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Abstract

The removal of a commercial herbicide, based on clopyralid, by means of Electro-Fenton (EF) was studied using a soil washing effluent obtained using synthetic ground water as washing fluid. From the results, it was observed that the degradation and mineralization yields of clopyralid were high, even without the addition of supporting electrolyte. The groundwater could be then used as a sustainable supporting electrolyte. The influence of the minerals constituents, the current and the ferrous ions regeneration was evaluated. The highest hydrogen peroxide production was achieved working at 200 mA but regeneration of ferrous ions was not efficient at this current. Iodide ions were one of the main responsible in the EF efficiency decrease due to their reaction with the produced hydrogen peroxide. Electrochemical study proved that clopyralid was not electroactive and that its degradation was mainly due to radical oxidation. Long duration electrolysis carried out at 200 mA in groundwater provided an improvement of the solution biodegradability after 480 min that can be linked to a significant increase in the carboxylic acids production. These results support the feasibility of applying an EF process in order to carry out a subsequent biological mineralization.

Keywords: Electro-Fenton; clopyralid; groundwater; soil washing effluent; biodegradability improvement.

1. INTRODUCTION

The pollution related to the use and production of pesticides is an issue which not only has impact on the environment but also concerns human beings and wildlife. The application of pesticides is an essential tool for the correct development of crops, however it became a serious problem during the green revolution, increasing the loss of soil fertility, the soil acidification, the nitrate leaching, the resistance of weed species and the loss of biodiversity (Tilman et al., 2002; Verma et al., 2013; Verma et al., 2014). Additionally, according to the literature (Pimentel and Levitan, 1986), less than 0.1% of pesticides applied for pest control reach their target pests. It means that more than 99.9% of pesticides move into the environment, polluting water, soil and air. Water pollution by pesticides is a widespread problem. Several pesticides haven been detected in surface and groundwater, as it has been described by a great number of research studies (Bortleson and Davis, 1997; Aydin et al., 2018; Xie et al., 2019). Moreover, human health is significantly affected by this kind of pollution, producing, among other problems, fertility diseases (Cano-Sancho et al., 2019).

The removal of organic pollutants from waters has been studied during years and it is a topic which can be faced by using different technologies, from the adsorption of the pollutants on carbon materials (Liu et al., 2018) to the use of microorganisms to degrade the organic compounds (De Lucas et al., 2007; Garcia-Becerra and Ortiz, 2018; Gaur et al., 2018; Kumar et al., 2018). One of the most effective technologies to remove organic molecules from water is the Advanced Oxidation Process (AOP). They are defined as processes which involve the generation of highly reactive oxidizing species able to attack and degrade organic substances. This concept was established in the 1980s (Glaze, 1987; Huang et al., 1993). The AOP processes have demonstrated good efficiencies treating

relatively low volumes of effluents at high concentrations. For this reason, they can be used after a concentration step such as membrane separation or adsorption processes (Pérez et al., 2010; Urtiaga et al., 2013; Wang et al., 2014; Liang et al., 2016; Bouaziz et al., 2017; Aboudalle et al., 2018a). One class of AOPs that is gaining attention over the last two decades are the electrochemical advanced oxidation processes (EAOPs) (Comninellis et al., 2008; Barrera-Díaz et al., 2014; Chaplin, 2014; Moreira et al., 2017). The main advantages of the EAOPs versus traditional AOPs are that this kind of technology is able to manage a wide range of pollutants and concentrations, can in situ generate H_2O_2, operates at mild conditions and can be easily scalable, amongst others. Additionally, this technology provides some upsides for the prevention and remediation of pollution problems because the electron is a non-polluting reagent (Sirés et al., 2014). Nevertheless, EAOPs have associated important downsides such as the electrical costs related to the energy supply and the consumption of chemicals as supporting electrolyte (Oller et al., 2011; Sirés et al., 2014). In order to reduce the costs of the EAOP processes, they can be coupled with cheap treatments such as the bioprocesses. The order in which the EAOP and the bioprocess are combined attends to different factors such as the biodegradability/toxicity of the effluents, the nature of the pollutant and the existence of acclimatized microbial cultures able to degrade the target pollutant amongst others (Oller et al., 2011; Ganzenko et al., 2014).

Electro-Fenton (EF) process is considered one of the most efficient EAOPs processes. The EF process is based on the electrogeneration of H_2O_2 at the cathode by reducing the fed dissolved oxygen. The addition of an iron catalyst and an acid pH are necessary conditions to produce oxidant •OH in the liquid bulk (Brillas et al., 2009; Barrera-Díaz et al., 2014; Aboudalle et al., 2018a). Fenton`s reaction involves H_2O_2 and ferrous iron to form •OH Eq. (1).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$

Electrochemical processes are usually characterized by the requirement of a supporting electrolyte, mineral salts which provide to the solution enough conductivity in order to decrease the cell voltage. However, the addition of mineral salts attained one important drawback, because in spite of improving the conductivity, it increases the pollution of the water (Belen Carboneras et al., 2018). Because of that, novel solutions must be reached.

In this context, this study focuses on the examination of the main parameters influencing the clopyralid removal and mineralization by means of the EF process. Moreover, a study of the influence of the operational variables over the enhancement of the biodegradability of the effluent caused by the EF process was carried out.

The EF clopyralid oxidation was implemented with and without the addition of any supporting electrolyte. To do that, a synthetic groundwater solution was used as soil washing fluid to enhance the conductivity, taking the advantage of this sustainable and non-polluting natural resource.

2. MATERIALS AND METHODS

2.1. Chemicals and soil washing effluents

In this work, the selected target pollutant was clopyralid. It was used in its commercial formulation, Lontrel® 72 (72% w/w), and was supplied by Dow AgroSciences. The polluted effluents used in this research were synthetic soil washing effluents. The soil washing fluid used to extract the pollutant from the soil was groundwater. According to the composition and concentration of typical groundwater and the results described in the literature (Minerales, 1985; Chair et al., 2017a; 2017b), the synthetic effluent presented the following concentrations: Na_2SO_4 50 mM; $MgSO_4$ $7H_2O$ 5.54 mM; NaCl 2.25 mM; $NaNO_3$ 1.53 mM; KI 0.15 mM; $CaCO_3$ 12.47 mM.

$FeSO_4 \cdot 7H_2O$ (purity 99%), Na_2SO_4 and the rest of the chemicals used in this work were purchased from Acros Organics (Thermo Fisher Scientific, Geel, Belgium).

In the literature, it has been described that the optimum pH to carry out the EF process is 3 (Diagne et al., 2007). Because of that, the pH of the wastewater was adjusted to 3 before the experiments by adding analytical grade sulfuric acid H_2SO_4 purchased form Acros Organics. All the solutions were prepared using Ultrapure water (Millipore Elga).

2.2. Electrochemical Apparatus and Procedures

The electrochemical reactor consisted of a batch undivided cylindrical glass compartment with a volume of 800 mL. The main components of the electrochemical cell were a cylindrical platinum anode (32 cm^2), which was placed at the centre of the reactor and a tri-dimensional piece of carbon felt of 112 cm^2 of geometrical area (Le Carbone Loraine RVG 4000 Mersen, Paris la Défense, France), which acted as cathode. The carbon felt electrode surrounded the platinum anode so as to get a good potential distribution. The main carbon felt characteristics were 35.3 $m^2\ g^{-1}$ of specific area, 500 g m^{-2} of area weight, thickness of 0.4 cm and 95% of porosity). Before starting the electrolysis, compressed air was bubbled into the solution during 15 min in order to provide the solution with an

appropriated O_2 concentration. The experiments were carried out in duplicate, at 20 ºC and galvanostatic conditions. The current was applied using a DC power supply (Metrix, model AX 322-Chauvin Arnoux Group, Paris, France). Just before the beginning of the EF reactions the catalytic Fe^{2+} was added into the reaction bulk as $FeSO_4 \cdot 7H_2O$. The Fe^{2+} concentrations studied were 0.1, 0.5, 1, 2 and 5 mM.

In order to select the optimal operating conditions in terms of clopyralid degradation and mineralization, several experiments were made changing one of the main parameters influencing the EF process, the current applied. In the literature it has been described that the current governs the formation of H_2O_2, the regeneration of ferrous iron and therefore the production of hydroxyl radicals (Oturan et al., 2008; Özcan et al., 2009; Feng et al., 2014; Aboudalle et al., 2018b).

2.3. Analytical procedure

2.3.1. High performance liquid chromatography (HPLC)

Clopyralid concentration was measured by HPLC using a Waters 996 system equipped with a Waters 996 PDA (Photodiode Array Detector) and Waters 600LCD Pump. The column was a Waters C-18 (4.6 mm x 250 mm x 5 µm). Acetonitrile (purity 99.9%) (HPLC grade) was purchased from Sigma Aldrich (Saint Quentin Fallavier, France). The mobile phase was a mixture of acetonitrile/ultra-pure water (20/80 v/v) with 0.1% of formic acid. The flow rate was 1 mL min^{-1} and the herbicide was detected at 280nm.

2.3.2. Total organic carbon (TOC)

TOC concentration was monitored by means of a TOC-V $_{CPH/CPG}$ Total Analyser Schimadzu. Organic Carbon compounds were combusted and converted to carbon dioxide; then it was detected by a Non-Dispersive Infra-Red (NDIR) Detector.

164

165 *2.3.3. Ion chromatography (IC)*

166 The carboxylic acids generated during the electrolysis were identified and quantified by
167 a DIONEX DX120 ion chromatography. The chromatograph was equipped with a
168 conductivity detector, using an anion exchange column AS19 (4 mm x 250 mm) as the
169 stationary phase, and solutions of KOH in water, prepared from KOH (12 M), as the
170 mobile phase. The analysis were carried out using a gradient elution mode, starting with
171 10 mM KOH during 10 min and then increasing linearly to 45 mM from 10 to 25 min.
172 Finally, from 25 to 35 min the concentration of KOH was 45 mM. The flow rate was set
173 at 1 mL min^{-1}.

174

175 *2.3.4. Ferrous ions and H_2O_2 concentrations*

176 The ferrous ions concentration in the reactor was measured by means of a colorimetric
177 principle, according to the Phenanthroline Method NF 90-017 (AFNOR, 1982). The
178 concentration of H_2O_2 was determined by the potassium titanium (IV) oxalate method
179 according to standard DIN 38 409, part 15, DEV-18 (Eisenberg, 1943).

180

181 *2.3.5. Chemical oxygen demand (COD) measurements*

182 CSB Nanocolor® tests were employed to analyse the COD of the samples. They were
183 supplied by Macherery-Nagel (Düren, Germany).

184

185 *2.3.6. Biochemical oxygen demand (BOD_5) measurements*

186 In order to evaluate the influence of the EF process on the biodegradability of the soil
187 washing effluents, BOD_5 test were carried out using Oxitop ISA technology (from WTW,
188 Alés, France). The tests were performed under the normalised conditions; 5 d at 20 ºC.

Before the test, it was necessary to adjust the pH of all the samples at 7 by adding NaOH. The innoculum required to perform the analyses was collected from the municipal wastewater treatment plant (Rennes Beaurade, France). For inoculation of the bottles, an initial biomass concentration of 0.05 g L^{-1} was necessary. The following trace mineral were used to ensure the nutrients availability along the BOD_5 tests (g L^{-1}): $MgSO_4 \cdot 7H_2O$, 22.5; $CaCl_2$, 27.5; $FeCl_3$, 0.15; NH_4Cl, 2.0; Na_2HPO_4, 6.80; KH_2PO_4, 2.80.

To check the viability of the seed used as inoculum, a control test containing glutamic acid (150 mg L^{-1}) and glucose (150 mg L^{-1}) was carried out. Additionally, a blank test, in absence of carbon source, was performed in order to determine the endogenous oxygen consumption.

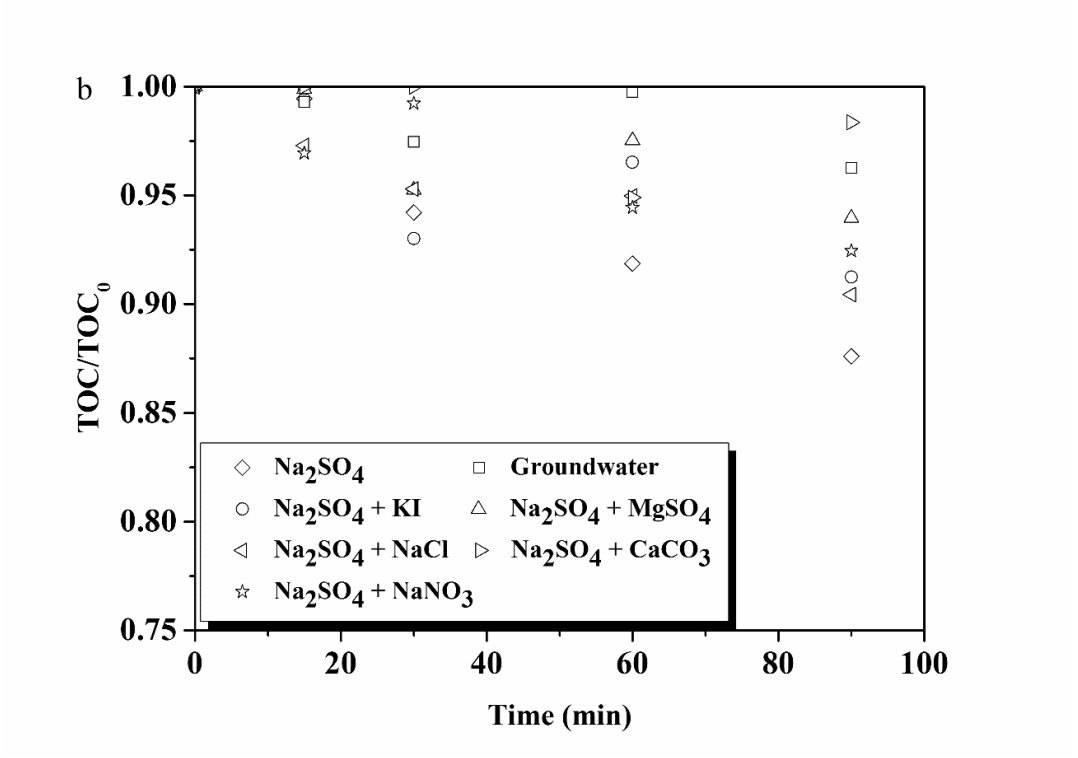
2.3.7. Electrochemical analysis

Voltammograms were obtained in a conventional three-electrodes cell with a scan rate of 100 mV s^{-1} using a BioLogic SP-150 potentiostat recorded to EC-Lab V10.36 software. As working electrode both, platinum and vitreous carbon, were tested. The platinum electrode (3.14 mm^2) was used to characterize the anodic oxidation processes while the carbonous electrode (7.07 mm^2) was used to study the cathodic reduction processes. In both cases, a Pt wire was used as the counter electrode and all the electrode potentials were measured with respect to a saturated calomel electrode (SCE) located near to the working electrode. Experiments were performed at ambient temperature under nitrogen atmosphere to avoid dissolved oxygen.

3. RESULTS AND DISCUSSION

3.1. Effect of the mineral salts contained in the groundwater on the EF experiments

213 Considering the composition of the soil washing solution, it must be highlighted that from
214 a thermodynamic point of view, redox reaction between the constituents cannot occur.
215 From Fig. 1, it can be seen that the composition of the supporting electrolyte directly
216 affected the clopyralid degradation and mineralization. As previously stated, the use of
217 groundwater could be a sustainable option for soil washing processes. In order to check
218 the influence of the different mineral salts, a set of experiments were carried out. To do
219 these experiments, 7 different electrolyte solutions were used. The first electrolyte
220 solution contained all of the components of the synthetic groundwater (Chair et al.,
221 2017b). As a reference, a tests containing the typical electrolyte solution, 50 mM Na_2SO_4,
222 was carried out. Finally, with the aim to study the individual contribution of the minerals
223 contained in the synthetic ground water, 5 extra electrolyte solutions were prepared.
224 These electrolytes were based on the typical supporting electrolyte, 50 mM Na_2SO_4, but
225 including in each case one of the minerals contained in the groundwater. The reaction
226 conditions were 0.1 mM of Fe^{2+}, 50 and 100 mA of current. These operational conditions
227 were identified as the optimum ones in a previous work carried out when operating with
228 a similar set-up (Dalle et al., 2017). The current intensities studied yield very similar
229 results. Because of that, only the results obtained at 50 mA are presented in Fig. 1.
230



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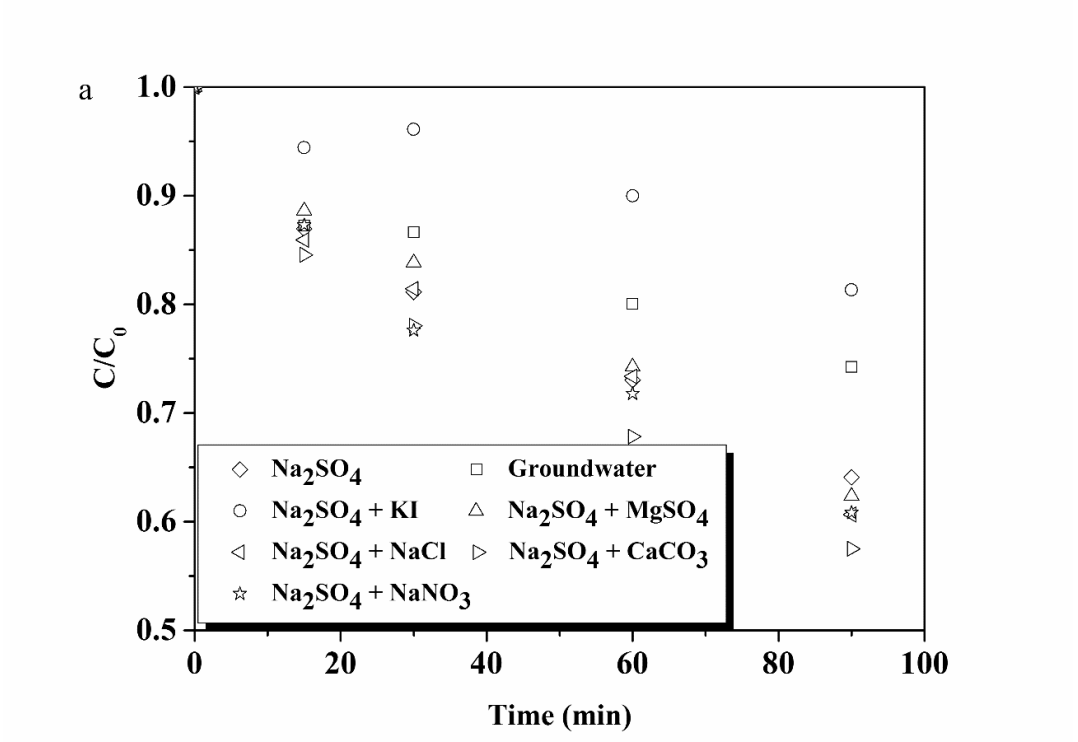


232

233 Figure 1. Influence of the electrolyte composition on the degradation (a) and
234 mineralization (b) of clopyralid (initial concentration 180 mg L^{-1}), 0.1 mM of Fe^{2+}, 50
235 mA of current and 0.1 mL min^{-1} of compressed air.

As can be seen in Fig. 1, the removal of the pollutant depended on the composition of the electrolyte used. The influence was mainly visible for the clopyralid degradation, which ranged from 20% to 40%. However, the mineralization yields presents very similar values in all the cases, about 10%.

When the synthetic groundwater was used as electrolyte, average removal efficiencies were obtained, presenting a removal rate of about 0.54 mg L^{-1} min^{-1}.

In most of the cases, except in the presence of iodide ions, the presence of single trace mineral from the groundwater had a slightly influence on the average degradation rates, presenting the best average removal rate the combination of the Na_2SO_4 and $CaCO_3$, 0.93 mg L^{-1} min^{-1}. This result indicates that these mineral ions, except the iodide ions, did not interfere on the clopyralid degradation. In Fig. 1a, iodide ions clearly worsened the clopyralid removal process. When the KI was present in the electrolyte, (groundwater electrolyte and Na_2SO_4 + KI electrolyte), only about 20% of the initial clopyralid was degraded after 90 min.

With regard to the mineralization, the best mineralization yield was obtained when using Na_2SO_4 as the sole supporting electrolyte. Anyway, the low mineralization observed in all the cases during the electrolysis could be explained by the reaction between the hydroxyls radicals and the inorganic compounds contained in the effluent. This reaction involves simple electron transfer of $^{\bullet}OH$ to form the hydroxide ion with the corresponding change in the oxidation state of the donor (Buxton et al., 1988). Inorganic ions are hydroxyl radical consumers, this statement justify the worse efficiency when mineral salts were used.

In this sense it must be highlighted that, considering the standard potentials of H_2O_2 / H_2O and I_3^- /I^- redox couple, iodide ions can react with the hydrogen peroxide produced at the cathode surface Eq. (2) interfering with the Fenton reaction.

$$H_2O_2 + 3I^- \leftrightarrow 2H_2O + I_3^- \quad (2)$$

Another ion interfering the Fenton reaction was chloride ion. According the literature, (Loaiza-Ambuludi et al., 2013) electrogenerated active chlorine can oxidize Fe^{2+} Eq. (3) or decompose hydrogen peroxide Eq. (4), reducing the production rate of the strong oxidant •OH by the Fenton´s reaction (Beqqal et al., 2017).

$$2\,Fe^{2+} + Cl_2 \rightarrow 2\,Fe^{3+} + 2\,Cl^- \quad (3)$$

$$2\,H_2O_2 + Cl_2 \rightarrow 2\,HCl + H_2O + O_2 \quad (4)$$

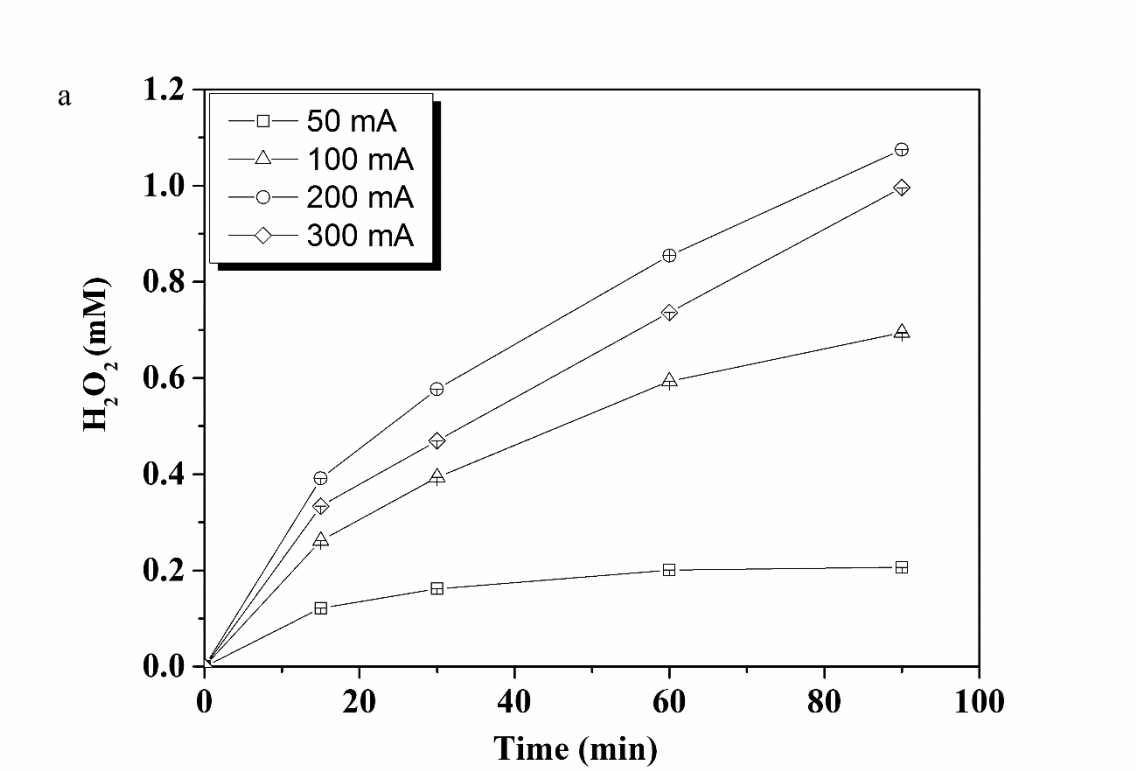
It should be noted that to allow chloride ions oxidation, the potential of the anode needs to be higher than about 1 V/SCE (E^0 (Cl_2/Cl^-) = 1.24 V/SHE) and then the production of chlorine depends on the operating conditions and mainly on the applied current.

3.2. Effect of the applied cathodic current on H_2O_2 production and ferrous regeneration

3.2.1. Effect of the current on the H_2O_2 production

Experiments were developed at different currents ranging from 50 to 300 mA. In these experiments, synthetic groundwater was used as supporting electrolyte, during 90 min at pH 3 and without the addition of Fe(II) and clopyralid to avoid EF reactions. The current

for H_2O_2 accumulation depended on some factors like reactor configuration, cathode material and operation conditions. 3D carbonaceous cathodes, such as carbon felt, have demonstrated good properties for H_2O_2 formation. Carbon is non-toxic, presents good stability and low catalytic activity of H_2O_2 decomposition (Petrucci et al., 2016; Das and Golder, 2017). The obtained results were compared with the same experiments using the typical electrolyte in electrochemistry, Na_2SO_4 (50 mM), with the aim to evaluate the influence of the mineral salts used as supporting electrolyte. The production of H_2O_2 as function of the electrolysis length and applied current is presented in Fig. 2.



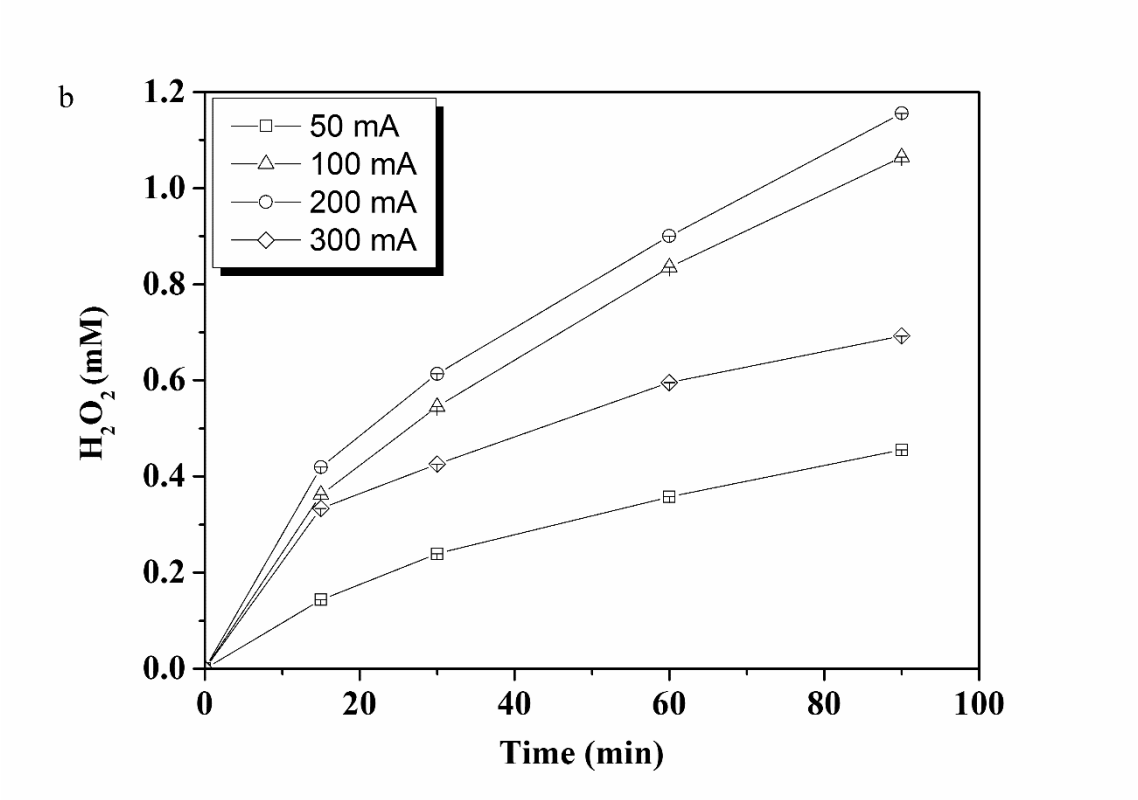


Figure 2. Effect of the current on the H_2O_2 production using (a) groundwater and (b) 50 mM Na_2SO_4.

The H_2O_2 production was not linear along the experiment due to the occurrence of parasitic reactions, mainly anodic oxidation of H_2O_2 Eq. (4) and cathodic reduction to water Eq. (5) (Pérez et al., 2017; Zhou et al., 2018).

$$H_2O_2 \rightarrow O_2 + 2e^- + 2H^+ \quad (4)$$

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \quad (5)$$

The evolution of the production of H_2O_2 during the experiment is directly related with the dissolved oxygen concentration. Usually, dissolved oxygen concentration remains constant at the beginning of the experiment until the polarization of electrodes takes place. After this stage, the concentration of dissolved oxygen in the solution depended on the applied current (Dalle et al., 2017).

303 The best H_2O_2 productions were achieved when working at 200 mA with both supporting
304 electrolytes: groundwater and Na_2SO_4. However, the concentrations reached with Na_2SO_4
305 as supporting electrolyte were higher compared with groundwater. The maximum
306 concentration of H_2O_2 obtained when working at 200 mA with Na_2SO_4 as supporting
307 electrolyte was about 1.16 mM; while it was about a 10% lower using groundwater at the
308 same current, reaching 1.08 mM. The difference could be, in part, explained by the
309 reaction of H_2O_2 with iodide ions contained in the groundwater can in part explain the
310 lower accumulated concentration.
311 Working with groundwater as supporting electrolyte, at 50 mA, the production of H_2O_2
312 increased during the first 30 min and then remained constant, showing the implementation
313 of an equilibrium between the anodic oxidation of H_2O_2 Eq. (5) and its cathodic
314 production Eq. (6). This effect was not observed at the other current applied, which
315 indicates that the production process outcompete the anodic oxidation process. Moreover,
316 the amount of O_2 produced at the anode, see Eq. (4), increases with the applied current
317 and then favours the production of hydrogen peroxide (Dalle et al., 2017).
318 $$O_2 + 2e^- + 2H^+ \rightarrow 2\ H_2O_2 \qquad (6)$$
319 When operating at higher current densities, the H_2O_2 production increased. However, at
320 the highest applied current, 300 mA, the accumulation of H_2O_2 did not show a
321 proportional improvement. This behaviour could be explained because the reduction of
322 O_2 to form H_2O becomes preferential (Özcan et al., 2008).
323
324 **3.3. Effect of the current on ferrous ions regeneration**
325 The next step was the study of the ferrous ion regeneration when working with the
326 groundwater medium during 90 min at pH 3 without the addition of clopyralid. A series

of experiments at different current intensities were carried out with at an initial concentration of Fe^{2+} of 0.5 mM. Fig. (3) shows the evolution of ferrous iron.

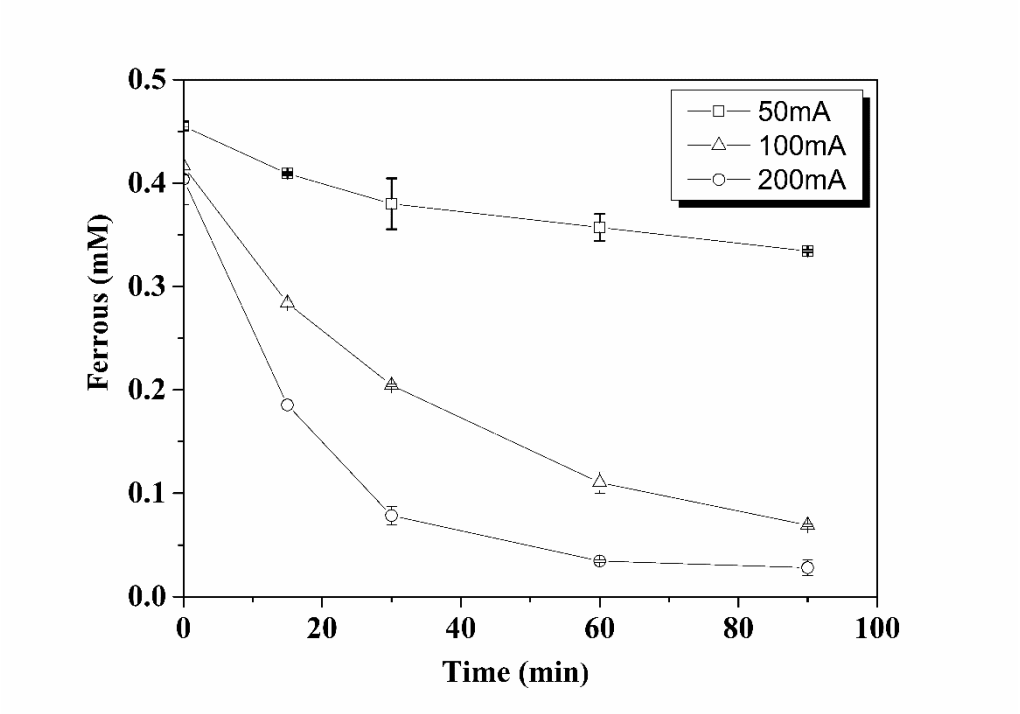


Figure 3. Effect of the applied current on the ferrous iron concentration.

In spite of getting the best H_2O_2 production at 200 mA, the worst regeneration of ferrous ions is achieved at the same current. A decrease of ferrous ions concentration about 25% was observed when the current reached 50 mA. For 100 and 200 mA a significant decrease in total iron concentration took place after 90 min of electrolysis. The ferrous iron concentration decreased from 0.45 to 0.07 and to 0.03 mM at 100 and 200 mA respectively.

Some of the reasons which explain the bad performance of the highest current intensities in the iron regeneration could be the followings:

- Water reduction can lead to a local alkalization of the solution caused by hydroxyl anions formation during H_2 release and then to the precipitation of iron as $Fe(OH)_3$ (Brillas et al., 2009; Petrucci et al., 2016).
- Iron hydroxide could be adsorbed onto the electrode surface or iron ions could be reduced to metallic iron considering standard potentials for iron redox couples (Aboudalle et al., 2018b).

These phenomena could explain a lower efficiency for the highest current densities.

3.4. Effect of the initial Fe^{2+} on the EF experiments

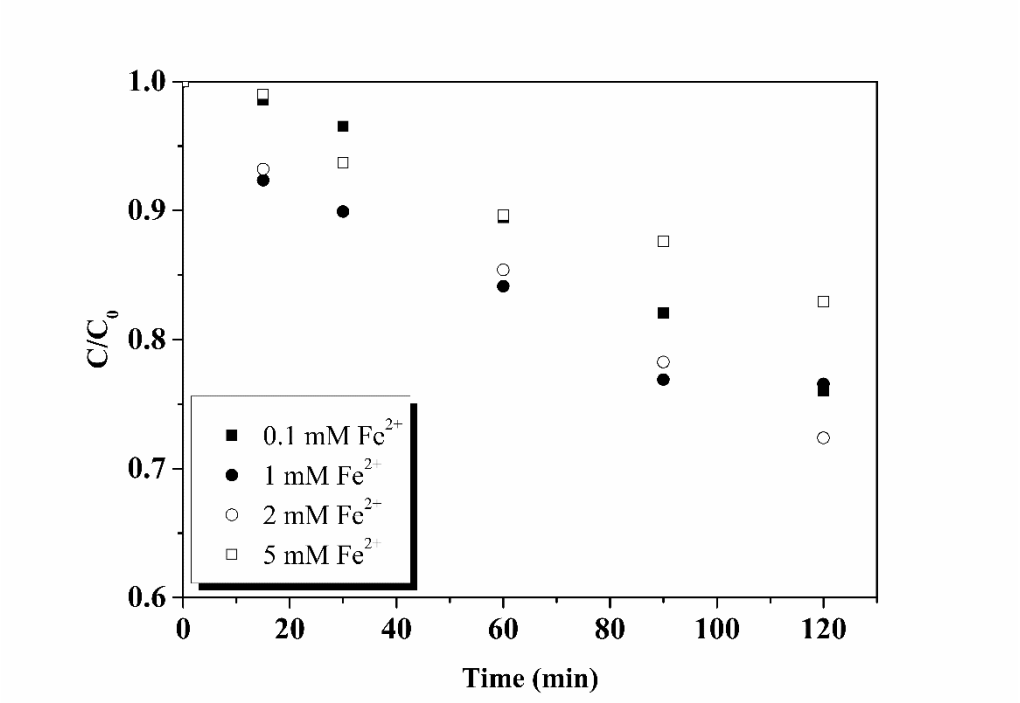
The initial ferrous ions catalyst concentration is another important parameter in the EF process. Taking into account that the highest production of H_2O_2 was obtained at 200 mA, even if the regeneration of the ferrous catalyst was not efficient throughout the electrolysis, the influence of the initial concentration of $FeSO_4 \cdot H_2O$ on the clopyralid degradation was studied with 4 different initial concentrations of Fe^{2+} ranging from 0.1 to 5 mM. As reported in Fig. (4), the initial concentration of ferrous ions influenced the degradation of the clopyralid, fluctuating the removal yield between 18 and 28%. Initial concentrations of 0.1 and 1 mM caused about 25% of clopyralid degradation. The clopyralid removal slightly increased when the initial concentration of Fe^{2+} was 2 mM reaching a clopyralid removal percentage of about 28%. Finally, when the concentration of Fe^{2+} was 5 mM the removal yield decreased to about 18%. This reduction in the clopyralid removal could be explained by the competitive effects between hydroxyl radicals, resulting from the Fenton`s reaction, and the excess of ferrous ions (Panizza and Cerisola, 2009; Aboudalle et al., 2018b), according to Eq. (7).

363 $Fe^{2+} + {}^{\bullet}OH \leftrightarrow Fe^{3+} + OH^{-}$ (7)

364

365 If ferrous ions concentration had a little influence on the clopyralid degradation, the
366 mineralization of organic compound was not influenced by the catalyst concentration
367 (data not shown). It can be then concluded that the influence of the ferrous ion
368 concentration, within the range studied in this work, does not present a significant effect
369 on the clopyralid removal.

370 This statement is in accordance with other studies, where the initial catalyst concentration
371 does not have a strong influence in the degradation and mineralization of organic
372 pollutants (Loaiza-Ambuludi et al., 2013; Aboudalle et al., 2018b).



373

374 Figure 4. Influence of the initial Fe^{2+} concentration on the clopyralid degradation. Initial
375 clopyralid concentration180 mg L^{-1}.

3.5. Effect of oxygen mass flow rate

One of the main reactions which manage EF is the cathodic reduction of oxygen to generate H_2O_2. Oxygen is transferred from the gaseous phase to the aqueous phase, and the dissolved oxygen in the liquid bulk is transferred to the cathode surface, where the reduction takes place. Consequently, it was expected that an increment in the oxygen flow could enhance the mass transfer rate and therefore the subsequent reactions (Do and Yeh, 1996). In order to increase the availability of oxygen in the liquid bulk, the O_2 flow rate was increased from 0.1 to 0.3 L min^{-1}. During the experiments, the current and the ferrous concentration were kept at 50 mA and 0.1 mM, respectively. As can be seen in Fig. 5, results indicate that an increment in the flow rate from 0.1 to 0.3 L min^{-1} had a slight influence on the removal but not on the mineralization efficiency.

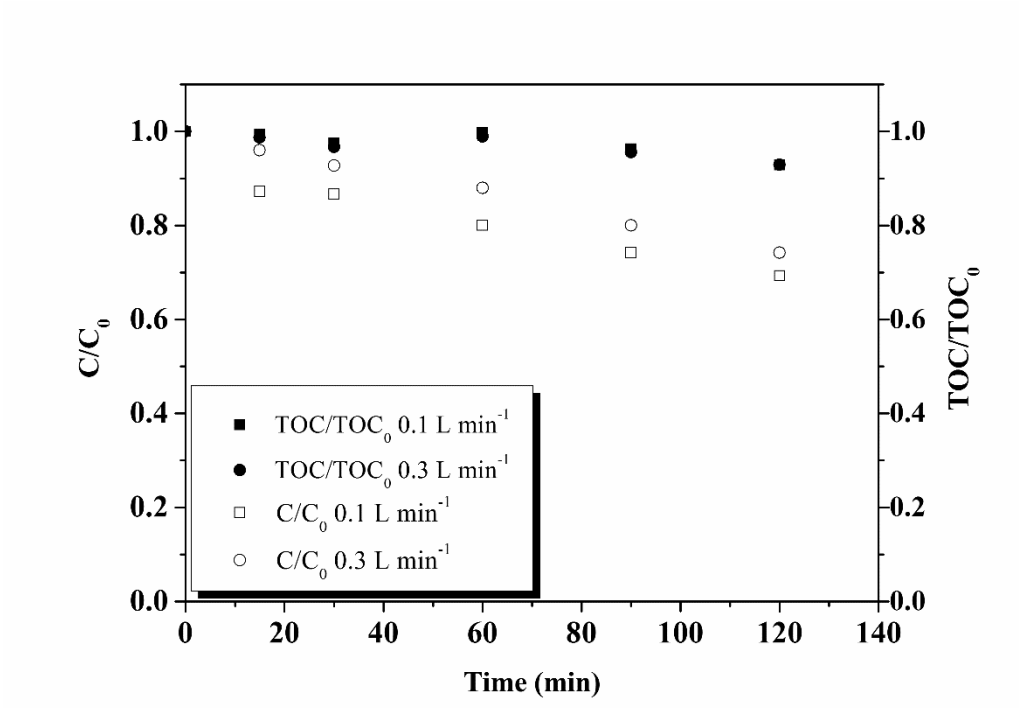


Figure 5. Effect of the oxygen mass flow on the removal efficiency. Clopyralid concentration (full symbols) and TOC concentration (empty symbols).

As can be seen in Fig. 5, the mineralization achieved was almost identical in both cases, whereas the clopyralid removal values were slightly different. Similar results were obtained in research previously reported in the literature (Dalle et al., 2017), where it was demonstrated that an increment from 0.5 to 3 L min^{-1} has not an important influence on the hydrogen peroxide production and hydroxyl radical concentration (Dalle et al., 2017). This behaviour could be explained by the very similar saturation of oxygen in the liquid bulk obtained in both cases (Dalle et al., 2017). In this sense, the slight enhancement obtained when operating at 0.3 L min^{-1} of oxygen flow rate could be explained by the higher turbulence caused which leads to a higher mass transfer coefficient on the surface of the electrode.

3.6. Anodic reaction during clopyralid degradation

In order to study the contribution of a direct oxidation and/or reduction of the clopyralid at the electrode surfaces during the EF process, the electrochemical behaviour of the target pollutant was also investigated. For this purpose, current potential curves were plotted and electrolysis with and without tert-butanol were implemented. Tert-butanol is used here as scavenger which reacts with hydroxyl radicals, generating inert intermediates. These inert compounds cause the termination of the radical chain reaction (Ma and Graham, 2000). The current potential curves, obtained by cyclic voltammetry, were carried out with a vitreous carbon electrode (S = 7.07 mm^2) as a working electrode when the curves were plotted in reduction, a platinum electrode in oxidation (S = 3.14

414 mm^2), a Pt counter electrode and SCE as reference electrode (r = 100 mV s^{-1}). These
415 measurements were carried out under nitrogen atmosphere, at room temperature, pH 3
416 and at a clopyralid concentration of 180 mg L^{-1}. In order to isolate the behaviour of the
417 clopyralid two current potential curves were carried out, one of them with groundwater
418 as supporting electrolyte, and the other one with groundwater and clopyralid. The
419 obtained results are presented in Fig. SM-1 and did not show any clopyralid reaction at
420 the electrodes surface.
421 The current-potential curves did not show any signal in reduction with vitreous carbon
422 electrode (data not shown). With a platinum working electrode, a reversible signal
423 appeared in both curves, due to the oxidation of one of the ions in the groundwater. The
424 peak detected on the platinum anode took places at +0.54V and could be related with the
425 oxidation of I^- into I_3^-. A signal was also observed around +1 V and can be attributed to
426 the oxidation of chloride ions. In this case, the formation of chlorine during the
427 electrolysis can influence the production of hydroxyl radicals.
428
429 Besides this analysis, the degradation of clopyralid on the anodic surface was studied
430 through a simple electrolysis and electrolysis but in the presence of tert-butanol. These
431 electrolyses, as well as an EF experiment in view of comparison, were made in the same
432 operating conditions, applying 50 mA of current during 120 min. Both electrolyses tests
433 achieved 10% of clopyralid removal, whereas EF led to 30% removal. These results
434 confirm again that the electrooxidation of clopyralid was negligible.
435
436 **3.7. Biodegradability of the electrolyzed soil washing effluents**
437 Due to the low mineralization yield, a longer EF treatment was considered in order to
438 improve the mineralization yield and the biodegradability of the wastewater after the

treatment. Two long electrolysis experiments were implemented at 50 and 200 mA and the generation of carboxylic acid was followed. In the literature, the ratio BOD_5/COD is usually employed to analyse the biodegradability of water samples (Zaghdoudi et al., 2017). If the ratio exceeds 0.4, the sample can be considered biodegradable (Carboneras et al., 2018). The obtained results are presented in Figs. 6 and 7 respectively. Experiments were carried out by adding 1 mM of ferrous ions and lasted 8 h.

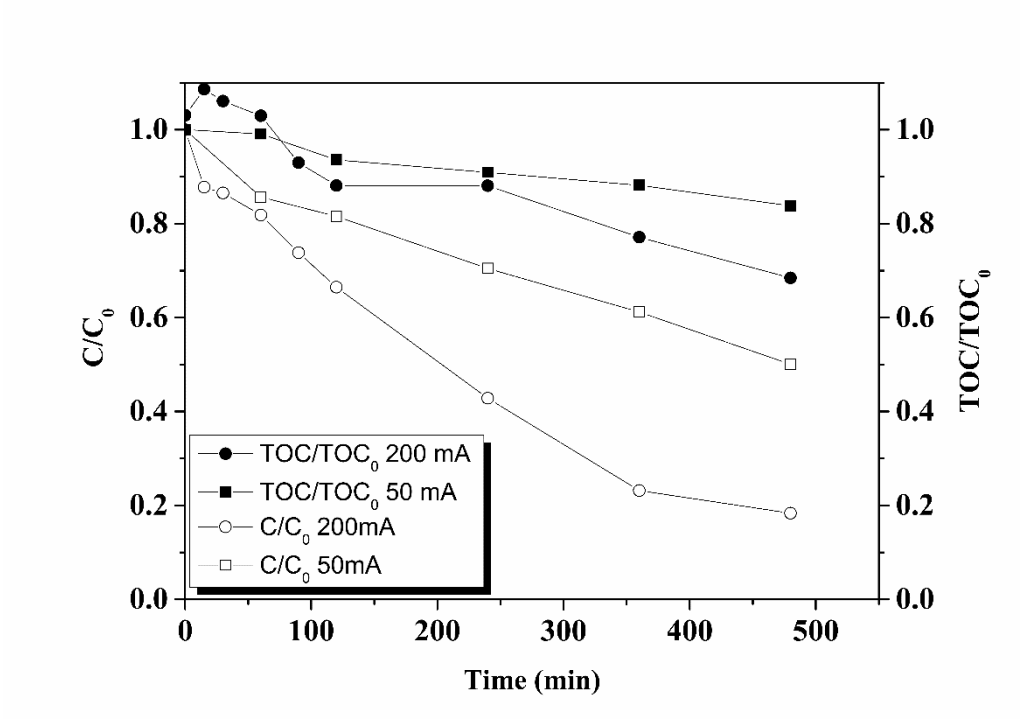
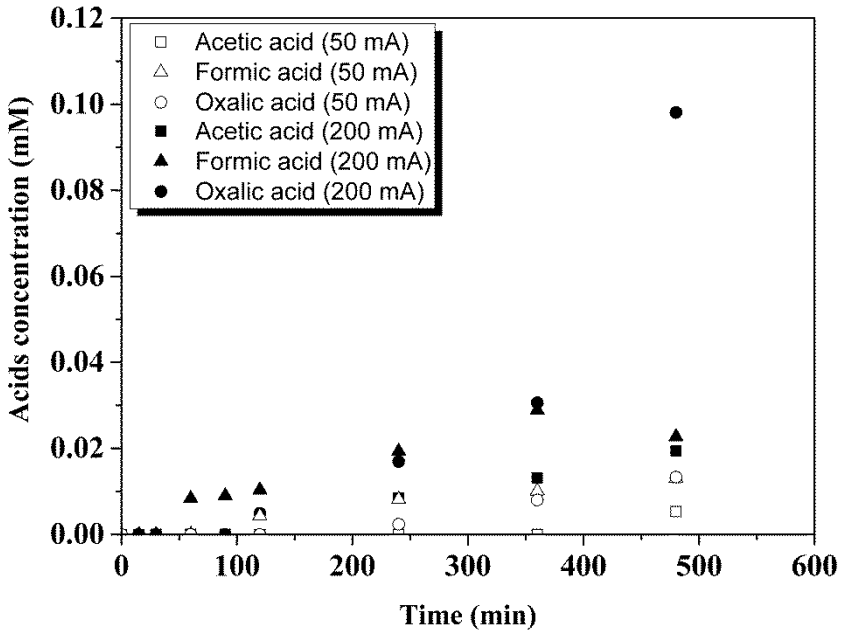


Figure 6. Time-courses of clopyralid degradation and its mineralization during EF at 50 and 200 mA.

A can be seen in Fig. 6, when operating at a current of 200 mA, a higher mineralization efficiency and a higher degradation of clopyralid was obtained, reaching 30 and 80% respectively. These results could be related to the higher production of H_2O_2 when the system was operated at 200 mA. However, in spite of getting a good removal of clopyralid, the mineralization yield reached only around 30%. This result can be

454 explained by the formation of a too low concentration of •OH linked to a non-efficient
455 regeneration of ferrous ions to completely mineralize clopyralid (Aboudalle et al., 2018a).
456 The IC analysis showed the formation of 3 carboxylic acids: acetic, formic and oxalic
457 acids. When clopyralid was removed, these three carboxylic acids appeared, increasing
458 their concentration during the experiments, reaching the highest concentrations at the end
459 of the experiment. Fig. 7 shows the acids concentration along the experiments.



460

461 Figure 7. Evolution of carboxylic acid concentrations along EF reactions at 50 mA (empty
462 symbols) and at 200 mA (full symbols).

463

464 With regard to the cumulative acids production, the electrolysis carried out at 200 mA led
465 to the highest concentration, 0.10 mM for oxalic acid, a concentration about ten times
466 higher than those obtained after the electrolysis at 50 mA.
467 During the electrolysis at 200 mA, the rate of carboxylic acids, especially oxalic acid,
468 seemed to significantly increase from 360 min. It can be then expected that the
469 biodegradability of the effluent can be improved with the significant increase in the

production rate of such carboxylic acids. In order to ratify this hypothesis, the BOD_5/COD ratios obtained after both experiments, carried out at 50 and 200 mA of current density, were determined. Table SM-2 presents the initial and final BOD_5/COD ratios obtained in the experiments carried out with 1 mM of ferrous ions and groundwater as a supporting electrolyte at 50 and 200 mA.

The initial solution of clopyralid was not considered biodegradable because of its BOD_5/COD ratio below 0.4. However, the initial value of this ratio, 0.33, means that some biodegradable compounds were present in the commercial clopyralid formulation (Fontmorin et al., 2014).

After 480 min of electrolysis at 200 mA the solution became biodegradable reaching BOD_5/COD ratios of 0.48 and 0.39 when applying 200 and 50 mA respectively (Table SM-2). This behaviour could be explained by the production of carboxylic acids {Fernandez, 2008, Evaluation of carbon degradation during co-composting of exhausted grape marc with different biowastes}. This improvement of the biodegradability can be explained by the significant generation of carboxylic acids and especially oxalic acid that can be easily metabolized by microorganisms (Fernández et al., 2008). Monitoring the evolution of carboxylic acids during the electrolysis could be then an interesting diagnostic tool for the estimation of biodegradability and could be easily inserted into the process. Regarding the electrolysis at 50 mA, biodegradability of the electrolyzed solution was nearly similar to the initial biodegradability, which can also be explained by the low mineralization of the organic compounds and then the presence of by-products structurally close to clopyralid (Mansour et al., 2012).

4. CONCLUSIONS

From this study, several conclusions can be extracted. Voltammetric study showed that clopyralid was not electroactive and then was not degraded at the electrode surface by a heterogeneous electron transfer. At a current of 200 mA, 80% of clopyralid was degraded and mineralization yield reached 30 %, improving the biodegradability ratio BOD_5/COD from 0.33 to 0.48 in 480 min. The evolution of the carboxylic acids was studied and the results seemed to show that the improvement of biodegradability can be linked to a significant increase of the carboxylic acids production rate and more especially oxalic acid. The EF process can be carried out using groundwater as sustainable supporting electrolyte. It allows the use of a natural resource, groundwater, avoiding the addition of synthetic electrolytes and the increase of the salinity of the natural water bodies receiving these effluents. The groundwater had a significant influence in the EF efficiency, reducing the H_2O_2 production and, therefore, the efficiency of the EF process. The mineral salt that presented the highest impact on the process was KI. In the studied operating conditions, neither the initial catalyst concentration nor the oxygen flow rate had a significant influence in the EF process. Because of that, an EF pre-treatment can be used to improve the biodegradability of polluted soil washing effluent using groundwater as a supporting electrolyte.

5. Acknowledgements

Authors wish to express their gratitude to the financial support from the Spanish Ministry of Economy, Industry and Competitiveness and European Union through project CTM2016-76197-R (AEI/FEDER, UE) and CYTEMA -Campus Científico y Tecnológico de la Energía y el Medioambiente- for the pre-doc CYTEMA-Net mobility grant of María Belén Carboneras.

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