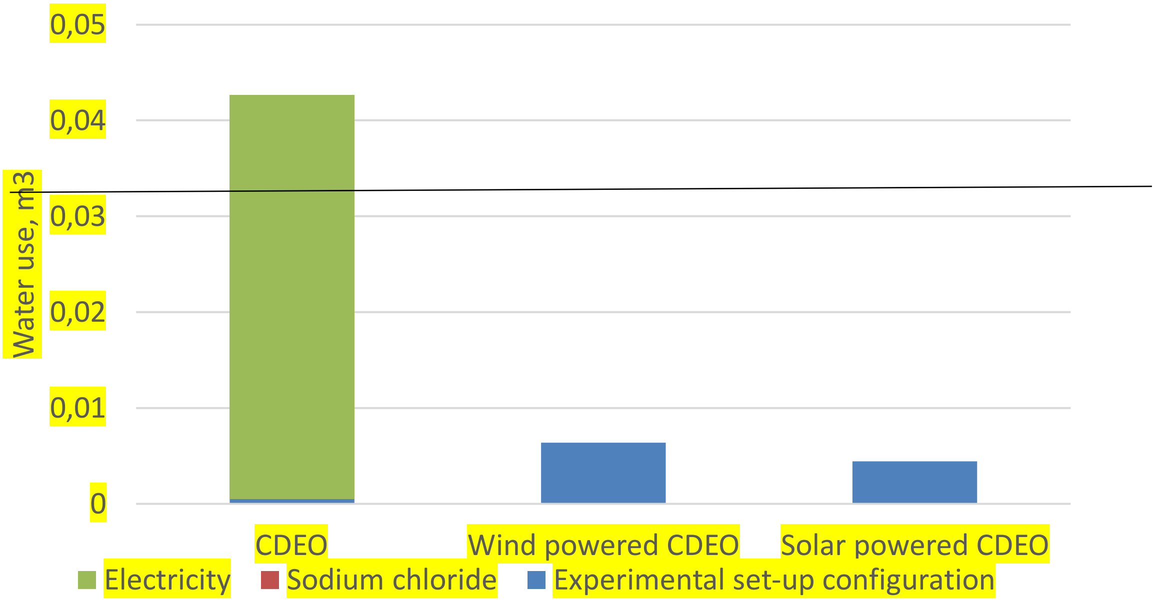


Figure 4a. Global warming potential as Kg CO_2 eq. per 0.1 g L^{-1} 2,4 D **b)** Ozone depletion as the kilograms of equivalent CFC-11 per 0.1 g L^{-1} 2,4 D.

Figure 5 shows the water use for the removal of 0.1 g 2,4 D L-1 of wastewater treated. In the CDEO process powered by electricity grid, the used water is 42.6 L and the 98.8 % is due to energy production. For this reason, when a wind turbine or a solar panel are used, the water use is reduced a 85 % and a 89.5 %, respectively, because only 6.37 and 4.45 L are needed. In these scenarios, water is used mainly during the manufacturing process of the brass, stainless steel and glass fiber. Rodriguez et al. 2016 and Morera et al., 2016 obtained similar water footprints for the treatment of pharmaceutical wastewater using heterogeneous Fenton processes: 65 and 75 L, respectively. These results are very interesting because, although the functional unit is the same (1 L) the scale is different and even so CDEO shows less water footprint that Heterogenous Fenton processes. Water footprint is a very important category in terms of sustainability of a process, mainly in dry regions like the south of Spain, where this resource is scarce.

Table 1. Comparison of the climate change impact category determined by IPCC method in this study with results reported in literature.

Autor (year)	**Process**	**Scale and location**	**Effluents**	**Functional Unit and location**	**Carbon footprint (kg CO_2 eq.)**	
Muñoz et al., 2005	Photocatalysis	Pilot unit	Kraft mill bleaching wastewater	1 m^3 (Spain)	90	kg CO_2 eq/m^3
	Solar Photocatalysis				0.48	kg CO_2 eq/m^3
	PhotoFenton				38	kg CO_2 eq/m^3
	Solar PhotoFenton				0.76	kg CO_2 eq/m^3
	Photocatalysis +H2O2				54	kg CO_2 eq/m^3
	Solar Photocatalysis +H2O2				1.2	kg CO_2 eq/m^3
	PhotoFenton +H2O2				16	kg CO_2 eq/m^3
	Solar PhotoFenton +H2O2				1.2	kg CO_2 eq/m^3
Foteinie et al., 2018	Solar PhotoFenton	Semi-industrial	pharmaceutical (antipyrine)	1 m^3 (Spain)	2.7	kg CO_2 eq/m^3
Ioannou-Ttofa et al., 2017	Solar PhotoFenton	Pilot unit	Urban Effluent	1 m^3 (Greece)	8.7	kg CO_2 eq/m^3
Zepon Tarpani and Azapagic, 2018	Solar PhotoFenton	Pilot unit	Pharmaceutical and personal care products	1 m^3 Cyprus (Spain)	0.3	kg CO_2 eq/m^3
Arzate et al., 2019	Solar PhotoFenton	Pilot unit	Urban Effluent	1 m^3 (Spain)	0.5	kg CO_2 eq/m^3
Gallego-Schmid et al., 2019	Nanofiltration +Solar PhotoFento	Pilot unit	Microcontaminants from real wastewater	1 m^3 (Spain)	0.31	kg CO_2 eq/m^3
Chatzisymeon et al., 2013	UV heterogenous Photocatalysis	Laboratory unit	Olive mill wastewater	1 g of COD per liter and 1 g of TPh per liter Chania (Greece)	5.2	kg CO_2 eq/l
	Wet Air Oxidation				0.8	kg CO_2 eq/l
	Electrochemical Oxidation				0.16	kg CO_2 eq/l
This study, 2020	Electrochemical Oxidation (CDEO)	Laboratory unit	2,4 D pesticide	0.1 g per liter (Spain)	0.14	kg CO_2 eq/l
	Solar CDEO				0.019	kg CO_2 eq/l
	Wind CDEO				0.020	kg CO_2 eq/l



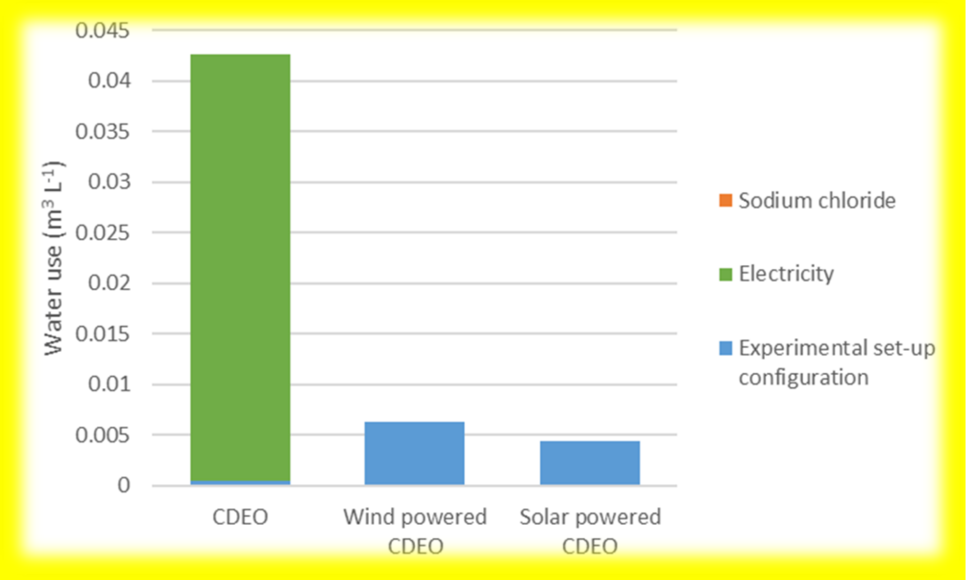
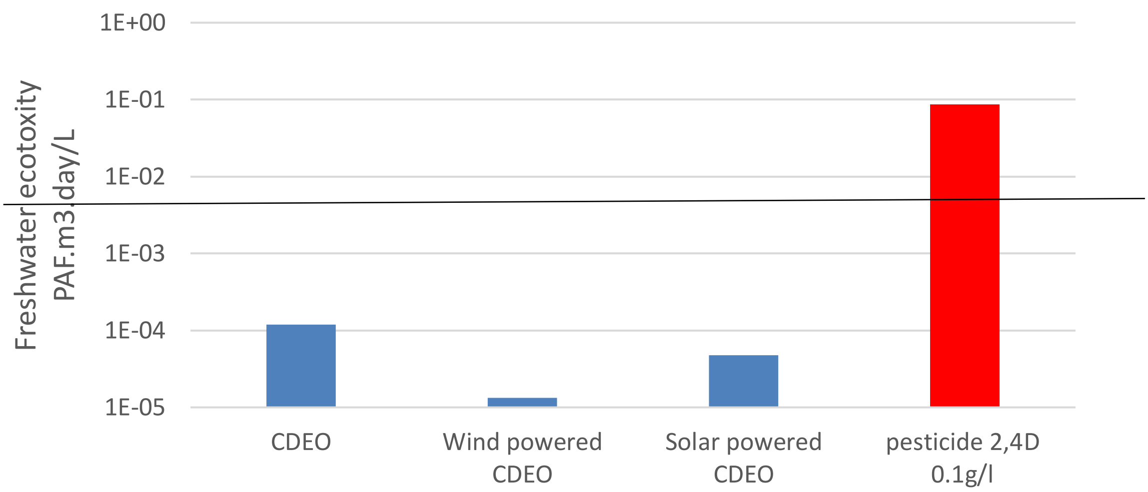


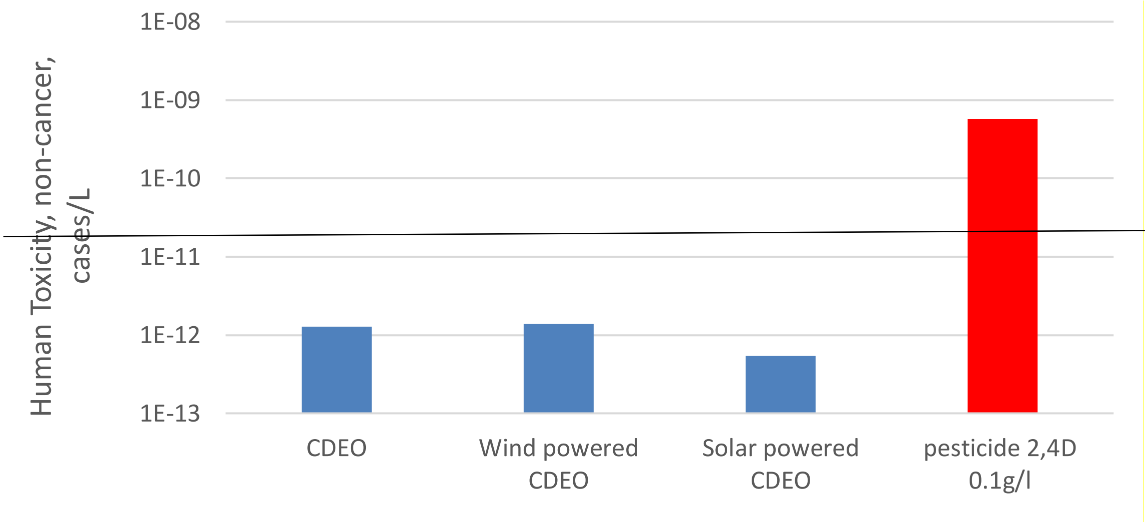
Figure 5. Water footprint as m^3 used.

The influence of the treatment on the Freshwater ecotoxicity impact category has been compared in Figure 6a. 0.1 g L^{-1} of 2,4 D in water generates an ecotoxicity of 0.0861 PAF.m^3.day. This Freshwater ecotoxicity impact is reduced to 1.4 % when the wastewater is treated by CDEO powered by Spanish electricity grid, 0.015% and 0.055% with wind and solar powers, respectively. In the case of CDEO powered by electricity grid, the 91 % of freshwater ecotoxicity impact is associated to the electricity consumed.

Human toxicity (non-cancer) impact category has also been compared and results are shown in Figure 6b. The Human toxicity is reduced to 99% with the different treatments. In the case of CDEO powered by electricity grid, the 95 % of human toxicity impact is due to electricity consumed. The impact in the case of wind power took values closer to power by electricity grid. Conversely, this impact was lower using a solar panel. Regarding, wind powering scenario, human toxicity is mainly due to the manufacturing processes of brass, stainless steel and glass fibre.



b)



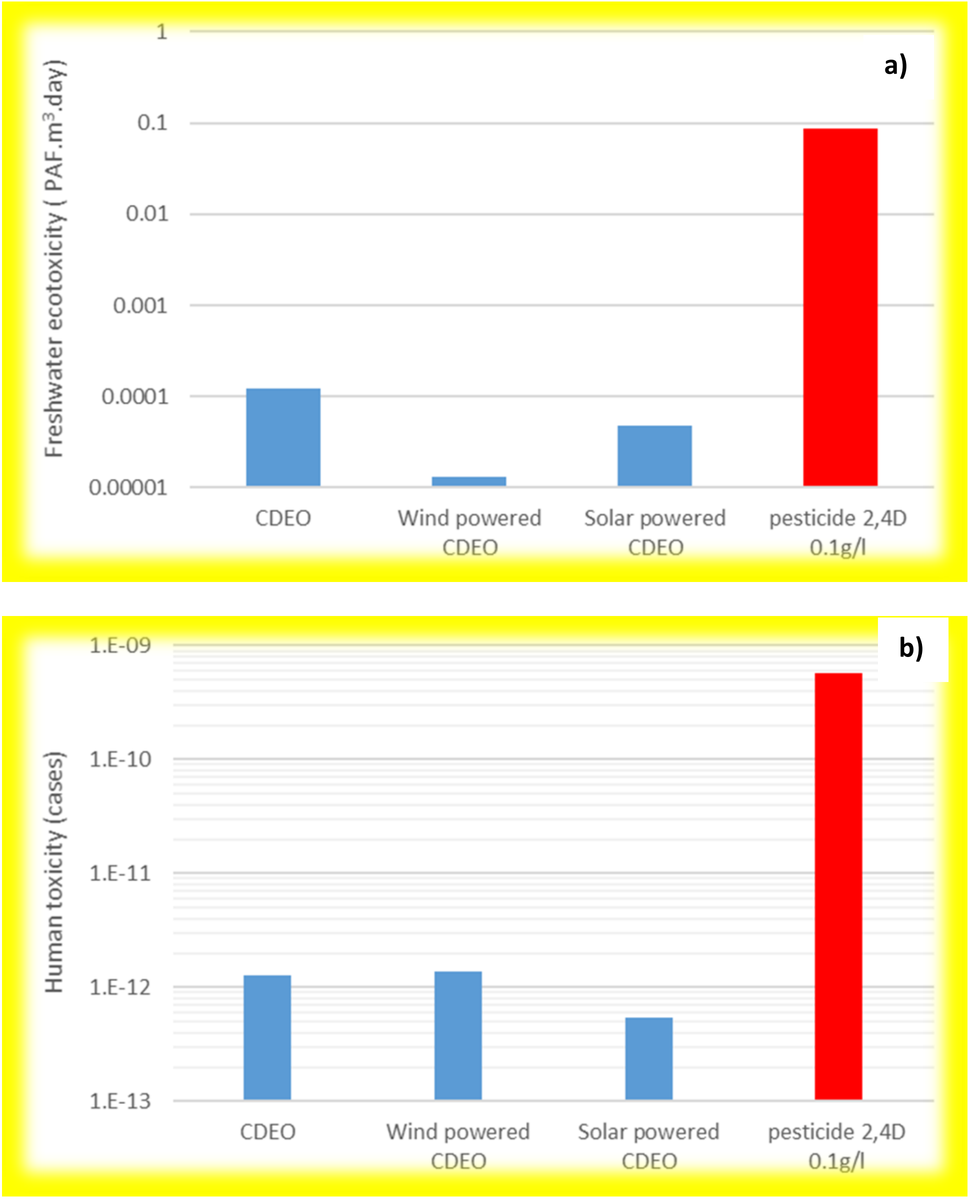


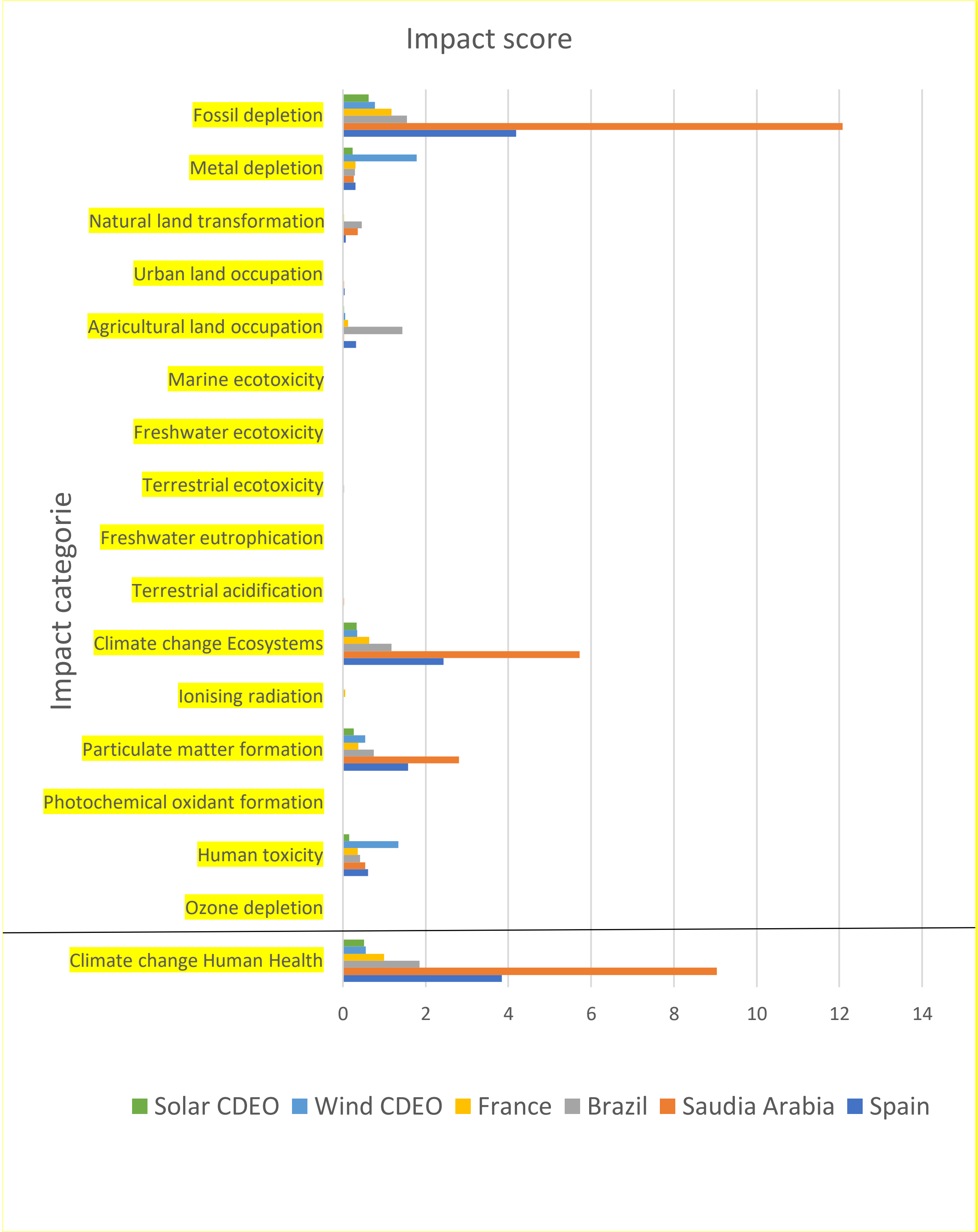
Figure 6a). Freshwater ecotoxicity as PAF.day per 0.1 g/l 2,4 D **b)** Human toxicity as cases per 0.1 g L^{-1} 2,4 D

Results discussed up to now demonstrate the importance of the use of green energies in combination with electrolytic remediation technologies. However, one important point to be considered is that the electricity mix is country-specific. This means that the environmental footprint of this process could have significant differences among different countries and energy sources and hence it is important to evaluate how these differences can influence on the sustainability of a given treatment technology Therefore, a sensitivity analysis was conducted to determine the influence of an electricity mix on the environmental footprint of the system. For this reason, it was evaluated the environmental footprint using three different energy mixes for countries that use a rather different mix as compared to Spain (Grid 4). These selected countries were France (Grid 1), Saudi Arabia (Grid 2) and Brazil (Grid 3), whose data are shown in Table 2.

Table 2. Shares of the global electricity production for the year 2008 based on the production volumes documented in this software (Itten et al., 2014)

	Grid 1 (France)	**Grid 2 (Saudi Arabia)**	**Grid 3 (Brazil)**	**Grid 4 (Spain)**
Fossil fuels (%)	9.08	**100**	12.46	**59.46**
Hydropower (%)	12.49	0	**80.29**	8.74
Pumped Storage Hydropower (%)	0.84	0	0	0.87
Nuclear Power (%)	**76.3**	0	2.88	18.74
Renewables (%)	1.39	0	4.32	12.31
Waste (%)	0.73	0	0	0.66
Other (%)	0	0	0.05	0.1

Results of this comparison using the ReCiPe method are shown in Figure 7, where it is also included the powering with pure green energies evaluated in this work for the sake of comparison. Thus, it is observed that climate change and fossil depletion impact categories yield a higher score in the case of CDEO powered by electricity grid. This statement is consistent with the results reported by other researchers, who observed that for advanced oxidation processes the energy consumption is the stage that generates the main environmental impact (Muñoz et al., 2006, Ioannou-Ttofa et al., 2016). If it is compared this work with Chatzisymeon et al., 2013, it is observed that the impact score change. In this work, fossil depletion and climate change impact categories have higher scores while for other advanced oxidation treatments the higher impact score is human toxicity impact category. In addition, we also observe that the fossil depletion and climate change impact scores of CDEO is significantly reduced when the energy supplied is green. As shown, each energy mix affects the same impact categories, and fundamentally depend on the amount of fossil fuels.


Impact score
Impact categorie
Fossil depletion
Metal depletion
Natural land transformation
Urban land occupation
Agricultural land occupation
Marine ecotoxicity
Freshwater ecotoxicity
Terrestrial ecotoxicity
Freshwater eutrophication
Terrestrial acidification
Climate change Ecosystems
Ionising radiation
Particulate matter formation
Photochemical oxidant formation
Human toxicity
Ozone depletion
Climate change Human Health
0
2
4
6
8
10
12
14
Solar CDEO
Wind CDEO
France
Brazil
Saudia Arabia
Spain

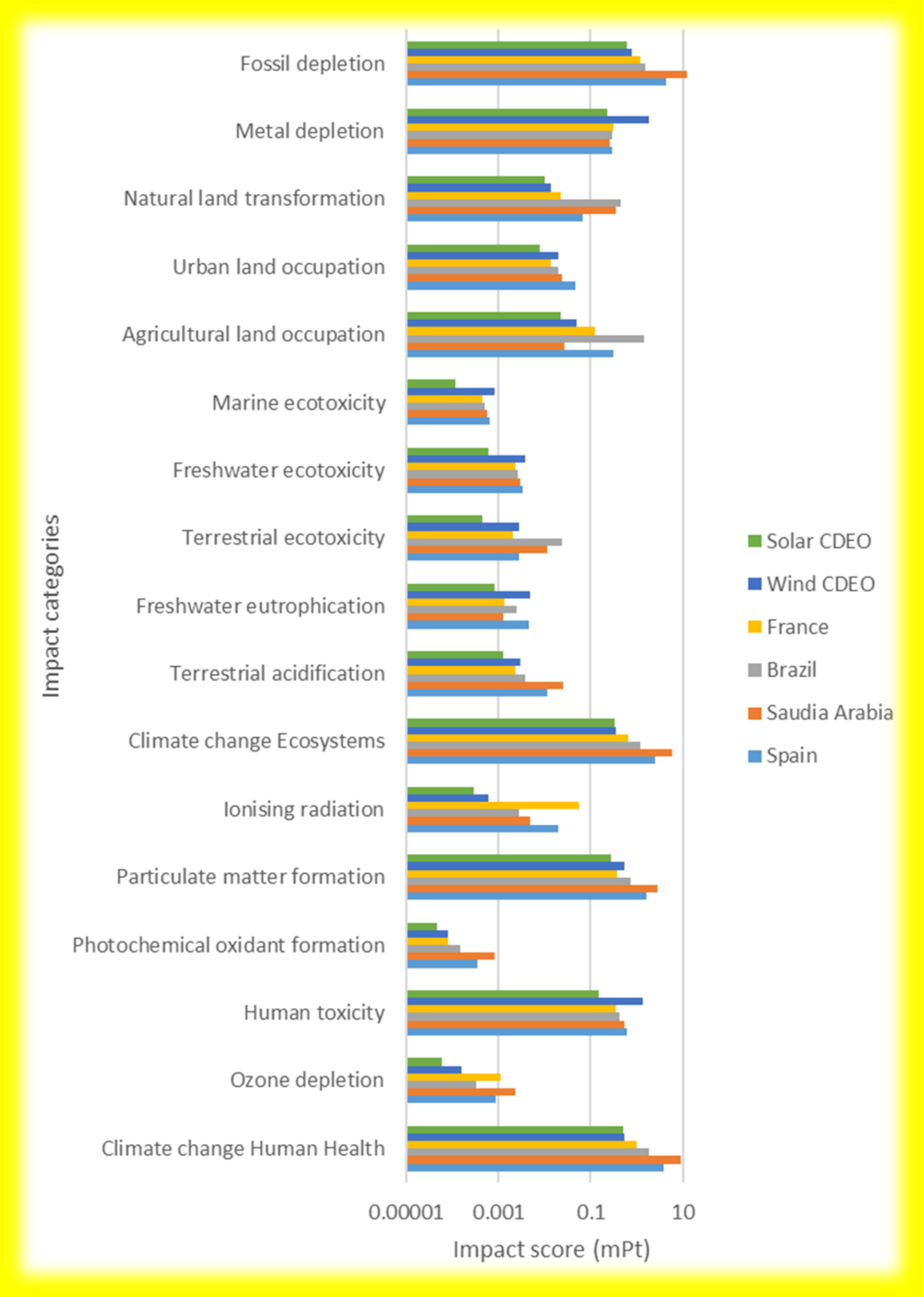


Figure 7. Effect of Grid Mix in the 17 endpoint impact categories. Values are presented per (0.1 g/l 2,4 D) FU.

Hence, the impact of applying this technology strongly depend on the energy grid mix used, which in turn is country-dependent. Thus, while the electrochemical technologies can be considered as green in countries like Brazil, with a much lower impact but not in countries such as Arabia, strongly dependent on the use of fossil fuels. In fact, these four countries represent four very different models of energy grid mix. There are three models clearly differentiated by having in their energy mix a main energy source (from which at least 75% of the energy is obtained). Thus, the predominant types of energy were fossil, hydraulic and nuclear energy for Arabia, Brazil and France, respectively. Opposite, Spain does not have a primary source and represents countries whose energy grid mix is more varied. Overall, given the origins of global energy, it accounts for 65% of energy well based on fossil resources, it is true that these percentages have now changed because more countries are betting on solar and wind energy as cleaner and more accessible energy vectors for all, because fresh water is a resource that very few countries can opt for. As we can see, the traditional fossil-based energy-based energy model has a significant impact on climate change and its consequences for human health and ecosystems, as well as the generation of suspended particles and fossil depletion. Renewable and nuclear energies have 10 times less effect on these impacts.

4. Conclusions

From this work, the following conclusions can be drawn:

- Direct powering with green energy of electrolytic processes can be successfully used to remediate wastes polluted with 2,4-D. Changing profiles in the exerted intensity have a significant influence on the efficiency of the processes, reflecting on higher concentrations of intermediates and more demands of electricity.
- Sustainability of environmental electrochemical technologies is significantly influenced by the type of powering applied to these technologies. According to the results obtained in this study, more than 90% of the impact caused (Carbon footprint, ozone layer depletion, water footprint, particulate matter formation) by CDEO treatments can be associated to energy fossil consumption.
- Despite the higher requirements of electricity, renewable powering is a suitable alternative to power electrochemical systems because according to LCA it can see that environmental impact and human health are significantly reduced.

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