



## Research article

# Toward more sustainable photovoltaic solar electrochemical oxidation treatments: Influence of hydraulic and electrical distribution

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## ABSTRACT

Powering electrochemical technologies with renewable energies is a promising way to get more sustainable environmental remediation techniques. However, the operational conditions of those processes must be optimized to undergo fast and efficient treatments. In this work, the influence of electrical and hydraulic connections in the performance of a set of two electrolyzers directly powered by photovoltaic panels was evaluated. Despite both electrolyzers were assembled using the same electrode material, they showed different performances. Results indicate that the electrolyzer with higher ohmic resistance and higher overpotential attained a greater production of oxidant species, being produced under the most efficient strategy around 4.8 and 15.1 mmol of oxidants per Ah by electrolyzer 1 and 2, respectively. Nevertheless, an excess of oxidant production because of an inefficient energy management, led to low removal efficiencies as a consequence of a waste of energy into undesirable reactions. Regarding the hydraulic distribution of wastewater between the cells, it was found to influence on the total remediation attained, being the serial connection 2.5 and 1.8 more efficient than a parallel wastewater distribution under series and parallel electrical strategies, respectively. Regarding electrical strategies, parallel connections maximize the use of power produced by the photovoltaic panels. Furthermore, this allows the system to work under lower current densities, reducing the mass transfer limitations. Considering both advantages, a hydraulic connection of the cells in series and an electrical connection in parallel was found to reach the highest specific removal of pollutant, 2.52 mg clopyralid (Wh)<sup>-1</sup>. Conversely, the opposite strategy (parallel hydraulic connection-series electrical connection) showed the lowest remediation ratio, 0.48 mg clopyralid (Wh)<sup>-1</sup>. These results are important to be considered in the design of electrolytic treatments of waste directly powered by photovoltaic panels, because they show the way to optimize the cells stack layout in full-scale applications, exhibiting significant impact on the sustainability of the electrochemical application.

## 1. Introduction

Society has increased its concern about the climate emergency that is currently taking place in the World. Human actions performed over the past decades have left very negative consequences on the environment. Among the harmful effects that can be discerned nowadays, the environmental pollution is one of the most important, being the consequence of the uncontrolled production and the misuse of hazardous chemicals (Nations, 2020). In this context, it is worth mentioning that noticeable

concentrations of pesticides can be found in soils and water effluents because of their use in crops production (Berberidou et al., 2017; Dominguez et al., 2020; Solís et al., 2019). Runoff and filtration processes transport these compounds from soils to underwater reservoirs. Thereby, these hazardous compounds could potentially reach the water supply chain and, consequently, affect human health (García-Segura et al., 2018; Repetto and Baliga, 1996). Furthermore, most of these compounds present a huge chemical stability and a low biodegradability, thus special treatments are necessary to remove them from the

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environment (Damalas and Eleftherohorinos, 2011; Jacob and Cherian, 2013).

Concerning remediation technologies, Electrochemical Advanced Oxidation Processes (EAOPs) have shown high removal efficiencies on the treatment of wastewater polluted by a wide range of hazardous compounds (Abdessalem et al., 2010; Brillas and Martínez-Huitle, 2015; Dewil et al., 2017; Frontistis et al., 2011; Martínez-Huitle and Panizza, 2018; Rodrigo et al., 2014; Sirés and Brillas, 2012). Among the large variety of EAOPs, the conductive diamond electrochemical-oxidation (CDEO) has demonstrated to reach very important mineralization degrees (Comminellis et al., 2005; Marselli et al., 2003; Quiroz et al., 2006; Rodrigo et al., 2010). The higher mineralization attained is partially associated to the performance of the boron doped diamond (BDD) anode regarding other electrode material, which is known to produce huge amounts of hydroxyl radicals due to its high oxygen evolution overvoltage (García-Segura et al., 2015; Guelfi et al., 2019; Nidheesh et al., 2018). Thus, organic compounds can be directly oxidized by the hydroxyl radicals ( $\cdot\text{OH}$ ) generated on the anodic surface or indirectly oxidized by redox reagents in the bulk of the solution (Moreira et al., 2017; Vasudevan and Oturan, 2014). EAOPs use the electron as almost the unique reactant, being able to recover environmental resources without the addition of further reagents and without waste production. Nevertheless, energy is essential to run these remediation treatments. Traditionally, these processes have been powered in galvanostatic mode, using power supplies directly connected to the grid. Despite the high efficiencies reported under this operational mode, the huge energy requirements associated with those technologies drop their sustainability regarding other remediation techniques (Poblete et al., 2019). To make them more sustainable, it has been recently proposed the use of renewable energies to power them, reducing the energy losses related to the distribution and conversion of electricity (Millán et al., 2020; Souza et al., 2015b, 2016). Furthermore, renewable sources contribute to reduce the dependency of fossil fuels, to prevent the lack of energy for future generations and to develop a more sustainable energetic system (Jafary et al., 2017).

Nevertheless, the intermittent production of solar energy can result in an unpredictable remediation. The solar power production depends on the solar radiation and, hence, the remediation treatment will depend directly on the weather conditions, hour of the day, etc. Until now, the photovoltaic solar electro-oxidation (PSEO) treatments have been previously studied by several authors working under different operational conditions and also in both, continuous and batch operation modes (Alvarez-Guerra et al., 2011a, b; Manuel Ortiz et al., 2007; Souza et al., 2015a; Thomson and Infield, 2003; Valero et al., 2014; Valero et al., 2010). In every case, different performances were reported. The continuous treatment of wastewater directly coupled by solar photovoltaic (PV) panels shows the drop of removal at low current densities, in short, when low sunlight irradiation is received by PV panels (Millán et al., 2019). To prevent this problem, the use of smart control systems has been tested in order to operate under a constant electrical charge density (Dominguez-Ramos et al., 2010; Marmanis et al., 2015; Valero et al., 2008) by modifying the flow rate as a function of the intensity supplied by the PV panels. Furthermore, energy storage systems have been used to smooth the power produced by renewable energies. This powering strategy accommodates energy production and demand, even though energy conversion losses may arise, reducing the specific remediation efficiency (de Melo Henrique et al., 2019; Ganiyu et al., 2019; Iyappan et al., 2014). In view of this fact, the most pragmatic and efficient coupling of PV plants and electro-oxidation treatments seems to be the random direct connection between both systems. Considering those facts, the solar powering of CDEO may lead to a cost drop (energy consumption) and a sustainability improvement. This later fulfils one of the targets exposed by the EPA (Environmental Protection Agency) according to the definition of *green remediation*: “to reduce the total energy use and to increase the percentage of energy from renewable resources into a remediation process” (EPA, 2011). In this way, Jiang et al.

reported that the use of solar powering technologies to recover a polluted water body showed a drop into the carbon emission of a 64% regarding a grid powering (Jiang et al., 2018), which confirms the environmental benefits of using renewable energies as power sources.

Considering this background, this work is focused on the management of the energy produced by PV panels to power more sustainable electrochemical environmental treatments. As aforementioned, the unique reagent of this electrochemical techniques is the electron. Furthermore, the energy required by those treatments is direct current (DC) as the PV panels produce. Hence those characteristics make the electrochemical technologies and the renewable energies the perfect tandem to reach a green remediation (Baek et al., 2012). Both setups can be directly connected without inverter devices which makes easier and cheaper their coupling. According to these premises, this combo can shed light on the water treatment field specifically in locations without energy supply. Despite the random direct coupling of CDEO treatments to an off-grid PV plant seems straightforward, an exhaustive analysis of both devices is essential to take advantage of the total energy produced by the PV panels and to manage it properly in order to reach the maximum remediation of the water effluent under the most sustainable conditions.

Considering the previous statements, the main aim of this work is to assess the optimum hydraulic and electrical strategy to undergo the most sustainable and efficient photovoltaic solar electrochemical oxidation. Thus, the influence of the electrical and hydraulic connections in the performance of a set of two electrolyzers powered by PV panels is evaluated in this work, with the aim of determining the management strategy that helps to reach the highest remediation efficiency in terms of pollutant removal and energy use. This will support that for getting sustainable processes, not only the connection of green powering devices with electrochemical cells is needed but also it is required to manage appropriately the way in which the connection between powering and treatment is made.

To face up the main aim of this work, firstly a set of two electrolyzers was electrochemically characterized under the different electrical strategies proposed (series and parallel). These previous tests allow to know the energy requirements of the electrochemical setup to check if the PV plant could work as power supply of the treatment. After that, to assess and quantify the removal performance achieved by each strategy, the concentration of a pesticide (taken as model of pollutant) was monitored during the treatment. To compare in equal terms the performance of the proposed hydraulic and electrical strategies, the distribution and use of energy were assessed by means of the currents and voltages supplied to each reactor for each configuration studied. As a result, the best hydraulic-electrical connection strategy was determined in terms of the highest specific removal of pollutant (per unit of energy powered). In this way, the optimum operational conditions were assessed in terms of efficiency and, thus, of sustainability. The experimental planning, the setups and the electrochemical and analytical techniques used in this paper have been detailed in Section 2. Finally, Section 3 and 4 shows the foremost Results and conclusions reached in this work, respectively.

## 2. Materials and methods

**Hydraulic & Electrical connections strategies.** As noted above, the main aim of this work is focused on the management of the solar energy coming from PV panels to power a set of two electrolyzers from the viewpoint of hydraulic and electrical connectivity, looking for the most sustainable and efficient wastewater clean-up in terms of grams of pollutant removed per unit of energy. Fig. 1 shows the operational strategies that will be faced up in the present work. Series and parallel hydraulic and electrical connections between two cells were assessed to get the highest remediation of a polluted effluent under a direct PSEO treatment in terms of sustainability according to the removal per unit of energy.

The hydraulic flows are expected to play an important role in the

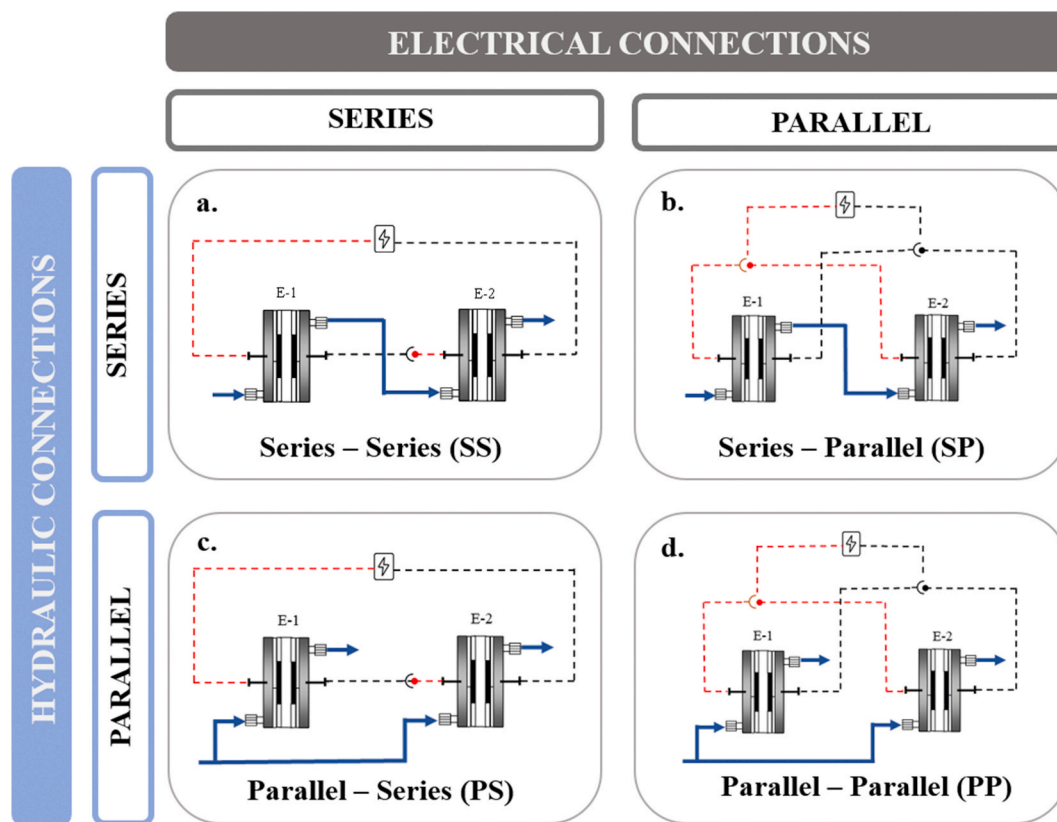


Fig. 1. Experimental test planning. (a) Series-Series, (b) Series-Parallel, (c) Parallel-Series and (d) Parallel-Parallel.

removal of a pesticide because of the hydraulic retention time (HRT) influences the period in which the waste is in direct contact with the electrodes. The higher is the retention time applied, the higher will be the removal of pollutant (Ejhed et al., 2018; Malinovic et al., 2018). Otherwise, the kinetic of an electrochemical remediation treatment directly depends on the applied current density (Comninellis and Chen, 2009; Frontistis et al., 2018; Oturan and Aaron, 2014). Thus, the oxidation processes can be current or mass transfer controlled when the applied current densities are under and over the limit current density (Comninellis et al., 2008; Kapařka et al., 2007; Panizza et al., 2008), respectively.

Higher current densities lead to faster remediation treatments but lower current efficiencies. Furthermore, the use of exceeded current densities can turn into non-desirable secondary reactions and higher wasted energy consumption (Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009). Nevertheless, considering the fluctuating current densities supplied by the PV panels, the process will work under different control mechanisms and it will turn into variable current efficiencies. Consequently, the current supplied to each electrolyzer, as a result of the different electrical connections proposed, will determine the rate and degree of remediation attained. Despite this green powering strategy seems to be a sustainable operational configuration to run electrochemical technologies, the fluctuating production of renewable sources may bring out unexpected remediation performances. For that reason, fluid and energy flows must be assessed and optimized before developing the design and performance of a PSEO treatment because of the influence of the way to connect devices can be of a great help (Mateo et al., 2018).

**Experimental setups & Characterization procedures.** Two commercial CDEO reactors, DiaCell® 101 (Adamant Technologies, France) were used to evaluate the remediation of 4.0 L of a synthetic wastewater polluted with an organochlorinated pesticide (clopyralid) directly powered by PV panels. This waste contained  $100 \text{ mg dm}^{-3}$  of clopyralid

(Zymit Química, Spain) and  $3000 \text{ mg dm}^{-3}$  of  $\text{Na}_2\text{SO}_4$  to simulate the ionic components. Both electrolyzers were equipped with two BDD electrodes ( $78.5 \text{ cm}^2$  of active area) supported on silicon substrate supplied by WaterDiam (Switzerland). They were named as E1 (Electrolyzer 1) and E2 (Electrolyzer 2). The tests were performed into a bench scale setup and batch mode. The total fluid was recirculated throughout the electrolyzers during the electrooxidation treatments, nevertheless, the effluent was conducted through each electrolyzer in a different way according to the hydraulic strategy used. Under a series hydraulic connection, Fig. 2 a and b, the total solution was pumped throughout the first electrolyzer by a peristaltic pump JP Selecta® Percom N-M. Electrolyzer 2 was fed through an overflow stream from a buffer tank. Conversely, under a parallel hydraulic connection (Fig. 2 c and d) the total wastewater effluent was equally distributed to two storage tanks and pumped to each single electrolyzer by means of peristaltic pumps. Considering both hydraulic strategies, the concentration of pollutant was assessed on the outlet stream of each electrolyzer. It is important to highlight that the series hydraulic configuration setup requires one less pump. Despite, pumps were directly powered by the grid and their energy consumptions have not been considered into the study, this fact is an advantage in terms of cost and sustainability.

Regarding the power source, two PV panels of 160 W connected in parallel (Atersa, Spain) were used as power supply in this work. In contrast to a conventional electro-oxidation treatment working at galvanostatic mode, the direct random coupling of a PV plant to an electro-oxidation setup does not allow the control of the current density supplied to the remediation treatment. Keeping this in mind, the current density supplied by the PV panels will be related to the solar radiation received each day and consequently it cannot be easily regulated. Fig. 2 shows the solar radiation profiles of each operational day.

Despite all experiments were performed under winter conditions during the month of January, the solar radiation profiles showed fluctuating conditions which will turn into a variable powering of the

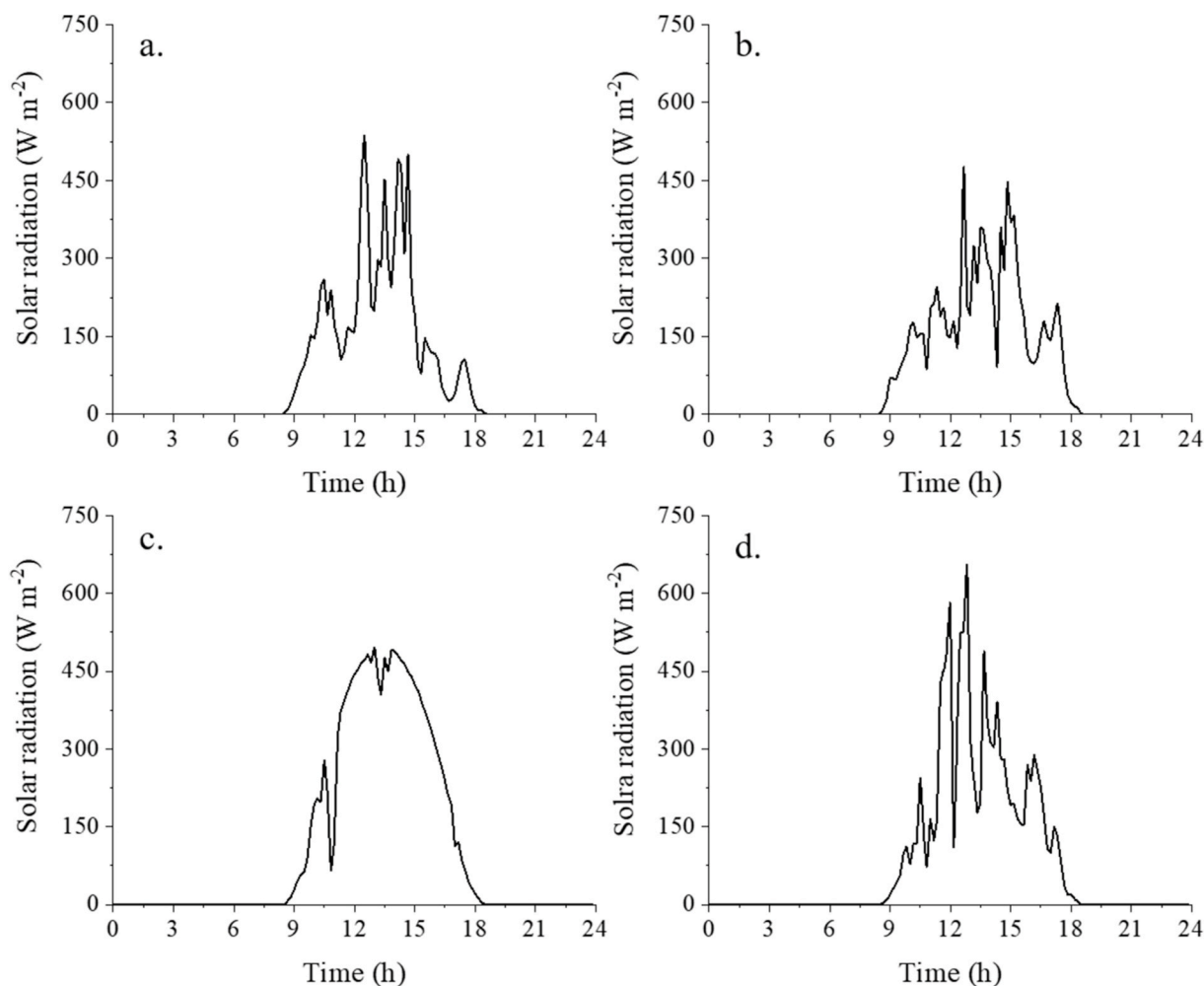


Fig. 2. Solar radiation received during electro-oxidation treatments powered by PV panels using different hydraulic and electric connections. (a) SS, (b) SP, (c) PS and (d) PP. Location: Ciudad Real (3.59N 3.55O), Spain. Data provided by METEO Ciudad Real: (METEO).

electro-oxidation treatment. Table 1 shows the total, average and maximum solar radiation received each day of operation. Data shows that the experiments performed under parallel conditions received higher solar radiation values which may turn into faster remediation treatments. Furthermore, the smoother solar radiation profile observed by the PS test explains its higher average solar radiation during the electro-oxidation treatment.

Firstly, a key aspect to be considered is the electrical supply of the power source used to supply electrically the electrochemical treatment (the PV plant) and the electrical requirements of the technology that is going to be powered (the PSEO setup). To undergo the most sustainable and efficient remediation treatment, the electrical features of both devices must fit. Thus, electrochemical characterization analyses were carried out to each electrolyzer to provide information about the powering operational limitations of the PV panels. Polarization curves (PC) were carried out manually using a Delta Elektronika ES-030-5 DC power

supply. Electrochemical impedance spectroscopy (EIS) measurements were made using an Autolab potentiostat/galvanostat (PGSTAT-302N) coupled with a FRA32M module. Despite those electrolyzers are going to be used to carry out electrochemical remediation techniques of wastewater effluents, their electrochemical characterizations were performed using a liquid effluent without pollutant. Thus, a solution containing only  $3 \text{ g dm}^{-3}$  of  $\text{Na}_2\text{SO}_4$  as supporting electrolyte, was used to carried out those analyses. On the other hand, to assess the performance of the photovoltaic solar electrochemical oxidation using the different hydraulic and electrical strategies, the concentrations of pesticide and oxidant species were monitored by high performance liquid chromatography, HPLC (Agilent 1260 Infinity) and by iodometric titration, (Metrohm 702 SM Titrino), respectively, as reported elsewhere (Cañizares et al., 2009; Millán et al., 2019; Rodríguez et al., 2018). pH and conductivity analyses were carried out using CRISON pH25+ and CRISON CM35+ instruments.

Table 1

Total, average and maximum solar radiation for each hydraulic-electrical strategy.

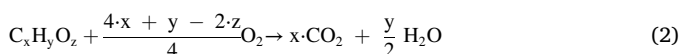
	Solar radiation		
	Total ( $\text{Wh m}^{-2}$ )	Average ( $\text{W m}^{-2}$ )	Maximum ( $\text{W m}^{-2}$ )
SS	1745.17	73.22	534
SP	1785.16	74.90	476
PS	2715.83	113.95	646
PP	2047.17	95.89	495

### 3. Results and discussion

As aforementioned, the main aim of this work is to optimize the operational conditions of a photovoltaic solar electrochemical oxidation treatment under the most sustainable and efficient way. To evaluate the best operational strategy, firstly it is essential to know in detail the features of the experimental setup. This fact becomes highly important when the remediation technology is directly powered by a renewable source which may involve an intermittent energy supply. According to

that, an electrochemical characterization of the power and remediation equipment was performed. Once known the electrical characteristics of both setups, the remediation performance of the PSEO was tested using different hydraulic and electrical strategies in order to assess the most optimum, sustainable and efficient operational conditions.

**Electrochemical characterization & electrical distribution.** The two electrolyzers were electrically characterized in a first stage of this study. Fig. 3 shows the PC and the results of EIS analyses. As it can be seen, despite both electrolyzers were assembled using the same electrode material (BDD electrodes supported on Si), their electrical performances were completely different. PCs show a higher oxygen evolution potential (OEP) for E2. Those results reveal a lower oxygen evolution and, consequently, an expected higher current efficiency for this electrolyzer in the production of oxidants (because of an expected higher production of hydroxyl radicals) (Panizza and Cerisola, 2009; Zhang et al., 2014). According to that, the production of the most powerful oxidant, hydroxy radical, may be easily attained by the oxidation of water on the anodic surface, as reaction 1 describes. Those radicals are capable of oxidizing faster a wide range of organic molecules until CO<sub>2</sub> (reaction 2) owing to its nonselective nature and its higher reaction rate, 10<sup>6</sup>-10<sup>9</sup> mol<sup>-1</sup> s<sup>-1</sup> (Andreozzi et al., 1999).



In addition, it has been proved that the hydroxyl radicals may interact between themselves or with other species to generate other powerful oxidants as H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> (Marselli et al., 2003; Sirés et al., 2014), as reaction 3 and 4 show, respectively.



Hence, the optimized production of hydroxyl radical may turn into efficient remediation treatments thanks to direct and mediated oxidation mechanisms. The production of oxidant species which may attack the pollutants contained into the bulk solution is directly related to the current density supplied to the electrochemical oxidation and, in turn, this variable depends on the electrochemical features of the electrolyzer and, in this particular case, on the solar radiation received by the PV plant. Considering those facts, the management of the solar power is essential to control the performance of an electrochemical remediation treatment directly coupled to a fluctuating renewable source as the solar

energy.

As noticed above, the PCs of the electrically connected electrolyzers may also provide information about the powering operational limitation of the PV panels. The electrolysis carried out under a parallel electrical connection allows the system to work under higher current densities, being limited at 9 A (current at maximum power). Conversely, the electrolysis running under series electrical connection can work below 35.7 V (voltage at maximum power).

Regarding Nyquist plots (EIS), electrolyzer E1 showed a lower ohmic resistance as compared to E2. Those Results agree with the information drawn from PCs. The lower is the PC slope, the higher is the ohmic resistance of the cell. Both electrochemical techniques showed the same trend which confirms the reliability of the data obtained. Nevertheless, those results claim differences between both electrolyzers despite of both setups were assembled with the same electrode material.

Santos et al. reported the different electrochemical behaviour of BDD electrodes associated with different boron contents (Santos et al., 2020). Thus, the lower ohmic resistance exposed by E1 could be directly related to a higher boron doping of the BDD installed, which provides the electrode of a higher electrical conductivity. Despite both anodes have the same BDD coating, the powering of higher current densities can wear the surface of the electrode reducing its active area which could explain the different resistances between both electrolyzers. Damages on the surface of the electrode due to boron losses can hinder the electron transference and consequently reduce its conductivity (Chaplin et al., 2013; Duo et al., 2004).

The lower ohmic resistance exposed by this electrolyzer leads to lower operational cell voltages, according to Ohm's law (Equation (1)). Concerning the equivalent resistances of each electrical connection, the use of a parallel electrical connection turn into a lower equivalent resistance and, consequently, into a higher energy consumption (see equations 2 and 3). Keeping these premises in mind, lower ohmic resistances can result as strengths or weaknesses that must be assessed in detail. In terms of energy consumption, the lower is the ohmic resistance, the lower is the power demand of the electrochemical setup and, consequently, the cheaper is the remediation treatment. According to the use of a renewable source, the lower the energy consumption of the setup, the higher the number of cells that may be coupled to the remediation system and therefore, the higher could be the wastewater flow to be treated in a day. Conversely, regarding mineralization efficiency, lower oxygen evolution potentials could lead to lower production of hydroxyl radicals and oxidant species, dropping down the organic compound oxidation capacity. It is important to note that despite series electrical configuration may power the PSEO at higher current densities,

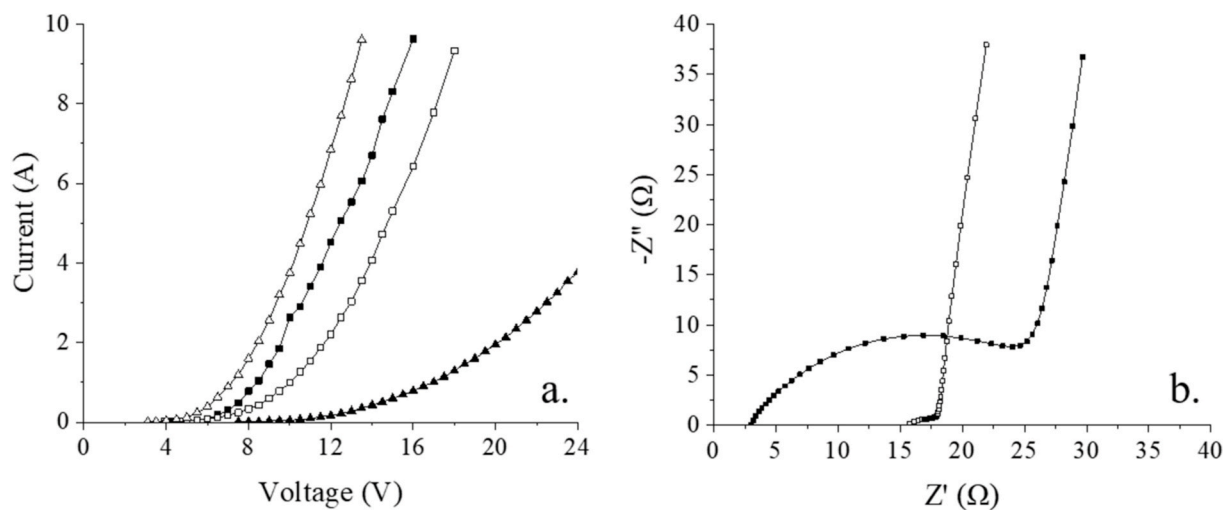


Fig. 3. Linear sweep voltammograms (a) and Nyquist plots (b) for different BDD electrolyzers (Electrolyzer 1 (■) and Electrolyzer 2 (□)) and electrical connections (Series (▲) and Parallel (△)). [Na<sub>2</sub>SO<sub>4</sub>] = 3 g dm<sup>-3</sup>.

and undergo a faster remediation, these operational conditions can turn into a waste of energy, dropping the efficiency and, hence, the sustainability of the treatment.

$$V = I \cdot R \quad (1)$$

where, V corresponds to the voltage of the device, I the current flowing through it and R its resistance.

- Series electrical connection:

$$R_{\text{TOTAL}} = R_{E1} + R_{E2} \quad (2)$$

- Parallel electrical connection:

$$\frac{1}{R_{\text{TOTAL}}} = \frac{1}{R_{E1}} + \frac{1}{R_{E2}} \quad (3)$$

where  $R_{\text{TOTAL}}$  corresponds to the total resistance of the electrochemical layout and  $R_{E1}$  and  $R_{E2}$  represent the individual resistance of each electrolyzer.

Consequently, to evaluate the best hydraulic and electrical connection for treating a wastewater with a set of two electrolyzers directly powered by PV panels, the energy consumption and the removal capacity of each setup were assessed. Firstly, to quantify the energy consumption of the remediation setup, the voltages and currents supplied to each electrolyzer were recorded. Simultaneously, in order to evaluate the efficiency and sustainability of the treatment in terms of remediation per unit of energy, the removal of pesticide was recorded. In this way, it

can be assessed if the total energy produced by the PV panels is being used satisfactorily or wasted, which may shed light of a wrong management of the green power resource which, in turn, can lead to an inefficient remediation.

Fig. 4 shows the applied current and the total electrical charges supplied to the four electrolytic systems evaluated. All figures show the applied current under solar power production hours. In all the cases, the PV panels started to supply energy around 08:10 a.m. As Kirchhoff's law (Browne, 2018; Lvov, 2014) exposed, when several resistors are connected in parallel, the total current flowing through them is equal to the sum of the individual current of each resistor. In contrast, in series connections, the current of the circuit will be the same in all its points and the total voltage will be the sum of the single voltage of each device connected. In agreement with this theoretical law, Fig. 4 a and c show a unique set of current values which correspond with the current flowing throughout both electrolyzers due to the use of a series electrical connection. Conversely, parallel electrical connections supply the same voltage to each device and current depends on the single cell resistance, Fig. 4 b and d. Regarding parallel electrical connections, as expected, lower currents were supplied to E2 as a result of the higher ohmic resistance exposed by this electrochemical reactor. According to literature, lower current densities could lead to slow but highly efficient treatment. Nevertheless, this hypothesis must be tested because of the huge variability of the current density supplied by the PV plant during the day.

Furthermore, it is important to highlight the differences observed among the total applied electrical charges each day, despite all the treatments were performed in winter days. The huge fluctuation of powering is representative of the important intermittence in the

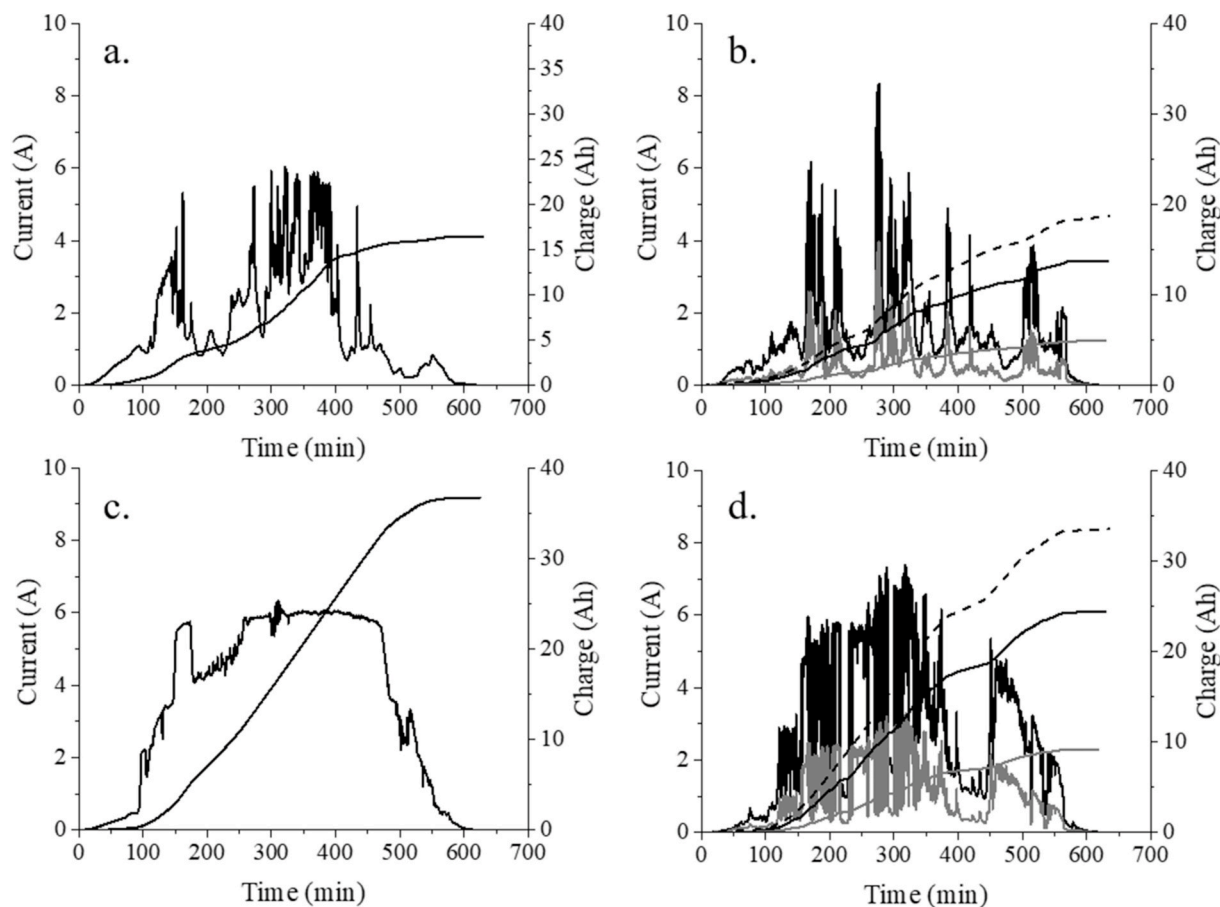


Fig. 4. Applied current and electrical charge under an electro-oxidation treatment powered by PV panels using different hydraulic and electrical connections. (a) SS, (b) SP, (c) PS and (d) PP. Electrolyzer 1 (black line) and Electrolyzer 2 (grey line). Total applied electrical charge in parallel electrical connection (Dashed line)  $[\text{Cloparylid}]_0 = 100 \text{ mg dm}^{-3}$ .

renewable power production and its important effects on the powering of electrolyzers (Cao and Hu, 2016; Islam et al., 2016). Those fluctuations have the same tendency observed into the solar radiation profiles. A smoother powering was observed into the PS test due to the solar radiation received during the day which exposed a lower fluctuation signal. These fluctuating operational conditions may power the PSEO at excessively high current densities which may turn into an efficiency drop because of the process will work under a mass transfer control (Comninellis and Chen, 2009).

Likewise, cell voltages values were recorded to assess the total energy consumptions of each electrolyzer and each operational combination strategy. Results are shown in Fig. 5. Opposite to the trend observed in the current values, the same voltage was supplied to the electrolyzers powered under parallel electrical connections. In the same way, different voltages values were noted in series electrical connections because of providing the same current to both electrolyzers. Thus, the higher was the ohmic resistance, the higher was the voltage observed. As expected, lower voltage values were recorded to E1 when the electro-oxidation treatment ran under series electrical connections, because of the smaller ohmic resistance showed by this electrolyzer in the EIS analyses.

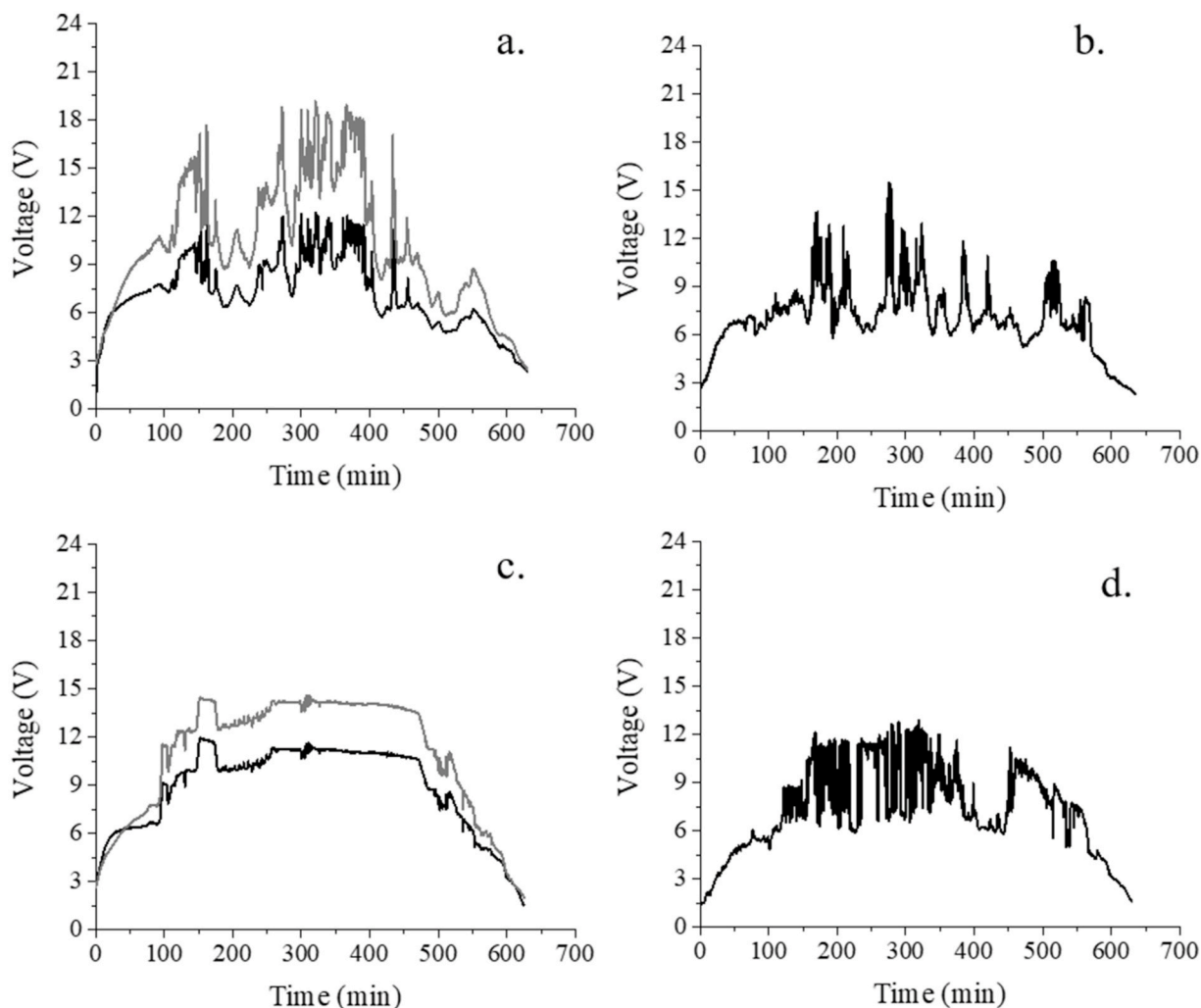
To compare the energy distribution between the different electrical connections proposed, Table 2 summarizes the values obtained, in terms of total applied electrical charge and total energy consumption for each combined setup and each single electrolyzer. It is important to highlight

**Table 2**  
Energetic data review.

	Applied charge (Ah)			Energy consumption (Wh)		
	E1	E2	Total	E1	E2	Total
SS	16.51		16.51	118.75	170.01	288.76
SP	13.78	4.92	18.70	96.41	34.42	130.83
PS	36.74		36.74	324.57	401.30	725.87
PP	24.36	9.16	33.52	178.56	67.14	245.70

the huge differences observed in the values of applied electrical charge among the tests performed under series and parallel hydraulic connections, despite the electrons flow does not depend on hydraulic features. Almost the double of electrical charge was supplied to the tests performed under parallel hydraulic connections, as compared to the test developed in series. Despite the treatments were carried out in the same period of the year (in fact in consecutive days of winter, and under similar conditions), different solar radiations were received each day, as Fig. 2 shows. Those results point out that PSEO treatments may expose unpredictable efficiencies according to the power supplied to the process. Hence, the sustainability of the treatment may vary according to the weather conditions and consequently of the time of the year.

As expected, the higher is the solar radiation, the higher is the total current supplied to the system. Thus, the values of total charge supplied to each test followed the same trend than the total solar radiation



**Fig. 5.** Recorded voltage under an electro-oxidation treatment powered by PV panels using different hydraulic and electrical connections. (a) SS, (b) SP, (c) PS and (d) PP. Electrolyzer 1 (black line) and Electrolyzer 2 (grey line).  $[\text{Clopyralid}]_0 = 100 \text{ mg dm}^{-3}$ .

received during the days of electro-oxidation treatment. Nevertheless, huge differences were observed by the applied charge. The aforementioned electrical limitation of the PV panels can narrow down the current supplied to the systems showing higher differences between experiments despite the similar values of solar radiation recorded. This means that one reached the maximum power of the PV plant, the voltage or current supplied to the electrooxidation system will be limited according to their values at the point of maximum power. Thus, despite the electrolyzer may be powered at higher current densities, according to its electrical features, this value is limited by the power that may be supplied by the PV plant.

Results suggest once again the important effects on the results of the uncontrolled and variable power supply by PV panels, which are directly related to weather conditions. It must be point out that differences could also be the result of ionic conductivity changes owing to the oxidation of the pollutant to other intermediate species and the production of oxidants. Nevertheless, those differences should not be as noticeable as those detailed in Table 2.

Considering the performance of each individual electrolyzer, differences were observed in terms of applied charge and energy consumption regarding the electrical operational strategy tested. As expected, the same charge was supplied to both electrolyzers when they were electrically connected in series. Consequently, the individual energy consumption of each electrolyzer will depend on its resistance. The higher ohmic resistance exposed by E2, turned into higher operational voltages

and consequently, into a higher energy consumption. Conversely, the opposite trend was observed when the electro-oxidation reactors were electrically connected in parallel. In this case, different charges were supplied to each cell, being higher for the electrolyzer that exposed the lower ohmic resistance. Thus, it can be concluded that working under parallel electrical connections leads to current intensities that depend on the ohmic resistance of the electro-oxidation reactor. Therefore, the same trend is clearly observed by the energy consumption of each electrolyzer. Thus, the lower is the ohmic resistance of the electrolyzer, the higher is its power consumption. Even though those data could shed light on interesting conclusions in terms of energy management and, hence, of sustainability, it is key to assess the performance of the treatment in terms of pesticide removal before making a statement about the most suitable powering mode.

Interestingly, despite the total applied charge took almost equal values for the same hydraulic operational conditions, the total energy consumptions were quite different depending on the electrical strategy. In both cases, series electrical connections showed higher energy consumption, being more than twice, and almost three times higher, for series and parallel hydraulic connections, respectively. In the light of those results, it can be claimed that working under a series electrical connection allows a greater use of the energy produced by the solar panel. Theoretically, the higher is the power, the higher is the remediation expected. Nevertheless, to claim this assumption, the degradation of pesticide must be quantified.

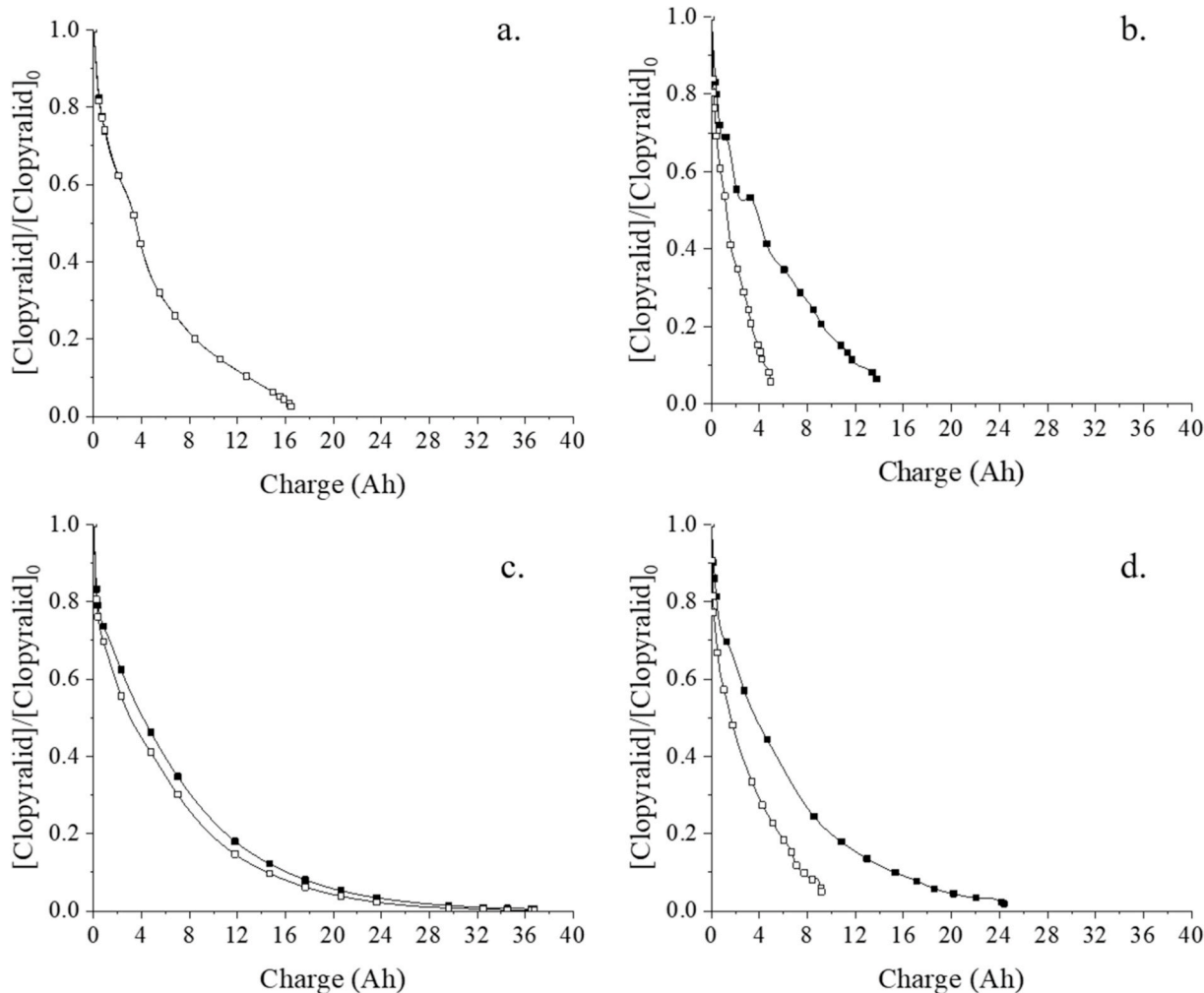


Fig. 6. Clopyralid removal profile vs applied electrical charge under an electro-oxidation treatment powered by PV panels using different hydraulic and electrical connections. (a) SS, (b) SP, (c) PS and (d) PP. Electrolyzer 1 (■) and Electrolyzer 2 (□).  $[\text{Clopyralid}]_0 = 100 \text{ mg dm}^{-3}$ ,  $[\text{Clopyralid}]$ :  $\text{mg dm}^{-3}$  of clopyralid remained into the water body during the treatment.



**Photovoltaic solar electrochemical oxidation (PSEO).** Once known the energy distribution from the PV panels to the different electro-oxidation setups, it is important to quantify the pollutant removal efficiency of each one to determine the best hydraulic and electrical strategy. Fig. 6 shows the degradation of clopyralid versus the applied electrical charge under the different hydraulic and electrical strategies proposed. In general terms, almost the same removal efficiency was observed in both electrolyzers, when they were electrically connected in series because of the same current density flows throughout both electrolyzers. Nevertheless, a slightly higher removal was observed by E2 when the setup worked under a parallel hydraulic connection. These results are in line with the preliminary electrochemical characterization results. The higher overpotential exposed by this electrolyzer turned into a more efficient remediation. The lowest variability observed in SS strategy is due to the electro-oxidation setup worked as a continuous stirred-tank reactor, showing almost the same pollutant removal in the outlet streams of both electrolyzers.

Conversely, under parallel electrical connections, huge differences can be seen. In both hydraulic strategies E2 showed a higher efficiency, reaching almost the same removal at lower electrical charges (over 93.5% in all cases). Regarding the differences of applied electric charge in each case, a 35.7 and a 37.6% of the charge supplied to E2 was powered to E1 under the series and parallel hydraulic connections, respectively. Those results exposed that despite lower ohmic resistances lead to lower energy consumption, which could be a competitive advantage in terms of energy efficiency and sustainability, working under lower voltage reduces the removal capacity of the CDEO treatment. As concluded previously, higher overpotentials lead to a higher removal efficiency (Zhang et al., 2014). Thus, it must be struck a balance between energy and removal efficiency in order to reach the most sustainable operational strategy.

To quantify the overall removal efficiency of each electro-oxidation setup, Fig. 7 shows the total removal of clopyralid as a function of electrical charge passed for each operational strategy proposed.

According to the experimental data, the higher remediation efficiencies were attained by the electro-oxidation setups running under series hydraulic connections. Indeed, the HRT is an important aspect to be considered. In view of the results obtained, the synergetic effect of working under series-series conditions allows a more efficient and faster removal, because of the higher current densities and the higher

retention times. Despite those results shed light on the removal efficiency of series-series configuration, it is essential to quantify the total energy consumption per unit of pollutant removal to claim in favour of the most suitable, efficient and sustainable PSEO configuration.

Given the complexity of the obtained data as a consequence of the different applied charge and with the aim of clarifying the results exposed, Table 3 shows the total grams of pollutant removed per unit of energy for each setup and each single electrolyzer.

Results show almost the same removal of pollutant for the four operational conditions,  $337.57 \pm 6.02$  mg of clopyralid, regardless the different charge applied in each case after a complete day of treatment. In agreement with the results exposed previously, the tests performed under series hydraulic connections showed a higher level of removal per unit of energy (specific removal) than the electro-oxidation treatment performed under parallel hydraulic connections, because of the higher retention times of the wastewater into the reactors in the first case (higher contact time with electrodes). Considering the individual efficiency of each electrolyzer, and contrary to expectations, E1 showed a slightly higher removal of clopyralid per Wh supplied to the system when both reactors were electrically connected in series (and, hence, the same current density was supplied to both electrolyzers). The higher OEV showed by E2 in the electrochemical characterization should lead to a higher hydroxyl radical generation and a higher remediation efficiency. Nevertheless, an excess of energy could arise undesirable reactions that reduce the removal efficiency and sustainability of the electro-oxidation process. Conversely, E2 showed the higher removal per unit of energy when the reactors were powered under a parallel electrical connection. The huge current densities supplied to E1 under parallel electrical connection can bring out more important mass transfer limitations (Ltaïef et al., 2017), because of parasitic secondary reactions which may produce an efficiency drop (Oturán and Aaron, 2014; Rodrigo et al., 2010). Therefore, lower current densities can reach a high pesticide removal, which turned into a higher ratio mg clopyralid removed/Wh powered. To test those hypotheses, the generation of oxidant species was quantified during each remediation treatment (Fig. 8). As expected, the series electrical connection strategies exposed a huge oxidant generation, because of the higher current values supplied to the CDEO reactors. Besides, a higher concentration of oxidants per applied charge was observed when the reactor worked under a series hydraulic connection. If those results are compared with the removal of pesticide per unit of energy, it can be claimed that most of the oxidant species generated during the treatment were wasted into undesirable reactions. Even though series electrical configuration was able to produce a higher quantity of oxidants, its removal per unit of energy was lower than under a parallel configuration. Thus, the misuse and waste of renewable energy may lead to a drop into the PSEO sustainability. Those results confirm once again the high influence of the current density on electrooxidation treatments. Furthermore, they point out the need to implement prediction and management analyses of renewable energies in order to take advantage of it and to avoid its waste.

Furthermore, it must be highlighted, that the E1 generated less oxidants in all cases. As aforementioned, the lower OEV exposed by this electrolyzer leads to a smaller oxidant generation capacity. Besides, its lower ohmic resistance limits the operation voltage values. Thus, the narrower is the operational electrochemical window, the lower is the

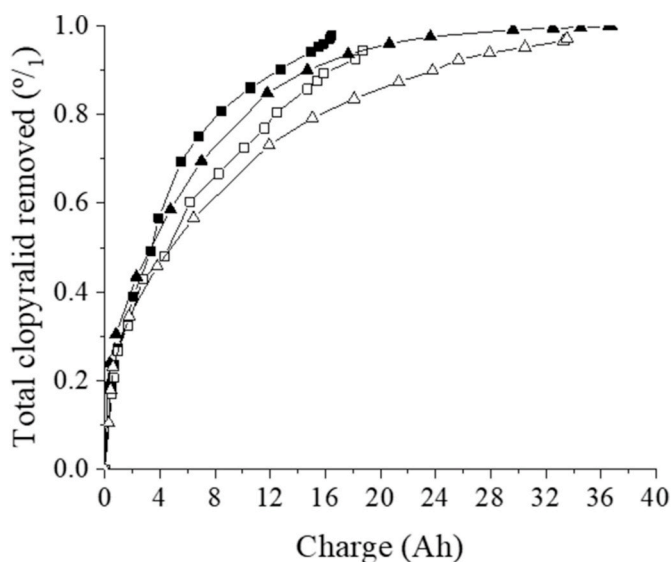
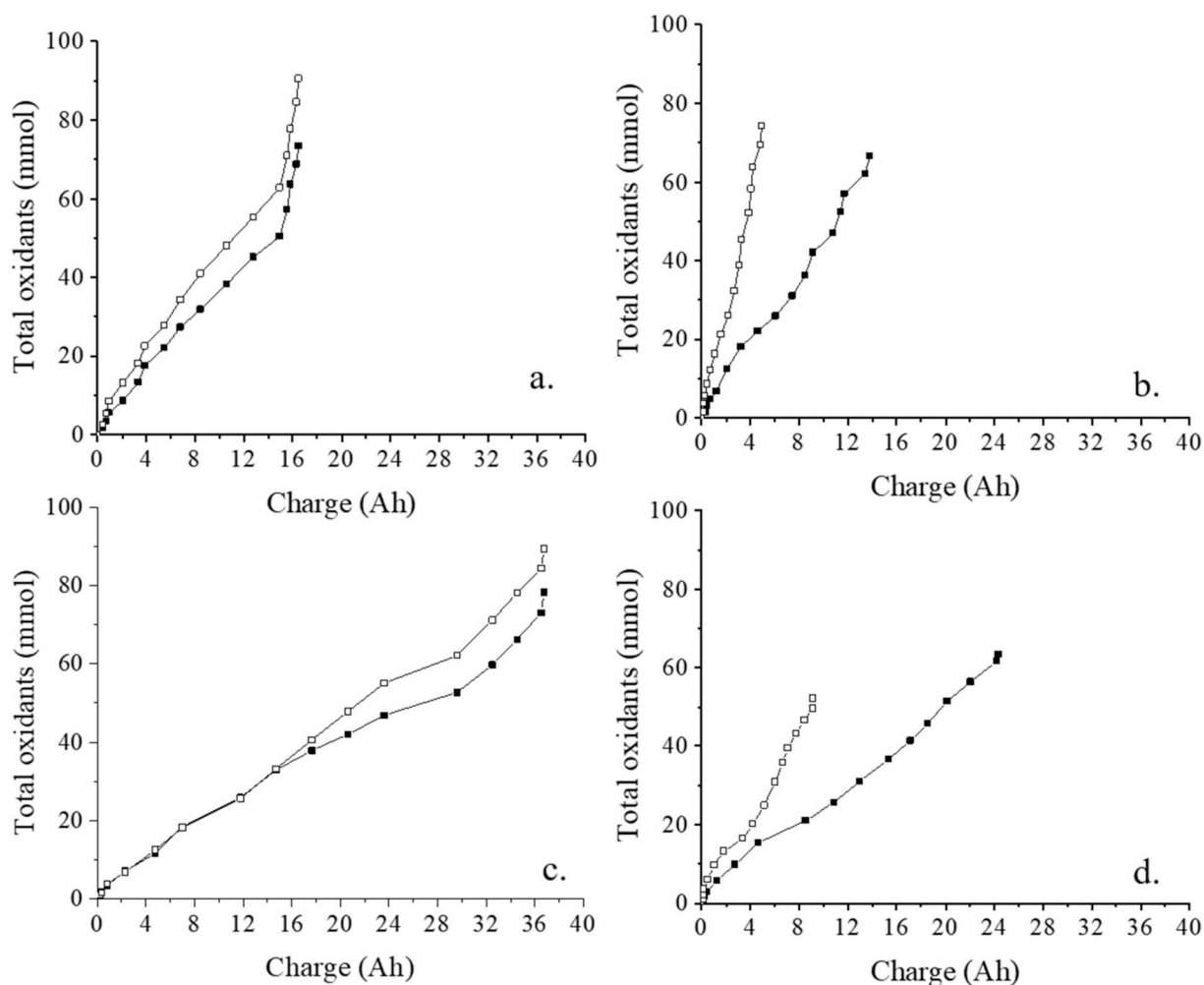


Fig. 7. Total clopyralid removal profile vs applied electrical charge under an electro-oxidation treatment powered by PV panels using different hydraulic and electrical connections. (■) SS, (□) SP, (▲) PS and (△) PP. [Clopyralid]<sub>0</sub> = 100 mg dm<sup>-3</sup>.

Table 3

Total clopyralid removed and removal of pesticide per used energy unit.

	Total clopyralid removed (mg)			Removal per unit of energy (mg clop (Wh) <sup>-1</sup> )		
	E1	E2	Total	E1	E2	Total
SS	147.90	194.44	342.34	1.25	1.14	1.19
SP	138.65	191.68	330.33	1.44	5.57	2.52
PS	172.54	173.32	345.86	0.53	0.43	0.48
PP	170.32	166.20	336.52	0.95	2.48	1.37



**Fig. 8.** Total oxidant species generation vs applied electrical charge under an electro-oxidation treatment powered by PV panels using different hydraulic and electrical connections. (a) SS, (b) SP, (c) PS and (d) PP. Electrolyzer 1 (■) and Electrolyzer 2 (□).  $[\text{Clopyralid}]_0 = 100 \text{ mg dm}^{-3}$ .

capacity of the electrolyzer to generate oxidant species capable of oxidizing the organic matter presents in the bulk of the solution.

Additionally, pH and conductivity were monitored under the four electro-oxidation tests to evaluate physical changes in the wastewater along the remediation treatment. Fig. 9 shows the pH and conductivity values versus time. The pH values indicate a slight basification at the second part of the treatment in the E1 when the tests were performed under a parallel hydraulic connection, regardless the type of electrical powering. The rest of the tests showed pH values close to 4.0 throughout the complete treatment. Regarding conductivity, values ranged from 3.0 to 4.0  $\text{mS cm}^{-1}$  and noticeable changes were not found.

In view of the obtained results, it is worth mentioning that working under different hydraulic and electrical connection strategies influences the ratio mg of clopyralid removed per unit of used energy being this effect noticeable when those treatments are directly coupled to a fluctuating power sources as solar energy. The use of a series hydraulic connection allows the setups to work under higher HRTs which favours the removal of organic pollutants because of the longer contact of the waste with the electrodes. Furthermore, the series electrical connections maximize the use of power supplied by the PV panels. Nevertheless, the distribution of current performed under parallel electrical connections allows to attain huge remediations under lower current densities. The higher currents recorded under series electrical connections can involve mass transfer limitations. Hence, the excess of power supplied in those cases can be wasted into parasitic secondary reactions showing an efficiency and sustainability drop.

From results discussed, it can be deduced that working under a series-parallel hydraulic-electrical connection between two electrolyzers directly powered by PV panels outperforms the remediation efficiency attained by the rest of the operational strategies proposed. This preliminary analysis showed a best management and a huge use of the solar power when it is distributed in parallel to both electrolyzers. In turn, the processes will be carried out under a most sustainable operational mode. In addition, these results may help to improve the real operation of drinking or wastewater treatment plants located in remoted places without grid energy supply.

#### 4. Conclusions

The most optimum and sustainable operational conditions of a photovoltaic solar electrochemical oxidation treatment have been tested in terms of hydraulic and electrical strategies. Results notice that the coupling of green powering devices (solar panels) and electrochemical setups of wastewater remediation requires an exhaustive assessment of the hydraulic and electrical configurations of both equipment in order to undergo the remediation process under the most efficient and sustainable strategy. Electrochemical setups equipped with several and equal cells showed different behaviour in terms of energy consumption and removal efficiency which could be due to damage or wear on the electrode surfaces. CDEO reactors with lower ohmic resistance attained lower production of oxidant species and consequently smaller removal efficiencies because of its lower overpotential. Under the most efficient

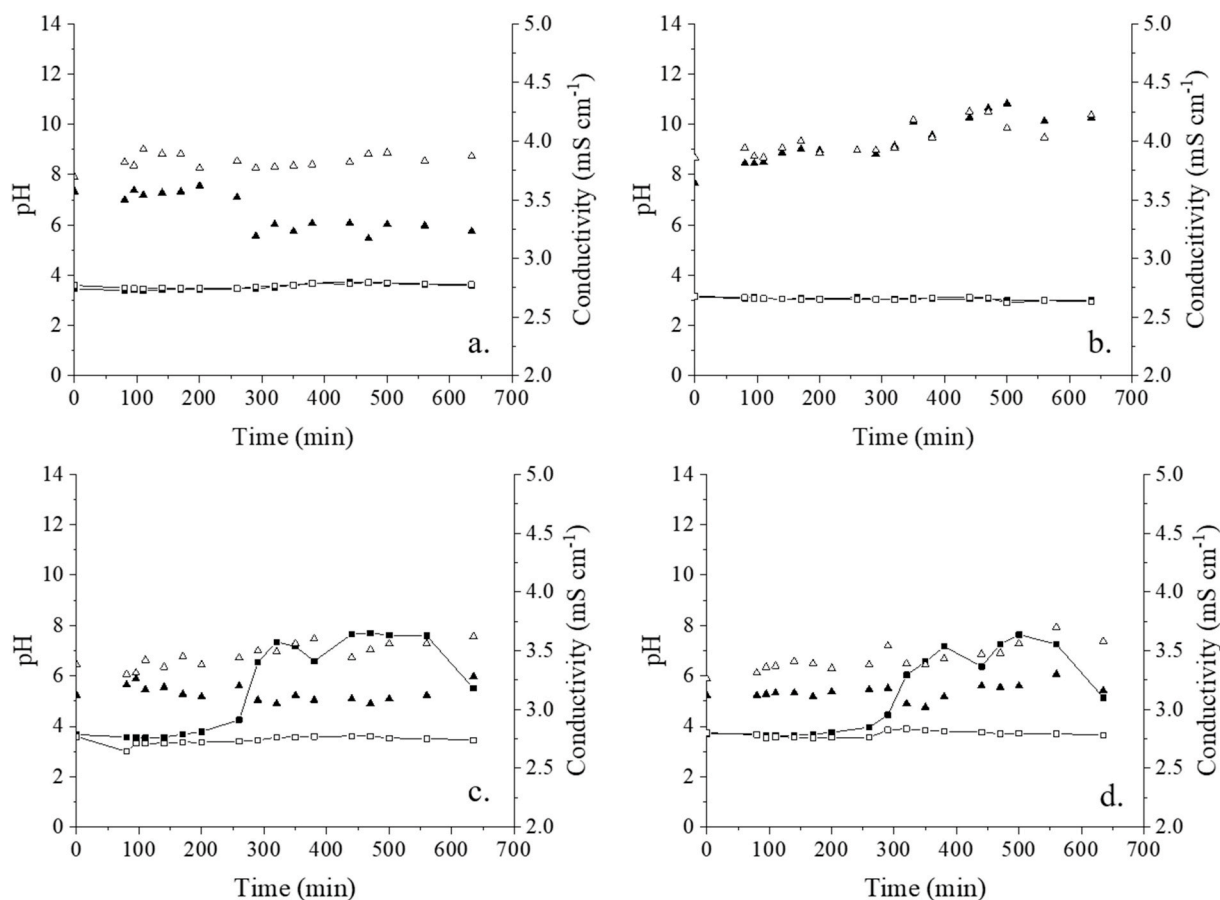


Fig. 9. pH (■) and conductivities (▲) values under an electro-oxidation treatment powered by PV panels using different hydraulic and electrical connections. (a) SS, (b) SP, (c) PS and (d) PP. Electrolyzer 1 (full symbol) and Electrolyzer 2 (empty symbol).  $[\text{Clopyralid}]_0 = 100 \text{ mg dm}^{-3}$ .

strategy around 4.8 and 15.1 mmol of oxidants per Ah were generated by electrolyzer 1 and 2, respectively. The hydraulic operational strategy allows to control the hydraulic retention time and therefore, the contact time between electrodes and waste. Thus, an electro-oxidation treatment performed with a set of electrolyzers reaches higher levels of remediation working under series hydraulic connections because of the higher HRT of the effluent into the CDEO reactors. Regarding the electrical connection, results noticed higher ratios of pesticide removal per Wh supplied under parallel electrical connections, being maximum for a series-parallel hydraulic-electrical connection. Data show that 2.52 mg clopyralid ( $\text{Wh}^{-1}$ ) were removed using the optimum hydraulic-electrical strategy regarding the 0.48 mg clopyralid ( $\text{Wh}^{-1}$ ) removed using the opposite strategy, parallel-series hydraulic-electrical connection. Those results claim that higher current densities can lead to mass transfer limitations that reduce the efficiency and sustainability of the electro-oxidation treatment because of non-desired reactions. According to the partial conclusions outlined by hydraulic and electrical strategies, it can be claimed that powering electrochemical technologies by solar panels under an off-grid connection requires an exhaustive study of electrical requirements and limitations of the remediation technique and the PV plant with the aim of reaching the highest remediation taking advantage of the energy produced by the PV panels and, consequently, avoiding its waste. Therefore, this study is essential to design sustainable PSEO treatment plants or other waste treatment plant working with electrochemical technologies directly coupled with renewable energies.

#### Credit roles

M. Millán: Investigation; Writing - original; draft; Methodology; Data curation, V.M. García-Orozco: Investigation; Writing - original; draft;

Methodology; Data curation. J. Lobato: Supervision; Funding acquisition; Validation; Formal analysis; Writing - review & editing, C.M. Fernández-Marchante: Supervision; Funding acquisition; Validation; Formal analysis; Writing - review & editing, G. Roa-Morales: Supervision; Funding acquisition; Validation; Formal analysis; Writing - review & editing, I. Linares-Hernández: Supervision; Funding acquisition; Validation; Formal analysis; Writing - review & editing, R. Natividad: Supervision; Funding acquisition; Validation; Formal analysis; Writing - review & editing, M.A. Rodrigo: Conceptualization; Funding acquisition; Supervision; Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix

Solar radiation ( $\text{W m}^{-2}$ ): Solar energy received by the PV plant each operation day.

V (V): Voltage of the device.

I (A): Current flowing through the cell.

R ( $\Omega$ ): Resistance of the device.

R<sub>TOTAL</sub> ( $\Omega$ ): Total resistance of the setup.

R<sub>E1</sub> ( $\Omega$ ): Resistance of electrolyzer 1.

R<sub>E2</sub> ( $\Omega$ ): Resistance of electrolyzer 2.

Charge (Ah): Amperes per hour supplied by the PV plant to each electrolyzer or the total electrochemical setup.

Energy consumption (Wh): Energy supplied to the electrochemical cell by the PV panels.

Total removal of pesticide (mg clop): Amount of pesticide oxidized during the PSEO treatment.

Removal per unit of energy (mg clop Wh<sup>-1</sup>): Amount of pesticide removed per unit of energy supplied by the PV panels to the electrochemical cell o setup.

pH.

Conductivity (mS cm<sup>-1</sup>).

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