Electro-irradiated technologies for clopyralid removal from soil washing effluents

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21 **Abstract**

22 In this work, electrolysis and electro-irradiated technologies, i.e. sonoelectrolysis, photoelectrolysis
23 and photosonoelectrolysis have been evaluated in order to improve the biodegradability of soil
24 washing effluents polluted with the herbicide clopyralid. Results obtained showed that simple
25 electrolysis with carbon felt anodes improved the biodegradability of the effluent and that
26 combination of electrolysis with irradiation technologies lead to very different operative results.
27 Photoelectrolysis produced a synergistic effect in clopyralid removal and mineralization, while
28 sonoelectrolysis and photosonoelectrolysis did not generate any positive effect, showing
29 antagonisms. Regarding the biodegradability of the effluents, photoelectrolysis was the only
30 technology which demonstrated a significant enhancement; nevertheless, it has associated an
31 important energy consumption in comparison to simple electrolysis processes.

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35 **Keywords**

36 Herbicide; electrochemical treatment; Ultrasound irradiation; Ultraviolet irradiation

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1. INTRODUCTION

Environmental pollution due to the uncontrolled use of pesticides has become one of the most alarming environmental and health related problem. Less than 1% of the pesticide sprayed arrives to the intended target [1], the rest, 99%, pollutes water, soil and air [2]. One of the most toxic and dangerous group of pesticides are organochlorine pesticides (OCPs). OCPs are considered as Persistent Organic Pollutant (POPs) because they are ubiquitous and persistent contaminants in all the environmental compartments [3, 4] and may become an important source for diffuse pollution [5]. Among the organochlorine pesticides, clopyralid (3,6-dichloro-2-pyridine-carboxylic acid) is one of the most widely used herbicide. It presents a very high solubility in water, because of that it can be easily dissolved in water and rapidly transported, promoting the problem of diffuse pollution [6]. Because of that, the pesticides have been detected very frequently, not only in the environment but even in drinking water [7, 8].

Regarding soil remediation technologies, the different technologies developed presents different drawbacks: Thermal treatments presents high economical costs and causes high perturbation in the soil texture; pump and treat technologies presents low efficiency and can be only applied to hydrophilic organic compounds, biotechnologies requires long treatment time, venting technologies can only be used with volatile organic compounds [9], etc. However, soil washing (SW) technology has showed a positive result during the lasts decades [10-12]. Sometimes SW technologies require the addition of surfactant to make easier the solubilisation of the target pollutant. Nevertheless, the high water-solubility of the clopyralid molecule makes the conventional SW process suitable for the removal of this herbicide without the addition of an extra surfactant or solvent.

Once the organic is extracted from the polluted soil, the resulting soil washing effluent (SWE) can be treated by different water remediation technologies. The final concentration of the SWE depends on the pollutant concentration of the soil treated and on the volume of soil washing liquid used, being the most convenient in most of the cases to obtain concentrated effluents.

Electrochemical Advanced Oxidation process (EAOP) have been pointed as an efficient technology to remove organochlorine pesticides from water effluents [13]. The coupling of electrolysis with

67 irradiated technologies such as photo- or sono-processes could increase the process efficiency,
68 avoiding the generation of refractory molecules during the oxidation of complex pollutants [14-17].
69 Photo-assisted treatments are based on the irradiation of a contaminated solution or a photoactive
70 electrode with ultraviolet (UV) or solar light [18-21]. Several researches have demonstrated that
71 combining photo and electrolysis technologies leads to a synergistic effect [14]. On the other hand,
72 sono-assisted processes have also been widely studied in the recent years, being proposed as an
73 adequate option for the treatment of different kinds of wastewaters, leading to good removal
74 efficiencies [22-24].
75 With this background, the objective of this work was to compare the clopyralid removal
76 effectiveness of a conventional electrolytic process with those obtained by processes assisted by
77 irradiation: photo and sono-electrolytic processes. To do that, the kinetic constants of clopyralid
78 degradation and mineralization were studied and the synergistic effect as well as the energy
79 consumption evaluated. Finally, the impact of the electro-irradiated technologies on the
80 biodegradability was determined.

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2. MATERIAL AND METHODS

2.1. Soil and Soil-Washing Effluent

The soil used in this work was a real clay soil provided by Cerámicas Millas Hijos S.A. from a quarry located in Toledo (Spain). The soil composition was determined by means of X-ray diffraction elemental analysis; the obtained results are presented in Table 1.

Table 1. Elemental analysis of the clay soil.

Mineral	%
Quartz	12
Feldspar	6
Calcite	1
Kaolinite	23
Glauconite	24
Muscovite	8
Montmorillonite	20
Illite	6
Dry density (g cm^{-3})	1.65
Hydroscopic moisture	0.115

This soil was polluted with Lontrel® 72 supplied by Dow AgroSciences. Lontrel® 72 is a commercial herbicide based on clopyralid, (3,6-dichloro-2-pyridine-carboxylic acid), presenting a concentration of 72% w/w. To prepare the polluted soil, 1.0 g of clopyralid was dissolved in 0.5 dm^{-3} of water and this solution was spiked over 1.0 kg of clay soil. Then, the polluted soil was subjected to the SW process. To do that, 5 dm^{-3} of synthetic groundwater was used as SW fluid. The synthetic groundwater was prepared according to the literature [25]. The concentration of the groundwater was the following: 0.6671 mg/dm^{-3} of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 0.1318 mg/dm^{-3} of NaCl; 0.1302 mg/dm^{-3} of NaNO_3 ; 0.0255 mg/dm^{-3} of KI; 0.2497 mg/dm^{-3} of CaCO_3 .

The SW process consists of mixing the polluted soil and 5.0 dm^3 of synthetic groundwater for 6 h.

Once finished the mixing procedure, the system was settled for 12 hours and the supernatant was

filtered through a 0.45 μm glass fibre filter (Whatman GF/C). The SWE presented a clopyralid concentration of 180 mg dm^{-3} , corresponding to a recovery of about 90% of the pesticide spiked in the soil. This SWE obtained was used in the electro-irradiated experiments. The use of synthetic groundwater as soil washing fluid ensured enough electrical conductivity to develop the electrochemical process without the addition of an extra electrolyte.

2.2 Irradiated and Electrolysis experiments

All the experiments were performed in the experimental set-up presented in Figure 1. This set-up consisted on a single compartment electrochemical flow cell. The anode was made of Carbon Felt (CF) Sigracell® GFA6EA manufactured by ElectroChem Inc. (USA) and presented a specific surface area of 35.3 $\text{m}^2 \text{g}^{-1}$ and 17700 $\text{m}^2 \text{m}^{-2}$, areal weight 500 g m^{-2} , porosity 95% and roughness 30 μm . An AISI 316 steel cathode was used in all the experiments performed. The electrode area was 100 cm^2 .

The UV lamp was a Filtered Lamp Vilber Lourmat VL-215.MC with a power of 4W. The wavelength used was 254 nm (UV-C). The UV light was irradiated directly to the reservoir tank. For the sono-electrolysis experiments the system was equipped with an ultrasound generator immersed inside the liquid bulk of the reservoir tank. The high frequency ultrasound generator used in this work was an EPOCH 650 Olympus (Barcelona, Spain), emitting 10 MHz of frequency, 450W.

Figure 1. Photoelectrolysis experimental set up. 1, Reservoir Tank. 2, Peristaltic pump. 3, Electrochemical reactor. 4, Thermostatic bath. 5, Power supply. 6, UV lamp/ultrasound generator.

The reactor was filled with 0.6 dm^{-3} of SWE polluted with clopyralid and samples were taken at defined times along the experiment or at the selected electrical charges. The monitored parameters were pH and conductivity of the solution, total organic carbon (TOC), clopyralid concentration, ionic species and oxidant concentrations. Table 2 presents the experimental conditions of the different experiments carried out. The initial clopyralid concentration was 180 mg dm^{-3} . The experiments were carried out in batch mode under galvanostatic conditions.

Table 2. Experimental conditions of the electro-irradiated essays.

Technology	Current density (mA cm^{-2})	US-radiation Frequency (MHz)	UV-radiation λ (nm) / Power (W)
Electrolysis	5	-	-
Photoelectrolysis	5	-	254 / 4
Sonoelectrolysis	5	10	-
Photosonoelectrolysis	5	10	254 / 4

The synergy effect (SI) was used to evaluate the effect of the coupling of the irradiated techniques to the electrolysis. The SI effect was calculated according to Equation 1.

$$SI = \frac{K_{\text{electro-irradiated process}}}{K_{\text{electrolysis}} + K_{\text{irradiated process}}} \quad (1)$$

Where: $K_{\text{electro-irradiated process}}$ corresponds to the pseudo first order kinetic rate of the electro-irradiated process, $K_{\text{electrolysis}}$ corresponds to the pseudo first order kinetic rate of the electrolysis process and $K_{\text{irradiated process}}$ corresponds to the pseudo first order kinetic rate of the irradiated process.

The energy consumption associated to each electrochemical technology was calculated by using to Equations 2-4 considering the individual contributions of each technique. The energy consumed by the electrolytic treatment in a discontinuous system can be determined from Equation 2, where Q is the applied electric charge, I is the cell intensity, V is the reaction volume, t is the treatment time and E is the cell potential.

$$W_{\text{electrolysis}} (kWh \cdot m^{-3}) = Q (kAh \cdot m^{-3}) \cdot E(V) = \frac{I (kA) \cdot t(h) \cdot E(V)}{V (m^3)} \quad (2)$$

The energy consumed by the electro-irradiated technologies were determined by means of Equation 3 and 4, where w_{uv} is the irradiated ultraviolet light power and w_{us} is the irradiated ultrasound power.

$$W_{\text{photoelectrolysis}} (kWh \cdot m^{-3}) = \frac{I (kA) \cdot t(h) \cdot E(V) + w_{uv}(kW) \cdot t(h)}{V (m^3)} \quad (3)$$

$$W_{\text{sono-electrolysis}} (kWh \cdot m^{-3}) = \frac{I (kA) \cdot t(h) \cdot E(V) + w_{us}(kW) \cdot t(h)}{V (m^3)} \quad (4)$$

2.3. Analytical techniques

Clopyralid concentration was determined by means of HPLC, using an Agilent 1260 Infinity equipment equipped with an Eclipse Plus C-18 (4.6 mm x 100 mm; 3.5 μ m). Samples were filtered with 0.2 μ m nylon filters before analysis in order to avoid particles. The mobile phase was a

mixture of 30% methanol and 70% formic acid (0.1%). The wavelength for the herbicide detection 280 nm, the flow rate was set at 1 mL min⁻¹ and the retention time was around 2.7 minutes. The reactions intermediates of clopyralid were identified by gas chromatography – mass spectrometry (GC-MS) and HPLC. Before using GC-MS, a freeze dryer was used in order to remove the water contained in the samples. The equipment was operated at -50°C and 0.02 bar. Once removed the water, ethyl acetate was added to the freeze-dried samples. The organic phase was analysed by GC-MS using a Thermo Scientific DSQ II Series Single Quadrupole GC-MS (Coolvauum Technologies) with a NIST05-MS library. The column was a polar TR-WAXMS (30 m x 0.25 mm x 0.25 mm). The temperature ramp was 40°C for 1 min, 5°C min⁻¹ up to 250°C and hold time 5 min. Acids were identified by a HPLC equipped with a Zorbax SB-Aq, column (4.6mm x 150mm), the mobile phase consists of 4 mM H₂SO₄ and the wavelength for the detection was 210 nm. The identifications of the intermediates was conducted by the retention time comparison and internal standard addition methods using standard solutions according to the procedure described in the literature [26]. The inorganic ions were determined by ionic chromatography in a Metrohm 930 Compact IC Flex device. The total oxidant concentration was iodometrically measured by using the I-/I₂ method. To do that KI was added in excess to the sample, 1 g approximately, 5 cm³ of H₂SO₄ (20%) were also added to 10 cm³ of liquid sample in order to ensure acidic conditions. This method quantifies all oxidants capable to oxidize iodide to iodate by means of a titration procedure with sodium thiosulphate, see Equation 5, starch was used as indicator. The total oxidants were quantified by Equation 6.

TOC concentration was determined by using a Multi N/C 3100 Analytic Jena analyser. Organic carbon compounds contained in the samples were calcined with a stream of pure oxygen at a temperature of 680 °C in a furnace containing a platinum catalyst supported on alumina. Then, the carbon dioxide generated was detected by a non-dispersive infrared detector. COD was measured using a Spectroquant® test CSB from Merck. The evolution of the pH was determined by a pH

meter Crison GLP 22 (Crison Instruments, Spain). The pH meter was calibrated regularly with standard pH solution of 4.00, 7.00 and 9.21 units. All the samples were measured in duplicate.

2.4. Biodegradability tests

Biodegradability of water samples was measured by respirometric analyses [27]. The short-term biodegradability was measured as Oxygen Uptake Rate (OUR) and the long-term biodegradability by means of the five days Biological Oxygen Demand (BOD_5) to COD ratio, BOD_5/COD . BOD_5 test for the long-term biodegradability measurements were performed in Oxitop IS 6-Var. According to the literature, a trace minerals solution was added to the samples in order to ensure minerals availability [28]. The samples were inoculated with 1 mL of activated sludge taken from a conventional wastewater treatment plant (WWTP) described elsewhere [29]. A blank reference test was performed to isolate and determine the endogenous oxygen consumption rate caused by the inoculum added.

Short-term biodegradability tests were carried out by measuring the OUR by conventional activated sludge, over a period of 30 min, using a Strathtox respirometer by Strathkelvin instruments. Before the respirometric tests, the activated sludge was aerated overnight in order to ensure the full consumption of the substrate contained in the sludge sample and the endogenous conditions. The tests were carried out using the same trace mineral solution and activated sludge from a conventional WWTP as in the BOD_5 tests.

3. RESULTS

The soil-washing procedure extracted the pesticide and also dragged anions and cations contained in the clay soil and in the synthetic groundwater used as washing fluid. Table 3 presents the ion concentrations in the SWE generated after the washing process.

Table 3. Anions and cations concentrations in the SWE.

Cation	Concentration (mg dm ⁻³)	Anion	Concentration (mg dm ⁻³)
<i>Na</i> ⁺	106.17	<i>SO</i> ₄ ²⁻	234.52
<i>Ca</i> ²⁺	66.35	<i>NO</i> ₃ ⁻	134.71
<i>Mg</i> ²⁺	32.69	<i>Cl</i> ⁻	83.98
<i>K</i> ⁺	3.41		

The high concentration of minerals in the SWE caused a conductivity of 1200 mS cm⁻¹, high enough to apply the electro-irradiated processes without adding any supporting electrolyte. Once extracted the pollutant, by means of the SW procedure, the electro-irradiated tests were performed. The results obtained in these tests were compared on the basis of the kinetics constants obtained for clopyralid removal and mineralization. Then, the SI effect as well as the energy consumption of the electro-irradiated technologies were studied. Based on the literature [8], the current density selected to carry out all the experiments was 5 mA cm⁻². Finally, the biodegradability of the effluent was evaluated.

3.1. Clopyralid degradation and mineralization

According to the literature [30, 31], a first-order kinetic model was used to describe the electrolytic and the electro-irradiated experiments (Equation 7).

$$\ln \frac{c_0}{c} = k \cdot t \quad (7)$$

Figure 2 presents the experimental results as well as the mathematical fitting of the pseudo-first order model to the experimental data obtained during the clopyralid removal by using the different

238 electrochemical technologies used. As can be seen in this Figure, good fitting results were
 239 obtained in all the cases, presenting square correlation coefficients between 0.97-0.99.
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242
 243
 244 Figure 2. Mathematical fitting of the pseudo-first order model to the experimental data of a)
 245 clopyralid and b) TOC.

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The kinetics constants, as well as the removal percentages attained in each experiment, are presented in Table 4. As can be observed, the UV-irradiation of the electrolytic process leads to an improvement of the clopyralid removal kinetic constant of a 52%, higher than that obtained when coupling the electrolysis with US irradiation, which only shows an improvement of 23%. In turn, the coupled application of UV-light and US irradiation with electrolysis did not change the kinetic constant, yielding a very similar value to that obtained for the single electrolysis process. Regarding the removal percentage, similar results were obtained in all the cases, ranging from 28 to 38%, presenting the highest value the photoelectrolysis process.

Table 4. Kinetic constants and synergistic effect of the electro-irradiated technologies in terms of clopyralid and TOC removal.

Technology	Clopyralid removal			TOC mineralization		
	Removal %	K_{app} (min ⁻¹)	SI	Removal %	K_{app} (min ⁻¹)	SI
Photolysis	5	$6.67 \cdot 10^{-7}$	-	3	$1.33 \cdot 10^{-8}$	-
Sonolysis	5	$5.00 \cdot 10^{-7}$	-	3	$1.30 \cdot 10^{-8}$	-
Electrolysis	31	$1.72 \cdot 10^{-3}$	1.0	32	$2.52 \cdot 10^{-3}$	1.0
Photoelectrolysis	38	$2.61 \cdot 10^{-3}$	1.2	38	$3.01 \cdot 10^{-3}$	1.2
Sonoelectrolysis	34	$2.11 \cdot 10^{-3}$	1.1	21	$1.32 \cdot 10^{-3}$	0.5
Photosonoelectrolysis	28	$1.70 \cdot 10^{-3}$	0.8	0	0.0	0.0

The improvement observed when applying UV light to the electrolytic treatment can be explained in terms of the modification of oxidants electrogenerated by UV light. Thus, peroxosulphates and chlorine produced electroodically from the sulphate and chlorine contained in the synthetic groundwater, are transformed into the more powerful sulphate and chlorine radicals [32-36]. This transformation into radicals does not only develop on the surface of the anode where the non-radical oxidants are produced but it extends to the bulk, improving the removal efficiency. The higher efficiency showed when coupling the US technology could be related to the improvement in the mass transfer that this technology generates. This is because the US application improves the turbulence by means of the implosion of microbubbles generated in the liquid bulk [37, 38]. At this point, it is worth to take in mind that low frequency US are not energetic enough to form hydroxyl radicals from water but they efficiently produce radicals from the breakage of chlorine and peroxosulphate.

As previously indicated, it is very interesting to evaluate the coupled effect of the technologies presented. With this aim, Table 4 presents a comparison of the SI effect in terms of clopyralid removal. The SI was calculated according to the Equation 1, for each electro-irradiated treatment of clopyralid solutions.

To calculate the SI, it was considered that the degradation of clopyralid by US and UV technologies was almost negligible as can be seen from the results presented in Table 4. In the literature, it has been previously reported the almost negligible clopyralid removal when only applying US or UV technologies [39, 40].

According to Table 4, the irradiation of UV light or US coupled with electrolysis with CF anode originates a synergistic effect. However, the photosonoelectrolysis shows an antagonistic influence. This antagonistic effect could be related to the fact that irradiation technologies lead to an excessive generation of radicals and to an enhanced mass transference, which could facilitate the radical recombination, generating less powerful and more stable oxidant agents, or that can decompose to oxygen, instead of reacting with the target pollutant. This means that these reactions may compete with organic oxidation and that active radicals are not available to oxidize the organic pollutants. In the literature, a similar antagonistic effect has been previously reported [41].

It is also important to evaluate the mineralization of the studied processes. To do that, the experimental data of the mineralization were fitted to a first-order kinetic model. The kinetic constants calculated in terms of mineralization and their fitting are represented in Figure 2b and in Table 4. In the case of photosonoelectrolysis, this technology did not exhibit any mineralization over the electrical charge applied, remaining the TOC constant along the test.

In terms of mineralization, the effect of photoelectrolysis was also better than that obtained when applying single electrolysis, increasing the kinetic mineralization constant by a 19%. Nevertheless, sonoelectrolysis presented a lower mineralization, reducing the kinetic constant by a 48%. In spite of the clopyralid removal by means of sonoelectrolysis, this technology was not able to degrade the by-products generated yielding a lower mineralization. Photosonoelectrolysis, according to clopyralid degradation, did not evidence any positive effect in SWE mineralization; in fact, the TOC

removal was near to 0%. These results indicated that the sonoelectrolysis and the
photosonoelectrolysis could not degrade the generated by-products.

As reported in clopyralid degradation, the SI produced by these technologies in terms of
mineralization was also determined. Table 4 compares the different SI caused in the mineralization
when using electro-irradiated technologies. As seen, and according to literature, it has been
considered that isolated sonoelectrolysis and photoelectrolysis technologies cannot mineralize
clopyralid [40].

Photoelectrolysis is the unique electro-irradiated technology which produced a synergistic effect in
both, clopyralid removal and mineralization. In fact, the SI reached in terms of clopyralid removal
and mineralization were the same, reaching a value of 1.2 in both cases. However, in the case of
the sonoelectrolysis a SI effect was obtained in the clopyralid removal, but an antagonism effect in
the mineralization.

The negative effect produced by the coupling of UV-light and US irradiation with electrolysis has
been previously reported in the literature. *Vidales et al.* [42] observed an antagonism effect in the
mineralization of caffeine applying conductive diamond by means of sono-photo-electrochemical
oxidation technology. On the other hand, *Silva et al.* [41] reported also an antagonism in the
degradation of amoxicillin and ampicillin using a similar technology.

In order to justify the efficiency of each process, the oxidant concentrations along each experiment
was determined. As previously indicated, the SWE used in this work consists of a complex mixture
of soluble organic pollutants and different inorganic salts coming from the washing fluid used,
synthetic ground water, and the polluted soil matrix. The synthetic ground water contained Cl^- ,
 NO_3^- , SO_4^{2-} as the main anions and Na^+ , K^+ , Ca^{2+} and Mg^{2+} as the main cations. In literature, it has
been reported the formation of oxidants from the anions contained in this SWE [43]. The results
obtained are presented in Figure 3.

Figure 3. Evolution of oxidants as function of the applied electric charge during the electrolysis of SWE.

For all technologies, it can be seen an important production of stable oxidants in solution, with not very significant variations in comparing the performance of the four technologies. In fact, it can be seen that the highest oxidant concentration was achieved in the photoelectrolysis process but the value reached is only 25% higher than that obtained in the worse technology (sonoelectrolysis). This higher production can be directly related to the best performance of photoelectrolysis in terms of clopyralid removal and mineralization. The oxidant concentration increased during the first moments of the electrolysis. Then, its concentration remained almost constant over electrical charged applied indicating an equilibrium between the production and the destruction of the oxidants. Thus, the steady concentration reached in all the cases can be explained by the balanced generation and consumption reached in the steady state. Regarding the other technologies employed, the oxidant concentration was similar, being sonoelectrolysis the technology that generated the lowest oxidant concentration. However, this technology reached a higher clopyralid degradation and, as reported previously, the explanation could be that the sonoelectrolysis improves the mass transport, leading to a more efficient clopyralid removal in the bulk.

Attending to inorganic salts, the concentration of these species was determined in order to clarify its role in the generation of oxidants associated to the formation of radicals from the interaction of the salt anions and the hydroxyl radicals massively formed from the water oxidation. Then, the recombination of these radicals allows to the formation of other species which can extend or limit the effects of the oxidation to the liquid bulk.

Chloride ion concentration was increased in all the electrolyses performed. This parameter gives information about the dechlorination of clopyralid molecule. This process could be related to the anodic oxidation of clopyralid mineralization according to Equation 8, but it is most likely from the cathodic hydro-dehalogenation of the molecule [40, 44], see Equations 9-10.

No formation of chlorate and perchlorate was detected during the process, which is in accordance with the absence of chloride depletion. According to the clopyralid mineralization, the formation of ammonium was expected. However, a very low concentration of this ion was detected in the liquid bulk at the end of the electrolyses experiments. The concentration of sulphate, which was contained in the SWE was expected to lead the formation of peroxodisulphate [45]. Moreover, UV irradiation is known to promote the production of sulphate radical from persulphate according to the Equation 11 [46, 47]. It is worth taking into account that the sulphate radical reacts typically 10^3 – 10^5 times faster than the anion persulphate [48].

If UV light had been irradiated over the anodic surface, the degradation of organic matter would have reach better results. The electrogenerated oxidant agents are on the anodic surface, so the activation of these oxidants may be more efficient [33-36, 49-51].

The highest efficiency showed in photoelectrolysis could be explained because of the formation of additional hypochlorite during electrolysis. The SWE contained NaCl, this chemical could be decomposed into chlorine radicals by means of UV irradiation (Equations (12-13)) [41].

However, the coupling of UV light and/or ultrasound with electrochemical oxidation of clopyralid polluted washing effluents did not exhibit a notable improvement in the clopyralid removal and mineralization rate.

According to the results, it can be concluded that although the irradiation of UV light or the application of US generates $(SO_4^{\bullet-})$ and $Cl^{\bullet}$ species and, in the first case, it also promotes the formation of $OH^{\bullet}$, these technologies do not reflect a relevant improvement of the degradation and mineralization process.

Regarding to the pH, in the electrolysis, sonoelectrolysis and photoelectrolysis experiments, a decrease from neutral to acid pH values was observed. The highest pH reduction was detected in photoelectrolysis, reaching a value of 3.5. This behaviour could be explained by the progress of the oxidation of the raw pollutants contained in the waste that generates higher H^{+} and short chain fatty acids concentrations.. On the other hand, the conductivity changes from $900 \mu S \text{ cm}^{-1}$ to $700 \mu S \text{ cm}^{-1}$ in all technologies, except for sonoelectrolysis, where the conductivity was kept constant. In this case, the complex interactions of the ions contained in the washing fluid can help to explain these trends.

3.2. Biodegradability measurements

To evaluate if the electro-irradiated technologies generated a positive effect in the biodegradability of clopyralid soil washing effluents, two different analytical techniques were applied. On the one hand, respirometric tests were used to evaluate the short-term biodegradability. On the other hand, the BOD_5 was determined in order to evaluate long-term effects in biodegradability.

Firstly, results are going to describe the changes in the short-term biodegradability test. The oxygen concentration profile along the experiment as well as the oxygen uptake rate (OUR) data obtained by using respirometric techniques are presented in Figure 4.

Figure 4. a) Dissolved Oxygen concentration profiles and b) Oxygen uptake rates measured with the respirometer before and after the treatments at 5 mA cm^{-2} .

Figure 4 shows the oxygen evolution when the different effluents were fed to a conventional activated sludge. As can be seen in Figure 4, the oxygen depletion presented different rates. The dissolved oxygen removal rate can be directly associated with to the degradation of organic matter [52]. Corresponding the higher slope of the oxygen concentration to the higher biodegradability.

According to the Figure 4b, the OUR obtained when feeding the photoelectrolysis was significantly higher than those obtained in the rest of treatments. This behaviour indicates that the photoelectrolysis was the process generating the most biodegradable effluent. This enhancement could be related to the generation of more biodegradable by-products, such as carboxylic acids, from the electrolysis of the pollutants. Carboxylic acids generation can also explain the higher reduction in the pH [53] observed in the photoelectrolysis process.

When comparing the OUR values it can be observed that the raw polluted water presented a higher biodegradability than the effluents obtained after the conventional electrolysis, the sonoelectrolysis and the photosonoelectrolysis, this behaviour could be explained by the presence of biodegradable compounds in the raw wastewater but not in the electrolysed ones. As described previously, the clopyralid used to develop the experiments was a commercial formulation, being a 72% of the commercial herbicide clopyralid. Unfortunately, the rests of additives are unidentified. Taking into account the respirometric results, it could be possible that these additives correspond to biodegradable compounds which could be oxidised in the electrolyses experiments. When taking the conventional electrolysis as reference, it can be observed that photosonoelectrolysis exhibited a slight improvement in the biodegradability. However, the sonoelectrolysis yield the less biodegradable effluents. This different behaviour could be explained by a more efficient oxidation which could remove biodegradable compounds.

In order to evaluate the long-term biodegradability, BOD₅ tests were performed to the raw wastewater and the effluents obtained after the different treatments. In the literature, the ratio BOD₅/COD is usually shown as biodegradability index (Figure 5).

Figure 5. BOD₅/COD ratio after electro-irradiated processes at 5 mA cm⁻².

In the cases of the photosonoelectrolysis and the sonoelectrolysis, the long-term biodegradability reached was significantly lower than that obtained when applying conventional electrolysis. These results indicate that despite the low mineralization experienced, the intermediates generated were hardly biodegradable. Sonoelectrolysis was the pre-treatment that produced the highest reduction in the biodegradability. However, this technology was pointed as a good treatment attending to clopyralid degradation, presenting a slight synergistic effect. Because of that, the coupling of US irradiation with the electrolysis just seems advisable if entails a high synergistic effect or can be achieved with low power consumptions.

Regarding the photoelectrolysis, in the short-term test it was observed an important increase in biodegradability. However, the long-term biodegradability measured as BOD₅/COD did not ratify this trend, being very similar the BOD₅/COD after the conventional electrolysis and the photoelectrolysis. This behaviour could be explained by the generation of biodegradable intermediates despite the high mineralization observed.

Opposite to the previous results, in which a synergistic effect was observed in the photoelectrolysis of the SWE, the ratio BOD₅/COD did not show an improvement. In fact, photoelectrolysis was the

treatment that enhanced most of the parameters studied: clopyralid degradation, mineralization, oxidant generation and short-term biodegradability, but does not enhance the long-term biodegradability.

From the beginning of the analysis, photosonoelectrolysis did not demonstrated good results in any analytical technique performed. Attending to biodegradability tests, it was expected that this technology did not generate any improvement, and the results confirmed this theory, showing a slight reduction in the ratio BOD₅/COD.

3.3. Energy consumption

Finally, the energy consumption of the processes was determined. The coupling of UV-light irradiation to electrolysis entails a slight increase of the energy consumption. When operating with conventional electrolysis, the energy consumption was 46.65 kwh m⁻³. However, the coupled photoelectrolysis increased the energy consumption up to 66.15 kwh m⁻³. In turn, the coupling with US irradiation originates an important increase in the energy consumption, due to the high power consumption associated to this technique [32] presenting an energy consumption of 3501.20 kWh m⁻³. For this reason, the application of US just seems to be advisable if entails a high synergistic effect with low applications periods of the US irradiation and therefore with lower power consumptions [37, 54]. Regarding the photosonoelectrolysis, its energy consumption was of 3542.50 kwh m⁻³, presenting the highest consumption but yielding very poor clopyralid removal and mineralization and hence, advising against its use.

4. CONCLUSIONS

From the results obtained in this work, the following conclusions can be drawn:

- Photoelectrolysis has shown a synergistic effect in clopyralid degradation and mineralization, improving the kinetic constants of both cases.
- Sonoelectrolysis shows a slight enhancement in clopyralid degradation, but it does not evidence any improvement in mineralization.
- Photosonoelectrolysis only causes an antagonism effect on the clopyralid removal and mineralization.
- The different improvements pointed in clopyralid degradation and mineralization could be related to the oxidants production, presenting the higher oxidant concentration the photoelectrolysis.
- The application of US irradiation presents an important energy consumption which could discourage its use from the economical point of view.
- Regarding biodegradability, results confirm that photoelectrolysis improves the biodegradability of the SWE.

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- 488 [1] D. Pimentel, L. Levitan, Pesticides: amounts applied and amounts reaching pests, *Bioscience*,
489 36 (1986) 86-91.
- 490 [2] A. Özkara, D. Akyıl, M. Konuk, Pesticides, environmental pollution, and health, in:
491 Environmental Health Risk-Hazardous Factors to Living Species, InTech, 2016.
- 492 [3] R. Dietz, F. Riget, M. Cleemann, A. Aarkrog, P. Johansen, J. Hansen, Comparison of
493 contaminants from different trophic levels and ecosystems, *Science of the Total Environment*, 245
494 (2000) 221-231.
- 495 [4] F. Carvalho, F. Gonzalez-Farias, J.-P. Villeneuve, C. Cattini, M. Hernandez-Garza, L. Mee, S.
496 Fowler, Distribution, fate and effects of pesticide residues in tropical coastal lagoons of
497 northwestern Mexico, *Environmental Technology*, 23 (2002) 1257-1270.
- 498 [5] C. Lei, Y. Sun, E. Khan, S.S. Chen, D.C.W. Tsang, N.J.D. Graham, Y.S. Ok, X. Yang, D. Lin, Y. Feng,
499 X.-D. Li, Removal of chlorinated organic solvents from hydraulic fracturing wastewater by bare
500 and entrapped nanoscale zero-valent iron, *Chemosphere*, 196 (2018) 9-17.
- 501 [6] S. Rodrigo, C. Saez, P. Cañizares, M.A. Rodrigo, Reversible electrokinetic adsorption barriers for
502 the removal of organochlorine herbicide from spiked soils, *Science of the Total Environment*, 640-
503 641 (2018) 629-636.
- 504 [7] C. Berberidou, V. Kitsiou, S. Karahanidou, D.A. Lambropoulou, A. Kouras, C.I. Kosma, T.A.
505 Albanis, I. Poulis, Photocatalytic degradation of the herbicide clopyralid: kinetics, degradation
506 pathways and ecotoxicity evaluation, *Journal of Chemical Technology & Biotechnology*, 91 (2016)
507 2510-2518.
- 508 [8] M.B. Carboneras, P. Cañizares, M.A. Rodrigo, J. Villaseñor, F.J. Fernandez-Morales, Improving
509 biodegradability of soil washing effluents using anodic oxidation, *Bioresource technology*, 252
510 (2018) 1-6.
- 511 [9] P. ROUDIER, Techniques de réhabilitation des sites et sols pollués, Ed. Techniques Ingénieur,
512 2005.
- 513 [10] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil:
514 a review, *Engineering Geology*, 60 (2001) 371-380.
- 515 [11] X. Mao, R. Jiang, W. Xiao, J. Yu, Use of surfactants for the remediation of contaminated soils:
516 A review, *Journal of Hazardous Materials*, 285 (2015) 419-435.
- 517 [12] C. Trellu, E. Mousset, Y. Pechaud, D. Huguenot, E.D. van Hullebusch, G. Esposito, M.A. Oturan,
518 Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review,
519 *Journal of Hazardous Materials*, 306 (2016) 149-174.
- 520 [13] M. Rodrigo, N. Oturan, M.A. Oturan, Electrochemically assisted remediation of pesticides in
521 soils and water: a review, *Chemical reviews*, 114 (2014) 8720-8745.
- 522 [14] F.L. Souza, C. Sáez, P. Cañizares, A.J. Motheo, M.A. Rodrigo, Coupling photo and sono
523 technologies to improve efficiencies in conductive diamond electrochemical oxidation, *Applied*
524 *Catalysis B: Environmental*, 144 (2014) 121-128.
- 525 [15] M.A. Oturan, N. Oturan, N. Bellakhal, M. Dachraoui, Comparative mineralization of textile dye
526 indigo by photo-Fenton process and anodic oxidation using boron-doped diamond anode AU -
527 Hammami, Samiha, *Desalination and Water Treatment*, 45 (2012) 297-304.
- 528 [16] S. Garcia-Segura, A. El-Ghenymy, F. Centellas, R.M. Rodríguez, C. Arias, J.A. Garrido, P.L.
529 Cabot, E. Brillas, Comparative degradation of the diazo dye Direct Yellow 4 by electro-Fenton,
530 photoelectro-Fenton and photo-assisted electro-Fenton, *Journal of Electroanalytical Chemistry*,
531 681 (2012) 36-43.
- 532 [17] M.A. Oturan, I. Sirés, N. Oturan, S. Pérocheau, J.-L. Laborde, S. Trévin, Sono-electro-Fenton
533 process: A novel hybrid technique for the destruction of organic pollutants in water, *Journal of*
534 *Electroanalytical Chemistry*, 624 (2008) 329-332.
- 535 [18] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical
536 technologies based on Fenton's reaction chemistry, *Chemical reviews*, 109 (2009) 6570-6631.
- 537 [19] I. Sirés, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based
538 on electrochemical separation and degradation technologies: a review, *Environment*
539 *international*, 40 (2012) 212-229.

- [20] R. Daghrir, P. Drogui, D. Robert, Photoelectrocatalytic technologies for environmental applications, *Journal of Photochemistry and Photobiology A: Chemistry*, 238 (2012) 41-52.
- [21] J. Georgieva, E. Valova, S. Armyanov, N. Philippidis, I. Poullos, S. Sotiropoulos, Bi-component semiconductor oxide photoanodes for the photoelectrocatalytic oxidation of organic solutes and vapours: a short review with emphasis to TiO₂-WO₃ photoanodes, *Journal of hazardous materials*, 211 (2012) 30-46.
- [22] C. Barrera-Díaz, P. Cañizares, F. Fernández, R. Natividad, M. Rodrigo, Electrochemical advanced oxidation processes: an overview of the current applications to actual industrial effluents, *Journal of the Mexican Chemical Society*, 58 (2014) 256-275.
- [23] A. Babuponnusami, K. Muthukumar, Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, *Chemical Engineering Journal*, 183 (2012) 1-9.
- [24] S. Balachandran, S.E. Kentish, R. Mawson, M. Ashokkumar, Ultrasonic enhancement of the supercritical extraction from ginger, *Ultrasonics Sonochemistry*, 13 (2006) 471-479.
- [25] K. Chair, A. Bedoui, N. Bensalah, F.J. Fernández-Morales, C. Sáez, P. Cañizares, M.A. Rodrigo, Combining bioadsorption and photoelectrochemical oxidation for the treatment of soil-washing effluents polluted with herbicide 2,4-D, *Journal of Chemical Technology & Biotechnology*, 92 (2017) 83-89.
- [26] A. Özcan, N. Oturan, Y. Şahin, M.A. Oturan, Electro-fenton treatment of aqueous clopyralid solutions, *International Journal of Environmental Analytical Chemistry*, 90 (2010) 478-486.
- [27] F.J. Fernandez, V. Sanchez-Arias, J. Villaseñor, L. Rodriguez, Evaluation of carbon degradation during co-composting of exhausted grape marc with different biowastes, *Chemosphere*, 73 (2008) 670-677.
- [28] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, M.A.H. Franson, American Public Health Association., American Water Works Association., Water Environment Federation., APHA., AWWA., WEF., Standard methods for the examination of water and wastewater, 21st ed., American Public Health Association, Washington, 2005.
- [29] L. Rodríguez Mayor, J. Villaseñor Camacho, F.J. Fernández Morales, Operational optimisation of pilot scale biological nutrient removal at the Ciudad Real (Spain) domestic wastewater treatment plant, *Water, Air, and Soil Pollution*, 152 (2004) 279-296.
- [30] C. Annabi, F. Fourcade, I. Soutrel, F. Geneste, D. Floner, N. Bellakhal, A. Amrane, Degradation of enoxacin antibiotic by the electro-Fenton process: Optimization, biodegradability improvement and degradation mechanism, *Journal of environmental management*, 165 (2016) 96-105.
- [31] C. Ridruejo, C. Salazar, P.L. Cabot, F. Centellas, E. Brillas, I. Sirés, Electrochemical oxidation of anesthetic tetracaine in aqueous medium. Influence of the anode and matrix composition, *Chemical Engineering Journal*, 326 (2017) 811-819.
- [32] M.J.M. de Vidales, M. Millán, C. Sáez, P. Cañizares, M.A. Rodrigo, Irradiated-assisted electrochemical processes for the removal of persistent pollutants from real wastewater, *Separation and Purification Technology*, 175 (2017) 428-434.
- [33] M. Catanho, G.R. Malpass, A.J. Motheo, Photoelectrochemical treatment of the dye reactive red 198 using DSA® electrodes, *Applied Catalysis B: Environmental*, 62 (2006) 193-200.
- [34] L. Pinheiro, R. Pelegrini, R. Bertazzoli, A. Motheo, Photoelectrochemical degradation of humic acid on a (TiO₂) 0.7 (RuO₂) 0.3 dimensionally stable anode, *Applied Catalysis B: Environmental*, 57 (2005) 75-81.
- [35] A. Socha, E. Sochocka, R. Podsiadły, J. Sokołowska, Electrochemical and photoelectrochemical degradation of direct dyes, *Coloration technology*, 122 (2006) 207-212.
- [36] M.E. Oslugi, G.A. Umbuzeiro, M.A. Anderson, M.V.B. Zanoni, Degradation of metallophthalocyanine dye by combined processes of electrochemistry and photoelectrochemistry, *Electrochimica Acta*, 50 (2005) 5261-5269.
- [37] M.J. Martín de Vidales, C. Sáez, P. Cañizares, M.A. Rodrigo, Removal of triclosan by conductive-diamond electrolysis and sonoelectrolysis, *Journal of Chemical Technology & Biotechnology*, 88 (2013) 823-828.
- [38] F.L. Souza, C. Sáez, P. Cañizares, A.J. Motheo, M.A. Rodrigo, Sonoelectrolysis of wastewaters polluted with dimethyl phthalate, *Industrial & Engineering Chemistry Research*, 52 (2013) 9674-9682.

- [39] M.-h. Wu, X.-y. Yang, G. Xu, N. Liu, R.-y. Guo, J.-q. Lei, L. Tang, UV-Based Oxidation Processes for Removal of Clopyralid: Optimal Conditions, Efficiency, and By-Products, *Environmental Engineering Science*, 32 (2015) 998-1006.
- [40] M.J. Martín de Vidales, M.P. Castro, C. Sáez, P. Cañizares, M.A. Rodrigo, Radiation-assisted electrochemical processes in semi-pilot scale for the removal of clopyralid from soil washing wastes, *Separation and Purification Technology*, 208 (2019) 100-109.
- [41] F. Silva, C. Sáez, M. Lanza, P. Cañizares, M. Rodrigo, The Role of Mediated Oxidation on the Electro-irradiated Treatment of Amoxicillin and Ampicillin Polluted Wastewater, *Catalysts*, 9 (2019) 9.
- [42] M.J.M. de Vidales, C. Sáez, J.F. Pérez, S. Cotillas, J. Llanos, P. Cañizares, M.A. Rodrigo, Irradiation-assisted electrochemical processes for the removal of persistent organic pollutants from wastewater, *Journal of Applied Electrochemistry*, 45 (2015) 799-808.
- [43] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, *Environmental Science and Pollution Research*, 21 (2014) 8336-8367.
- [44] C.C. de Almeida, M. Munoz-Morales, C. Saez, P. Canizares, C.A. Martinez-Huitle, M.A. Rodrigo, Integrating ZVI-dehalogenation into an electrolytic soil-washing cell, *Separation and Purification Technology*, 211 (2019) 28-34.
- [45] P. Cañizares, C. Sáez, A. Sánchez-Carretero, M.A. Rodrigo, Synthesis of novel oxidants by electrochemical technology, *Journal of Applied Electrochemistry*, 39 (2009) 2143.
- [46] Y.-T. Lin, C. Liang, J.-H. Chen, Feasibility study of ultraviolet activated persulfate oxidation of phenol, *Chemosphere*, 82 (2011) 1168-1172.
- [47] Y.-J. Shih, W.N. Putra, Y.-H. Huang, J.-C. Tsai, Mineralization and defluorization of 2, 2, 3, 3-tetrafluoro-1-propanol (TFP) by UV/persulfate oxidation and sequential adsorption, *Chemosphere*, 89 (2012) 1262-1266.
- [48] B. Petri, M. Crimi, H. Mosbæk, R.L. Siegrist, P.L. Bjerg, In Situ Chemical Oxidation of Contaminated Soil and Groundwater Using Persulfate: A Review AU - TSITONAKI, AIKATERINI, *Critical Reviews in Environmental Science and Technology*, 40 (2010) 55-91.
- [49] G. Li, J. Qu, X. Zhang, J. Ge, Electrochemically assisted photocatalytic degradation of Acid Orange 7 with β -PbO₂ electrodes modified by TiO₂, *Water research*, 40 (2006) 213-220.
- [50] A. Socha, E. Sochocka, R. Podsiadły, J. Sokołowska, Electrochemical and photoelectrochemical treatment of CI Acid Violet 1, *Dyes and Pigments*, 73 (2007) 390-393.
- [51] A.M. de Freitas, C. Sirtori, P. Peralta-Zamora, Photoelectrocatalytic degradation of camphor on TiO₂/RuO₂ electrodes, *Environmental Chemistry Letters*, 9 (2011) 97-102.
- [52] F.J. Fernández, V. Sánchez-Arias, J. Villaseñor, L. Rodríguez, Evaluation of carbon degradation during co-composting of exhausted grape marc with different biowastes, *Chemosphere*, 73 (2008) 670-677.
- [53] F.J. Fernandez-Morales, J. Villasenor, D. Infantes, Modeling and monitoring of the acclimatization of conventional activated sludge to a biohydrogen producing culture by biokinetic control, *International Journal of Hydrogen Energy*, 35 (2010) 10927-10933.
- [54] M.J.M. de Vidales, S. Barba, C. Sáez, P. Cañizares, M.A. Rodrigo, Coupling ultraviolet light and ultrasound irradiation with Conductive-Diamond Electrochemical Oxidation for the removal of progesterone, *Electrochimica Acta*, 140 (2014) 20-26.