Does intensification with UV light and US improve the sustainability of electrolytic waste treatment processes?

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Abstract

This work aims to assess the influence of ultrasounds (US) application or ultraviolet (UV) light irradiation on the efficiency and sustainability of the treatment of wastes by conductive diamond electrochemical oxidation (CDEO). To do this, a life cycle assessment (LCA) is carried out in order to quantify the environmental impacts of the intensified CDEO processes. Inventories of three bench scale remediation plants (CDEO, Sono-CDEO and Photo-CDEO) in which the different technologies are implemented are performed by means of 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. Photo-CDEO attains the faster and more efficient removal in terms of energy consumed. All impact categories are lower in the case in which UV light irradiation is coupled to the CDEO treatment, particularly if the electrolyte does not contain chloride anions. From the point of view of toxicity and ecotoxicity, it is essential to achieve a complete mineralization, because of the intermediates generated into wastes containing chloride anions can become more hazardous than the initial pesticide. The operation of these technologies at large current densities shows positive results from the sustainability point of view, despite the huge environmental impact related to the energy production. Data notice that almost a 99.0 %

of the total global warming potential is mainly due to the electricity required during the electrochemical treatment, being higher by the sono and photo CDEO treatments because of the use of additional devices. Nevertheless, this issue can be overcome by means of using renewable energies as power sources of these remediation treatments. According to results, it can be claimed that the electrochemical technologies may successfully compete with other AOPs in terms of sustainability.

Keywords

Life cycle assessment; electrolysis; wastewater; photo-electrolysis; sono-electrolysis, intermediates.

Highlights

- UV irradiation has a great impact on the sustainability of CDEO treatments
- US dosing has a great negative impact on the sustainability of CDEO treatments
- Great dependence of the environmental impact on the energy consumption
- Powering large current densities favors the sustainability of CDEO processes
- Chloride ions have a negative impact on the sustainability of CDEO processes.

1. Introduction

Electrolysis is best-known as an industrial technology highly used in processes such as the chloralkaline process. **Notwithstanding**, this electrochemical technique has also demonstrated to be an efficient technology for the removal of organic pollutants **from** aquatic environment whose origin can be domestic or industrial. Those wastewater bodies may contain metals, pesticides, hydrocarbons, dyes and personal care and pharmaceutical products (Dewil et al., 2017; Martín de Vidales et al., 2018; Martínez-Huitle et al., 2015; Sirés et al., 2014). Besides, urban and agricultural run-offs are the most significant emitters of organic chemical traces to wastewater treatment plants (Miklos et al., 2018). In this context, 2,4-dichlorophenoxyacetic acid (2,4-D) is one of most hazardous and widely used herbicide and defoliant in the world (Souza et al., 2016). The treatment of wastewater **effluents polluted by** organic persistent compounds by means of electrochemical technologies has recently attracted the scientific community interest. Although it is widely extended the idea of the huge costs related to these technologies, exhaustive studies (Canizares et al., 2009) demonstrated that costs are within the range of other advanced oxidation processes (AOPs). Nevertheless, its mineralization efficiency allows to reduce the pollution below the limits fixed by local environmental regulations. **Furthermore**, many studies have demonstrated that electrolysis is a very robust and effective technology for the treatment of wastewaters polluted with a great variety of organic pollutants (Martin de Vidales et al., 2014; Martín de Vidales et al., 2017). The great success of this technology is based on the production of many types of oxidants from the anodic oxidation or cathodic reduction of species contained in the waste (Barrera-Diaz et al., 2014). Examples of anodically formed species are ozone, peroxosulfate, chlorine or peroxocarbonates (Cañizares et al., 2009). Conversely, hydrogen peroxide is the most representative cathodically formed oxidant (Lim and

Hoffmann, 2019; Perez et al., 2017). These oxidants are not **active or** powerful in their molecular form. However, they can be easily activated by different mechanisms that favor their transformation into radicals (Barrera-Diaz et al., 2014). Among **the wide variety of activation** mechanisms, the interaction between chemical species (case of the Fenton based processes, or the synergism observed in peroxone) and the application of external energy sources, **such as** ultraviolet (UV) light or ultrasounds (US), **are the most efficient mechanisms to increase the remediation efficiency of electrochemical processes** (Martínez-Huitle et al., 2015).

The impact of **coupling intensified techniques and electrochemical processes** (photo-electrolysis and sono-electrolysis) **on wastewater remediation has** been **widely** studied in the recent years **showing promising results in terms of mineralization efficiency** (Souza et al., 2014; Souza et al., 2013; Souza et al., 2015; Vieira dos Santos et al., 2017; Vieira dos Santos et al., 2018). In addition, the experimental setups required to transform an electrolytic **treatment** into an **intensified** process are very simple. UV lamps or US probes **must be** located **into the storage** tank, just in the point where **the** oxidants produced electrochemically are found at high concentrations and **the** chemical oxidation reactions may take place (Rubí-Juárez et al., 2016). There are other types of photo- and sono-electrochemically assisted processes, which try to improve the electrodic formation of oxidants, but this work is not going to be focused on them. Among the electrolysis techniques, the conductive diamond electrochemical oxidation (CDEO) breakthrough opened a novel research line in terms of remediation technologies. The use of Boron Doped Diamond (BDD) anodes has reported the total mineralization of a wide range of pollutants of a different nature (Mena et al., 2017; Miklos et al., 2018). The **straightforward** experimental setups and the faster removal of pollutants **by means of intensified CDEO treatments**, claim that the combination of **those** technologies is more

efficient than the bare CDEO. However, doubts arise in terms of energy consumption, especially in the case of the sono-based processes.

The huge impacts of human activities on the planet has led to an environmental emergency. This emergency is changing the paradigms for the development of environmental remediation technologies. These technologies must not only remove pollutants from liquid, gases streams or from soil, but they should be sustainable, and they must minimize other potential environmental impacts. According to those facts, application of Life Cycle Assessment (LCA) tools are becoming mandatory in the recent years for environmentalist, because these tools give a more complete view of the real impact of the remediation technologies on the environment. LCA is a technique to analyze and evaluate resources and environmental impacts associated with all the stages of a product's life including raw material, production process, packaging, energy, and some other human activity, as the collection of raw material, production, transportation, consumption, and final disposal (Lam et al., 2020). This tool allows to assess the potential impacts associated to the entire life cycle of a product or a process (Burgess and Brennan, 2001; Domènech et al., 2002; Guinée et al., 2001). In the specific case of a chemical reaction, the application of LCA requires an inventory of the energy, reagents and auxiliary materials consumed, as well as the emission and wasted generated, thus giving a holistic view of the environmental implications of the reaction (Muñoz et al., 2005). The toxicity, ecotoxicity, carbon and hydric footprints are one of the most important data that can be obtained from the LCA. The LCA of different advanced oxidation processes has been reported in literature (Arzate et al., 2019; Foteinis et al., 2018; Muñoz et al., 2005; Zepon Tarpani and Azapagic, 2018). However, there are few data related to electrochemical oxidation (Chatzisyneon et al., 2013) and, to the authors' knowledge, no LCA studies of electrochemical assisted oxidation with UV light and US intensification

have been found until now. In addition, there are data related to intermediates which have been generated in these processes (Brillas et al., 2004; Souza et al., 2016) but there are few studies related to their overall toxicity (San-Román et al., 2020).

Considering this background, this work aims to assess the environmental impacts related to the removal of 2,4-D from wastewater effluents by means of different assisted CDEO treatments using LCA tools. The environmental costs and the advantages and drawbacks of the combination of CDEO and photo and sono assisted technologies, co-called in this work as CDEO, photo-CDEO (UV irradiation coupled to CDEO) and sono-CDEO (US coupled with CDEO) will be evaluated. To do this, a specific methodology following the ISO 14040 was used to evaluate the environmental risks of the three CDEO studies. Firstly, the aim of the study was defined, and the input and output of the systems were specified. According to that, an inventory of each of the three lab-scale setups was performed using Ecoinvent 3.3 database. Considering those approaches, IPPC, ReCiPe, AWARE and USEtox methodologies were used to quantify the environmental burden into 5 midpoint (carbon footprint, ozone layer depletion, water footprint, human toxicity, freshwater ecotoxicity) and 17 endpoint impact categories. Those environmental impacts were assessed and compared in the results section. Finally, conclusions were drawn into the last section of the manuscript.

2. Materials and methods

2.1. Experimental data

The LCA was performed using experimental data previously reported by our group (Souza et al., 2015, 2016). The CDEO treatments were carried out into a bench scale plant working on batch mode and fed with $26.4 \text{ dm}^3 \text{ h}^{-1}$ of a wastewater effluent polluted with 100 mg dm^{-3} of 2,4-D. A Diacell® (type 101) single-compartment electrolytic flow-cell

manufactured by Adamant Technologies was used as electrooxidation reactor. The photo and sono CDEO treatments were coupled with a UV lamp VL-215MC (Vilber Lourmat) and an US generator UP200S (Hielscher Ultrasonics GmbH), respectively. More experimental details of the experimental tests can be found elsewhere (Souza et al., 2015, 2016).

2.2. LCA analysis

- *Functional Unit Definition and inventory*

1 L of wastewater effluent polluted with 100 mg dm⁻³ of 2,4-D was taken as functional unit for the three CDEO treatments. It is important to note that before performing the inventory of the treatment, it is essential to determine the systems boundaries that will be considered into the LCA study. Thus, it must be pointed out that in this case some assumptions were considered to simplify the study. According to that, the CO₂ emission generated by the organic mineralization of the pesticide were not considered. Despite the CO₂ is one of the hazardous gasses that contribute to the greenhouse effect, the amount of CO₂ emitted during the mineralization of pesticides is negligible regarding the amount discharged by the electricity production processes. In this case, considering a total mineralization of the functional unit, 2·10⁻⁴ kg of CO₂ will be emitted to the atmosphere. A slight percentage compared to the overall Global Warming Potential (GWP) of a remediation treatment. Furthermore, it must be highlighted that post-treatments related to an incomplete remediation of the water effluent or additional gasses emissions have not been included into the system boundaries and, consequently, they have not been considered in this study. The inventory of the three-laboratory setups is shown in Table 1. That inventory was simulated using the Ecoinvent 3.3 database and include the equipment that made up each CDEO setup.

175 **Table 1.** Life cycle inventory of CDEO processes

	Life span	CDEO	Photo-CDEO	Sono-CDEO
<i>Experimental set up configuration</i>				
Diacell (type 401)	10 years		0.26 g Diamond 0.1 g Boron 0.15 kg Silicon 1.6 kg Steel 0.7 kg Polypropylene 1.8 g Polyethylene	
Ultraviolet lamp	1.4 years	-	0.4 g Mercuy 46.1 g polypropylene 0.169 kg Silica sand 30 g Cable	-
Glass tube	10 years	-	50 g Borosilicate	-
Ultrasound generator	5 years	-	-	0.245 kg Titanium 10 g Electronic materials 1.15 kg Polyethylene 0.69 kg Steel 30 g Cable
Reactor	10 years		0.6 kg Borosilicate glass	
Piping system	2 year		50 g Silicone 0.15 kg Synthetic rubber	
Electronic conditioner hardware	15 years		50 g Electronic materials 0.7 kg Polyethylene 0.25 g Steel 50 g Cable	
Peristaltic pump	15 years		10 g Electronic materials 1.87 kg Polypropylene 1.08 kg Steel 30 g Cable	
<i>Reagents</i>				
NaCl (g L⁻¹)			3	
<i>Operating parameters</i>				
Treatment time (h)		4	2.7	2.7
Current density (mA cm⁻²)		128	128	128
<i>Energy requirements</i>				
Energy- Spain grid		coal (16%), natural gas (17 %), nuclear (20%), hydro (15%), wind (19%) other sources (12%)		
Energy consumption (kWh for 0.1 g 2,4-D per L removed)		0.291	0.256	0.669

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2.3 Methods

The LCA was carried out using the SimaPro 9.0 software. The IPCC, ReCiPe, AWARE, USEtox Mid-point and ReCiPe End-point methods were used in order to assess a large variety of impacts associated with each of the three processes presented and to determine the environmental performance as a whole (Fernandez-Marchante et al., 2019; Gorrée et al., 2002; Huijbregts et al., 2003; Parascanu et al., 2018). These methodologies were used to quantify the environmental burden into water footprint (Ansorge and Beránková, 2017; Boulay et al., 2018), GWP (Houghton, 1992), ozone layer depletion (World Meteorological Organization, 1991) human toxicity, freshwater ecotoxicity (Rosenbaum et al., 2008) and 17 endpoint impact categories. Thus, all those impact categories were studied for a bare CDEO and photo and sono assisted CDEO processes.

3. Results

Fig. 1 shows the changes of 2,4-D and Total Organic Carbon (TOC) versus the energy applied under a single CDEO treatment and its combination with the irradiation of UV light (photo-CDEO) or the application of ultrasounds (sono-CDEO). Noticeable differences were found in terms of energy consumption required to reach a total mineralization. Thus, the photo-CDEO process is the most efficient technology. It requires 3-times less electricity than a single CDEO and 7-times less than a sono-CDEO. Those differences are higher when the synthetic waste contains sulfate species (Fig. 1b). In fact, this technology can mineralize the waste 2-times faster than the CDEO, what turns into shorter reaction times. However, when the synthetic waste contains chlorides, the coupling of intensified sources does not show significant enhancements regarding the bare CDEO (Fig. 1 a). On the other hand, it is important to highlight that the decrease of

the 2,4-D concentration fits well with the increase in the mineralization (TOC), which points out a low production of intermediates species.

It is worth mentioning that despite the coupling of UV or US techniques to CDEO treatments may speed up the remediation of a wastewater effluent, higher energy consumptions are required to power the UV and US devices. Nevertheless, it is important to perform a complete analysis that includes not only the mineralization efficiency of those technologies but also the environmental cost related to the manufacturing of the setups and the operation process. Furthermore, it is essential to evaluate the level of remediation reached after the treatment.

In Fig. 2, the three processes, using NaCl as electrolyte, are compared regarding three impact categories: Part a shows the GWP impact category, which indicates the equivalent emissions of carbon dioxide and Part b shows the contribution of these processes in the ozone layer depletion. Both analyses were performed by means of the IPCC method. Finally, Part c shows the water used for the removal of this pesticide which was estimated under the AWARE method.

Fig. 1. Influence of the power on the removal of pollutant (full symbol) and TOC (empty symbol) during the electrochemical assisted processes using NaCl (a) and Na₂SO₄ (b) as supporting electrolytes.

Regarding GWP effect, it can be observed that the process that generates the highest impact in terms of carbon dioxide emissions is the sono-CDEO (0.32 kg CO₂ eq.) followed by the single CDEO. The CDEO process emits less than half of CO₂ (0.14 kgCO₂ eq) than the sono-assisted treatment. Contrary to expectation, the photo-CDEO showed the lowest GWP, 0.12 kg CO₂ eq. According to the ozone depletion, the same trend observed in the GWP studies was noticed in this case. The highest impact was observed by the sono-chemically assisted technology (153.3 µg CFC11eq L⁻¹) followed by the photo-CDEO treatment (58.9 µg CFC11eq L⁻¹). These effects are mainly related to the amount of energy consumed by each treatment. Results noticed that the impact generated by the setups manufacturing is much lower than the impact of the energy consumed in all cases. In fact, the energy consumption impact is strongly influenced by the energy mix of the grid used to power the treatment technologies. In this work, carbon footprint and ozone depletion impact categories were assessed considering the Spanish grid mix.

The impact associated to the overall water use of a wastewater remediation treatment follows the same trend aforementioned by the carbon footprint. Nevertheless, lower differences are noticed in this case, being the water consumption associated with the sono-CDEO only 2.6 times higher than of photo-CDEO. The total water consumptions to remediate a 1 L of wastewater of polluted with 100 mg dm⁻³ of 2,4-D are 43, 37 and 97 L under bare CDEO, photo-CDEO and sono-CDEO, respectively. As in the previous cases, a huge percentage of the water footprint of those treatments is related to the production of energy required to power those technologies. Furthermore, this impact may be highly influenced by the energy mix used. It is important to keep in mind the magnitude of these data, because according to the functional unit studied, the water required to reach a complete mineralization is 100 times higher than the amount of water to be treated.

Fig. 2. Global warming potential (a), ozone depletion (b) and water footprint (c) per 0.1 g L⁻¹ of 2,4 D removed. Electrolyte: NaCl.

This trend is not only observed in electrochemically based processes but in many others remediation treatments shown in literature. Thus, (Morera et al., 2016; Rodríguez et al., 2016) obtained huge water footprints of heterogeneous Fenton processes for the treatment

of pharmaceutical wastewater, being those water consumptions of 65 and 75 L, respectively. It is important to note that water footprint is one of the most important environmental impact categories to be studied, mainly in regions such as the south of Spain, where this resource is highly scarce.

Environmental and human toxicities are also one of the most important impact categories to be assessed when a remediation treatment is performed (Aljerf and AlMasri, 2018) being essential to quantify the overall sustainability of a remediation process.

Freshwater ecotoxicity and human toxicity (cancer and non-cancer) are shown in Fig. 3. The categories of freshwater impact ecotoxicity, human toxicity (non-cancerous) and human toxicity (cancer) have been studied taking into account the effect generated by the different treatments and also considering the effect of the intermediates present at the end of the treatment when all 2,4-D has been removed. These scenarios have been compared with the initial pollution, 0.1 g 2,4-D L⁻¹. As expected, the treatment significantly reduces the initial toxicity of the pollution after the remediation process. Nevertheless, the intermediate species generated during the electrooxidation treatment increase the overall toxicity of the treatment. 0.1 g L⁻¹ of 2,4-D in water generates an ecotoxicity of 0.0861 PAF.m³.day (Potentially Affected Fraction of species per cubic metre of water in a day), as shown in Part A of Fig. 3. Nevertheless, this value increases a 33.3 % and a 66.75 % when the wastewater is treated by single CDEO and a sono-CDEO treatment, respectively as a consequence of the intermediate species remaining into the water body once the 2,4-D has been removed. Conversely, the ecotoxicity of the initial pollution drop a 99 % using a photo-CDEO process because of the lower concentration of intermediate noticed at the end of this assisted CDEO treatment. In the case of CDEO and sono-CDEO, the 99.9 % and 99.8% of freshwater ecotoxicity impacts are associated to the intermediate generated (3 mg L⁻¹ and 3.75 mg L⁻¹ of hydroquinone, respectively). On the other hand, the 0.1 %

and 0.2 % of freshwater ecotoxicity impact is mainly associated with the electricity consumed. In the case of photo-CDEO the 66.2 % is associated to treatment because low concentrations of intermediates were identified at the end of the remediation treatment. The human toxicity (non-cancer) of an initial pollution of 0.1 g L⁻¹ of 2,4-D showed an impact of $5.76 \cdot 10^{-10}$ cases. This toxicity is reduced more than 99% after the three proposed treatments. Thus, the initial impact was reduced a 99.2, a 99.6 and a 98.8 % when the wastewater was treated by CDEO, photo-CDEO and sono-CDEO, respectively. Those results suggest again that the main impact contribution is related to the electricity supplied to the treatment technologies (around a 95 % of human toxicity impact is due to energy consumption). Thus, those results point out the great influence of this input nature on the sustainability of the electrochemical wastewater treatment technologies. At this point, coupling of electrochemical technologies with green energies could be an innovative solution in order to make these processes even more sustainable. Regarding cancer-human toxicity, the final toxicity exceeds the initial toxicity of the pollution ($9.98 \cdot 10^{-14}$ cases) due to the huge toxicity showed by the intermediates remained into the water effluent after the treatment. Those results point out the importance of a total mineralization in order to get rid of the toxicity of the initial pollution from the environment.

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298 **Fig. 3.** Freshwater ecotoxicity (a) and human toxicity for non-cancer (b) and cancer (c)

299 impacts per 0.1 g L⁻¹ 2,4 D removed. Electrolyte: NaCl.

Several authors have indicated the possible degradation mechanisms of 2,4-D for the different supporting electrolytes (Brillas et al., 2004; Souza et al., 2016). The intermediates that are formed in the 2,4-D degradation process in the presence of NaCl are 2-Chlorophenol, Hydroquinone, 4-Chlororesorcinol and Dichlorophenol. The figures show the effects caused by hydroquinone (3 mg L^{-1} CDEO and $3,75 \text{ mg L}^{-1}$ sono-CDEO), which could be derived from a non-complete mineralization. It is observed that from the point of view of freshwater ecotoxicity the hydroquinone is much more dangerous than the raw pesticide, being this effect noticeable for human toxicity, specifically referenced to cancer cases (Part C) (Anku et al., 2017). In general terms, intermediates are highly aggressive in the environment because of smaller organic molecules are more easily assimilable by microorganisms. This could prevent against incomplete treatment alternatives, frequently proposed in the literature, such as the biological processes. Nevertheless, those results suggest that complete treatments up to mineralization are worth from a holistic point of view.

To the best of our knowledge, the main operation parameter in the electrolytic treatments of waste is the current density applied. This operational parameter fixes the reaction rate and the efficiency of the process. Thus, huge current densities turn into faster treatments but lower removal efficiencies due to undesirable secondary reactions. In order to quantify the influence of this parameter on the sustainability of the treatment technology, a study at a low (10 mA cm^{-2}) and a high (128 mA cm^{-2}) current densities was performed for the photo-CDEO technology, because of its most sustainable performance. This technology showed a better technical and environmental viability, without a significantly increase in the energetic and equipment costs. Furthermore, the presence of salts into the water body may contribute or reduce the efficiency of the remediation process. According to this fact, the influence of the supporting electrolyte (NaCl or Na_2SO_4) into the

environmental impact of a remediation treatment has been evaluated. The environmental risks related to these operational conditions (current density and supporting electrolyte) have been evaluated for 17 endpoints impact categories and are summarized in Fig 4.

Fig. 4a shows the influence of the current density on the sustainability of a photo-CDEO treatment. Results clearly point out lower impacts working at higher current densities, despite initially this option may seem less environmentally-friendly, because the oxidation of pollutants competes with the unproductive oxidation of water, promoted at higher current densities. Nevertheless, the much shorter treatment time required, associated to the higher production of stronger oxidants, become this operational condition into an environmental advantage

The most significant impact categories are, again, those related to the energy production, fossil depletion and climate change. Those results are tied to the energy mix used to perform this study, a Spanish energy mix (60% of the total energy came from fossil origin).

Fig. 4b shows the influence of the supporting electrolyte on the sustainability of a photo-CDEO treatment. Results notice a lower environmental cost when chloride species are not discerned at the end of the treatment. Thus, the most meaningful impact categories drop at least a 65 % in sulphate medium. Carbon and water footprints showed a reduction of 67 and 65 % regarding the photo-CDEO performed in chloride medium, showing values of 0.04 kg CO₂ eq and 13 L, respectively. Nevertheless, the ozone layer depletion impact showed a drop of 96 %, 2.1 µg CFC11eq L⁻¹. Those results can be explained in terms of the production of more efficient oxidants, such as persulfates or hydrogen peroxide when Na₂SO₄ is used as supporting electrolyte.

Fig. 4. Effect of current density (a) and electrolyte nature (b) in sensitivity studies of a photo-CDEO for 17 different endpoint impact categories. Current density supplied: 128 mA cm⁻² (black) and 10 mA cm⁻² (gray). Supporting electrolyte: NaCl (black) and Na₂SO₄ (gray).

Finally, Table 2 compares the results obtained in this study with other reported in literature by means of the carbon footprint. As it has been demonstrated in this work, the energy demand required to reach a total mineralization of a wastewater effluent is the most important input to be considered to assess the sustainability of electrolytic technologies. The strong influence of the energy mix grid into carbon and water footprints may showed fluctuating impact scores according to the nature of the energy mix, mainly made up of renewable or non-renewable sources. Considering a Spanish energy mix grid,

those impacts must be higher than in Iceland or Norway, countries which produce more than a 90 % of its energy by means of renewable sources.

As it can be seen, electrochemical technologies may compete satisfactorily with other AOPs in terms of sustainability according to the carbon footprints showed in Table 2. It is important to note that the coupling of green energies and electrochemical technologies could reduce the environmental impacts related to the energy production, becoming these technologies into more sustainable remediation processes.

Table 2. 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 and electrolyte	Functional unit and location	Carbon footprint (kg CO2 eq.)
Muñoz et al., 2005	· Photocatalysis	Pilot unit	Kraft mill bleaching wastewater	1 m ³ (Spain)	90.00
	· Solar Photocatalysis				0.48
	· PhotoFenton				38.00
	· Solar PhotoFenton				0.76
Chatzisyneon et al., 2013	· UV heterogenous photocatalysis	Laboratory unit	Olive mill wastewater	1 g L ⁻¹ of COD and 1 g L ⁻¹ of TPh Chania (Greece)	5.2
	· Electrochemical Oxidation			0.16	
Fernández-Marchante et al., 2020	· CDEO	Laboratory unit	2,4-D (NaCl)	0.1 g L ⁻¹ (Saudi Arabia)	0.14
	· Solar CDEO			0.1 g L ⁻¹ (Spain)	0.019
	· Wind CDEO				0.020
	· CDEO			0.1 g L ⁻¹ (Brasil)	0.328
	· CDEO			0.1 g L ⁻¹ (France)	0.0685
	· CDEO				0.0365
This study, 2020	· CDEO	Laboratory unit	2,4-D (NaCl)	0.1 g L ⁻¹ (Spain)	0.1405
	· Photo CDEO				0.124
	· Sono CDEO				0.322
	· PhotoCDEO				0.228
	· PhotoCDEO				(Na ₂ SO ₄)

According to the aforementioned results, it can be claimed that the combination of UV irradiation with CDEO treatments demonstrates a superb performance in terms of sustainability. The higher performance reached by the photo-CDEO thanks to the UV irradiation joined to the lower environmental impact showed by this experimental setup and its operation, make this assisted technology one of the best sustainable alternative to the single CDEO. Hence, those results support the need for further research in the sustainability of remediation technologies in order to develop the most suitable treatments in terms of removal and sustainability performance.

4. Conclusions

From this work the following conclusions can be drawn:

- CDEO, sono-CDEO and photo-CDEO can face the treatment of wastes polluted with 2,4-D. The most efficient process from the viewpoint of energy consumption is the photo-CDEO, which attains the faster removal to a complete mineralization of the waste.
- The lowest impacts on carbon footprint and ozone depletion are obtained by photo-CDEO, followed by CDEO and sono-CDEO which can be explained by the amount of energy consumed and the level of remediation attained in each case. The impact generated by the installation manufacturing is much lower than that impact of the energy consumed in all cases. Those results point out that the impact of the grid mix used to power the electrochemical devices is extremely relevant, being a 99 % of the total GWP of the treatment.
- The impact associated to the water use also follows the same trend. The water consumption associated with the sono-CDEO is 2.6 times higher than the water

consumption of a photo-CDEO treatment. It is important to keep in mind the magnitude of the total water consumption associated to each technology, because of the use of water exceed the amount of water that it is aimed to be treated.

- The human toxicity is reduced to 99.2 %, 99.6 % and 98.8 % when the wastewater is treated by CDEO, photo-CDEO and sono-CDEO, respectively. Those results point out the good prospective of these technologies to reduce the hazardousness of discharges. Nevertheless, data showed huge toxicities of the intermediate species generated during the electrooxidation treatment which make essential a complete mineralization of the organic matter present into the wastewater body, getting rid of the toxicity of the water effluent.
- Running these technologies at large current densities shows important benefits from the sustainable point of view. Likewise, low concentrations of chlorides showed lower environmental risks. Electrochemical technologies seem to compete satisfactorily with other AOPs in terms of sustainability according to their carbon footprints.
- The huge environmental cost related to the energy consumption of these electrochemical technologies may be overcome coupling renewable energies to these processes which could become them into more sustainable techniques to remediate environmental resources.

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