

1 **A comparison of the electrolysis of soil washing wastes with**
2 **active and non-active electrodes.**

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13
14 **Abstract**

15 A comparison between the performance of electrolysis of three different soil-washing
16 wastes with platinum and boron doped diamond (BDD) anodes is carried out in this work.
17 Results demonstrate that the treatment is more efficient with BDD for perchloroethylene
18 and clopyralid but not for the case of lindane, because in this case there is a competitive
19 oxidation between lindane and Sodium Dodecyl Sulphate used to extract this pollutant
20 from soil. First order kinetics are observed in each compound with higher removal at the
21 early stages and generally better results are obtained when using BDD as anode. The
22 evolution of pH and a voltammetry study indicate a higher direct oxidation rate in the
23 case of platinum and more importance of hydroxyl radical mediated processes with
24 diamond anodes. Similar speciation is obtained during the electro-oxidation using BDD
25 and platinum electrodes although the concentration of intermediates vary significantly.

26

27

28 **Keywords**

29 Perchloroethylene; clopyralid; lindane; soil washing; anodic oxidation

30

31 **Highlights**

32 • Important differences between electrolysis of SWF with diamond and platinum
33 anodes

34 • More important direct electrolysis processes with platinum electrodes

35 • More important hydroxyl radical mediated processes with diamond electrodes

36 • Intermediates found were nearly the same, although the concentration differs
37 importantly

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39

40 **1. Introduction**

41 Occurrence of chlorinated hydrocarbons in environment is an issue of the major
42 significance. They can be associated to industrial or agricultural activities and because of
43 its anthropogenic nature and properties (such as high volatility and strong recalcitrance
44 to degradation), the potentiality of damages that they can cause in the environment when
45 they are discharged accidentally is extremely high (Huang et al., 2014; Rodrigo et al.,
46 2014).

47 One of the most effective treatments for acute spills of pollutants is soil washing. It allows
48 the fast removal of the pollutants from soil preventing their diffusion. As it is widely
49 reported, soil washing is not a complete treatment, but it only transfers pollution from soil
50 to a liquid (soil washing fluid) that must be further treated. As pollutants separated from
51 soil are typically refractory to biological treatments, Electrochemical advanced oxidation
52 processes (EAOPs) are the technologies used to remove these species from the liquid
53 waste. Among them, anodic oxidation uses to exhibit a good performance, in particular,
54 when considering that soil washing effluents contains naturally salts (also extracted from
55 soil) and, hence, that they can be treated as produced, without the addition of reagents.
56 Thus, there are many works in the literature describing successful applications of this
57 technology (Mousset et al., 2014a; Mousset et al., 2014b, c; Huguenot et al., 2015; Trelu
58 et al., 2016a; Trelu et al., 2016b).

59 When speaking about anodic oxidation, there are two different processes which are
60 related to the anode material employed. Some types of anodes, such as platinum, lead to
61 a soft oxidation with the production of a very large number of intermediates (including
62 sometimes polymers) and not very high mineralization efficient. (Pulgarin et al., 1994;
63 Subba Rao and Venkatarangiah, 2014) In a pioneering work of Comninellis (Foti et al.,
64 1999), these electrodes were named as active electrodes and their performance was

65 explained in terms of the use of the hydroxyl radicals (formed during oxidation of water)
66 for the oxidation of the surface of the anode which, in turn, was the main responsible for
67 the oxidation of the pollutant. Thus, the oxidation of the pollutant was a simple chemical
68 reaction between a component of the electrode surface in a higher oxidation state and the
69 pollutant. On the contrary, the anodic oxidation carried out by other anodes such as those
70 based on conductive diamond coatings (so-called non-active electrodes) was much more
71 efficient. It was explained in terms of the lack of possibilities of interactions between the
72 surface of these electrodes and the hydroxyl radicals formed during the oxidation of the
73 water molecule. Thus, once produced and during their very low lifetime, hydroxyl
74 radicals cannot combine with the species contained in the surface but only with those
75 contained in wastewater, promoting complete oxidation of the organics to CO₂ (Panizza
76 and Cerisola, 2009) . Among them, it is not only important to consider the pollutants but
77 also ions such as sulfate, phosphate or carbonate that can be transformed into longer-
78 lifetime oxidants, which expands the oxidation region from the very nearness of the
79 electrode surface to the bulk (Cañizares et al., 2009). In addition, hydroxyl radical can be
80 recombined to form hydrogen peroxide and oxygen and it can also oxidize oxygen and
81 form ozone, resulting in the production of a very efficient oxidation cocktail, as it is
82 pointed out by many researchers (Canizares et al., 2007; Tang et al., 2019).

83 In the literature, there are works focused on the comparison of the performance of active
84 and non-active electrodes from the late nineties of the last century, which have been
85 extensively discussed in recent reviews (Sirés et al., 2014; Martínez-Huitle et al., 2015;
86 Martínez-Huitle and Panizza, 2018). However, most of them are related to synthetic
87 wastewater with only one electrolyte (mainly sulfate or chloride) and they have a
88 mechanistic interest. To the knowledge of the authors, no previous comparison has been
89 made with the fluid obtained after washing soil directly with a suitable soil washing fluid.

90 In this work, the performance of the anodic oxidation of soil washing effluents polluted
91 with perchloroethylene, clopyralid and lindane with platinum and boron doped diamond
92 electrodes is compared. The treatment of these wastes by anodic oxidation was
93 exhaustively studied with boron doped diamond, finding that it was an efficient treatment
94 in which the interactions of the pollutant with the waste matrix are a point of the major
95 significance (Cotillas et al., 2017; Muñoz-Morales et al., 2017; Muñoz-Morales et al.,
96 2019) . Opposite we did not evaluate platinum before, as the treatment expectations were
97 much poorer according to previous works of other authors. So, the aim of this work is not
98 to describe these treatments but to shed light on the mechanisms involved in the processes
99 and clarify which of the two types of electrolysis exhibits better performance for this
100 innovative advanced oxidation process.

101

102 **2. Materials and methods**

103

104 **2.1 Chemical Products**

105 Perchloroethylene (PCE, C_2Cl_4 , >99%), was chosen as a volatile and non-polar pollutant,
106 lindane ($C_6H_6Cl_6$, 97%) as a model of non-volatile and non-polar species and clopyralid
107 (99 %) as a model of non-volatile and polar compound. These three chlorinated
108 hydrocarbons were obtained from Sigma Aldrich and they were used as received. Sodium
109 Dodecyl Sulfate (SDS, 99% by Sigma Aldrich) has been used as solubilizing agent.
110 Hexane (C_6H_{14} , 97%) was used to solubilize PCE and Lindane during the pollution
111 process. The hydrophobic lubricant oil Serie FORTE was obtained from Josval
112 (Zaragoza, Spain) and it was used to mix with perchloroethylene and pollute the soil.
113 Hexane and ethyl acetate (HPLC grade) were obtained from VWR INTERNATIONAL
114 EUROLAB S.L (Barcelona- Spain) and they were used as extraction solvent of

115 perchloroethylene and lindane respectively for using Gas Chromatography with an
116 electron capture detector (GC-ECD). Methanol and formic acid were obtained from VWR
117 INTERNATIONAL EUROLAB S.L. Double deionized water (Millipore Milli-Q System,
118 resistivity: 18.2 M Ω cm at 25 °C) was also used.

119

120 **2.2 Analytical Techniques**

121 To determine the concentration of non-polar pesticides (perchloroethylene and lindane)
122 and their intermediates in liquid phase an extraction process was used before the analysis.
123 This process was carried out in separator flasks of 10 cm³ using hexane and ethyl acetate
124 respectively. The ratio chlorinated organic vs solvent was 3:1 for PCE and 1:1 for lindane.
125 After that, all samples extracted from electrolyzed solution were filtered with 0.25 μ m
126 nylon filters before analysis by GC ECD (Thermo Fisher Scientific) using analytical
127 column using a TG-5MS capillary column (30 m \times 0.25 mm 0.25 mm), 63 Ni micro-
128 electron capture detector, a split/splitless injector and ChromCard Software. Under these
129 conditions the limit of detection was 0.25 mg dm⁻³ for PCE and 0.1 mg dm⁻³ for lindane.
130 The flow rate of gas He was 1.0 cm³ min⁻¹. The temperature of the oven was programmed
131 as follows: 50 °C for 1 minute, ramp at 10 °C min⁻¹ to reach 260 °C followed by 2 minutes
132 hold. The temperature of the injector was 260 °C. The concentration of the clopyralid and
133 intermediates were quantified by HPLC (Agilent 1200 series) using a ZORBAX Eclipse
134 Plus5 C18 analytical column with a limit of detection of 0.5 mg dm⁻³. The mobile phase
135 consisted of 30% methanol / 70% water with 0.1% of formic acid (flow rate: 0.8 mL min⁻¹).
136 The detection wavelength of Diode Array Detector (DAD) was 280 nm, the
137 temperature was maintained 25 °C and the injection volume was 20 μ L. The concentration
138 of carboxylic acids was quantified by HPLC (Agilent 1100 series) filtering with 0.22 μ m
139 Nylon Supelco filters before analysis using a Hi-Flex H, 300x7.7mm analytical column.

140 The mobile phase consisted of H₂SO₄ solution (5mM) (flow rate: 0.5 mL min⁻¹). The
141 detection wavelength of DAD was 210 nm, the temperature was maintained 35 °C and
142 the injection volume was 100 µL. The total organic carbon (TOC) concentration was
143 monitored using a Multi N/C 3100 Analytic Jena analyzer. Measurements of pH and
144 conductivity were measured using a CRISON pH25+ and CRISON CM35+. The
145 colorimetric method used to determine the concentration of the SDS surfactant has been
146 described elsewhere (Jurado et al., 2006). Finally, the anions present in the wastewater
147 were characterized using an Ion Chromatograph with a Shimadzu LC-20A system.

148

149 **2.3. Voltammetry experiments**

150 Voltammetric measurements were carried out in an Autolab potentiostat/galvanostat
151 controlled with the Nova 2.0. Software. All the electrochemical experiments were
152 conducted at room temperature in a three-electrode single-compartment glass cell, using
153 a 3 cm² working electrode of p-Si/BDD (doped with 500 ppm B; 250 of sp³/sp² ratio)
154 obtained from Adamant Technologies (Switzerland) or platinum (99,9% purity). An
155 Ag/AgCl (3.0 M KCl) were used as reference electrode. Voltammetry experiments were
156 performed in unstirred solutions (150 cm³). BDD and platinum were anodically polarized
157 during 5 min with a 1 M H₂SO₄ solution at 0.1 A prior to each experiment.

158

159 **2.4. Preparation of polluted soil and soil-washing fluid**

160 The soil used in this study was obtained from a quarry located in Toledo (Spain). This
161 soil is characterized by its inertness, low hydraulic conductivity (10⁻⁸ cm s⁻¹) and lack of
162 organic content. Procedure for soil contamination and soil washing is extensively describe
163 in previous works of our group (Cotillas et al., 2017; Muñoz-Morales et al., 2017)

164

165 **2.5. Experimental set-up**

166 Surfactant-Aided Soil Washing (SASW) effluents were treated by anodic using a bench-
167 scale stirred electrochemical setup. P-Si Boron doped diamond (500 ppm of boron
168 concentration and 250 of sp³/sp² ratio) or platinum electrodes (99.9% purity Metrohm)
169 were used as anodes and graphite as cathode. The surface of the electrodes were 3 cm².
170 The electrical current was applied using a Delta Electronika ES030 (0–30 V, 0–10 A) and
171 the electrolysis were carried out galvanostatically at 300 A m⁻². Prior to use in
172 galvanostatic electrolysis assays, the electrode was polarized for 10 min in a 0.035 M
173 Na₂SO₄ solution at 150 A m⁻² to remove any impurities from its surface. Temperature
174 was kept constant (25 °C) using a thermo-regulated water bath.

175

176 **3. Results and Discussion**

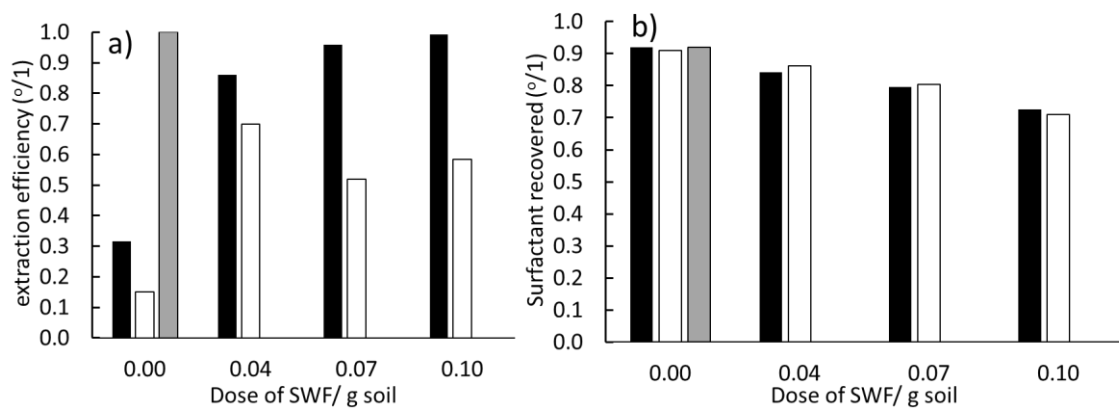
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178 The first stage in the treatment of the soils studied in this work consists of the extraction
179 of pollutants using a soil washing fluid (SWF). This operation has been extensively
180 described in previous papers of our group. Thus, as already explained in those previous
181 works (Saez et al., 2010; dos Santos et al., 2016; Muñoz-Morales et al., 2017; Vieira dos
182 Santos et al., 2017), this is a critical stage in the overall remediation process and reaching
183 high efficiencies depends on:

- 184 1) the application of intense mixing conditions during the soil washing process and,
185 2) the use of a suitable concentration of surfactant reagent which helps to drag the
186 pollutant from soil, in the case of pollutants with low solubility in water.

187 **Fig. 1** shows the extraction efficiency of three chlorinated hydrocarbons tested and
188 confirms this information by showing that clopyralid can be completely exhausted from
189 soil without the need of surfactant by using ratios SWF soil⁻¹ of only 2.5 L kg⁻¹, while the

190 concentration of surfactant (SDS) added influences on different ways with the other two
191 pollutants studied, which have a much lower solubility in water.



192

193 **Fig.** 1. (a) Extraction efficiency of chlorinated hydrocarbons in the liquid wastes and (b)
194 volume of soil washing fluid recovered after the soil washing process using different
195 ratios surfactant soil with similar mixing conditions. Perchloroethylene (black bars);
196 lindane (white bars) and clopyralid (grey bars).

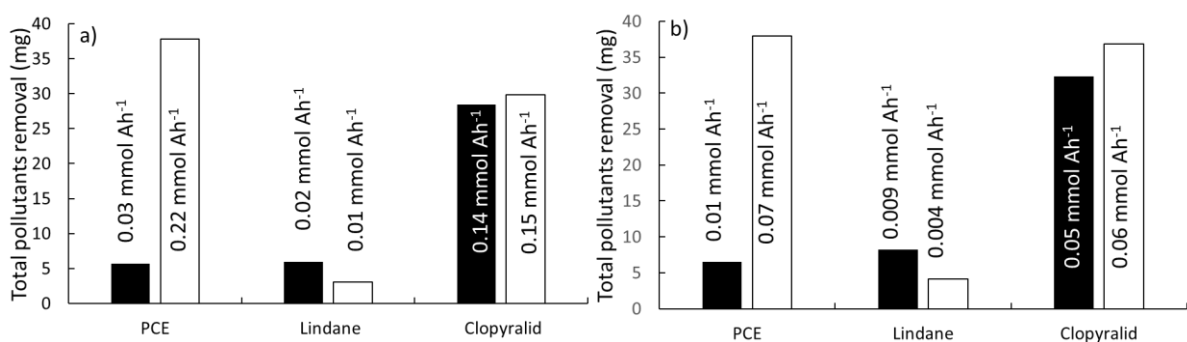
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198 In the case of PCE, the higher the dose applied, the higher is the extraction efficiency
199 attained, reaching the almost complete exhaustion with a dose of 0.1 g SDS g⁻¹ soil.
200 Opposite, in the case of lindane, a more complex relationship is observed, although the
201 efficiency is lower, mainly because of the higher solubility of PCE in water. The
202 surfactant promotes the extraction of lindane, but it remains mainly in the interphase with
203 the micelles formed by soil and surfactant. Thus, the clarified phase does not show a direct
204 relationship with the dose of SDS and, in fact, higher dose seems lower lindane contained
205 in the upper phase, because it is concentrated in the interphase, which was kept with the
206 soil. This behavior is caused by the complex interaction of the surfactant with the
207 pollutant and soil. However, considering the further electrolysis process, upper phase is
208 the most useful to study the differences of depletion of lindane with BDD and Pt anodes
209 and it was the phase used for later stages of this work. At this point, it is worth to consider

210 the SWF retained in the soil after the treatment depends on the amount of surfactant dosed
 211 and, in this case, there is a direct relationship between the water that can be retained, and
 212 the amount of surfactant added. For an efficient treatment, the lower the amount of SWF
 213 retained the better is the performance of the overall process.

214 After the extraction, the soil washing fluid becomes a highly polluted waste (soil washing
 215 wastes, SWW) with a high concentration of ions extracted from soil and a conductivity
 216 that is always over 1 mS cm^{-1} , high enough to undergo electrolysis at a suitable cell
 217 voltage without the necessity of adding salts. By applying electrolysis with diamond and
 218 platinum electrodes, the expected first-order decays already discussed in the literature
 219 were obtained. However, here we are focusing on the comparison of the performance
 220 among different pollutants and electrodes. Thus, Fig. 2a, compares the removal of
 221 pollutants (mg) and the electrical efficiencies (mmol Ah^{-1}) reached for an arbitrarily
 222 selected applied electric charge passed of 1.05 Ah and Fig. 2b for a larger applied charge
 223 of 3.30 Ah. It was chosen these 2 values to compare the efficiencies of the process with
 224 the applied electric charge.

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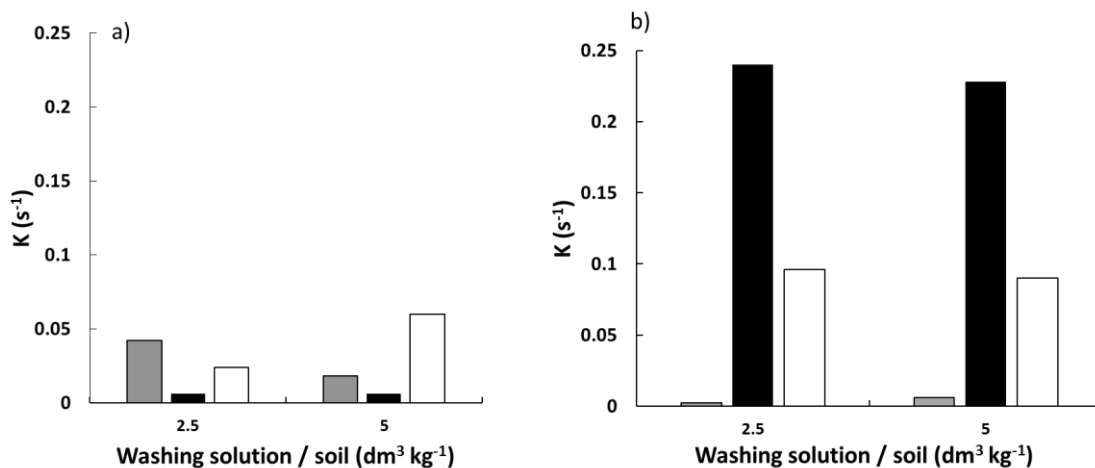
227 **Fig. 2.** Total removal of pollutants from the SWW after applying an arbitrarily electric
 228 charge of (a) 1.05 Ah and (b) 3.30 Ah. Platinum anodes (black bars), BDD anodes (white
 229 bars). $J = 300 \text{ A m}^{-2}$; $V = 150 \text{ cm}^3$.

230

231 As seen, in all cases the efficiency in the removal of the pollutant decreases during
232 operation. That is, it is more efficient the degradation in the first moments of the
233 electrolysis, and this behavior can be explained in terms of the well-known first order
234 kinetic undergone by the pollutants during electrolysis (Aquino et al., 2014; Sopaj et al.,
235 2015), which reflects on a linear dependence on the concentration. In addition, there are
236 important differences between the removals of the different pollutants. Clopyralid is
237 slightly more oxidizable by BDD than by Pt, although both electrolysis lead to similar
238 values. On the contrary, large discrepancies occur when emulsified wastes are treated.
239 PCE is very efficiency degraded with diamond electrodes and this is not the case for
240 platinum. Contradictory, lindane exhibits exactly the opposite behavior, although in this
241 case the degradation of SDS can help to explain this unexpected behavior. Thus, oxidation
242 of SDS (data not shown) is more important with BDD ($13.15 \text{ mmol Ah}^{-1}$) than with
243 platinum ($1.16 \text{ mmol Ah}^{-1}$) and this difference helps to explain the lower removal
244 obtained in the case of the electrolysis of lindane. SDS is a very complex linear molecule
245 whose concentration in the SWF is 3-logs over the concentration of lindane. It is known
246 to be easily oxidized by BDD anodes, leading to the formation of sulfates and persulfates
247 which mainly increase the conductivity of the SWF. In the case of the oxidation of PCE,
248 its influence is much lower, and this can be explained considering that SDS is also
249 combined with the oil extracted during the soil washing and this helps to explain a more
250 important decrease in the removal of PCE, which behaves as a very easily oxidizable
251 molecule.

252 Results obtained in the treatment of soil washing wastes obtained with a SWF soil⁻¹ ratio
253 of 2.5 L kg^{-1} are reproduced when higher amounts of soil washing fluid are added during
254 the extraction and this can be seen in Fig. 3, in which the kinetic constants obtained after
255 the fitting of experimental results to first order kinetics are obtained. Fig. SM-1 shows the

256 decay trend from which kinetic constants have been estimated. Except for the case of
 257 lindane (which is explained because of the concurrent oxidation of SDS), electrolysis with
 258 platinum is always much less efficient than with BDD anodes and kinetic constants
 259 reflects the differences in the oxidation capacity of the different pollutants. Again, results
 260 obtained with PCE washing fluids demonstrate to be the most easily oxidizable wastes by
 261 diamond and it exhibits a very poor efficiency for Pt. The fitting of electrolytic results to
 262 first order kinetic indicates that it is important to obtain wastes as much concentrated as
 263 possible. For this reason, concentration techniques such as those recently proposed in
 264 works of our group for these pollutants can be of extreme significance for the
 265 development of successful treatments (Muñoz et al., 2017; Raschitor et al., 2017; Llanos
 266 et al., 2018).



267 **Fig. 3.** Kinetic constants obtained by fitting the experimental decay of organochloride
 268 compounds to first order kinetics during 8 hours of treatment of SWW using (a) platinum
 269 and (b) BDD anodes. Perchloroethylene (white bars); lindane (grey bars) and clopyralid
 270 (black bars).
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 273 A very important point when comparing the anodic oxidation of pollutants with different
 274 electrodes is the production of oxidants. In this work, they are measured in a globalized

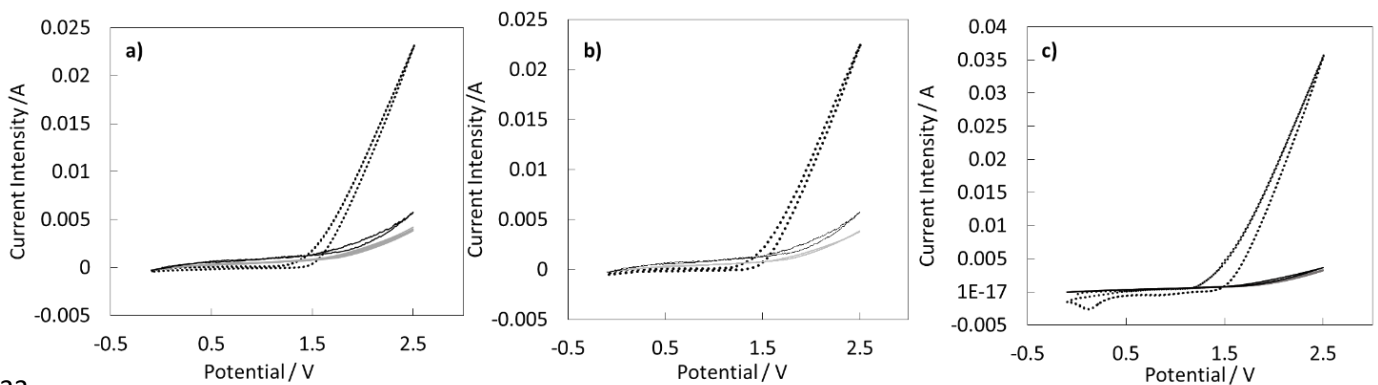
275 way by considering the concentration of oxidants capable to oxidize I^- to I_2 . This means
276 that we are considering all stable oxidants in this measurement but not others, like the
277 hydroxyl radical, whose action is almost instantaneous. As seen in Fig. SM-2, there are
278 not very important differences in the concentration of stable oxidants formed in the
279 electrolyte during the electrolysis and, in fact, they seem to be higher in the case of using
280 platinum than when using BDD, which initially is an unexpected outcome because the
281 formation of persulfates is only efficient with the BDD anode and because the oxidation
282 with diamond was found to be more efficient (even in the case of lindane in which higher
283 concentration of SDS is oxidized). However, this result can be easily explained in terms
284 of the chemistry of chlorine in the system. Platinum anodes can transform the chloride
285 contained in the SWF (and that obtained by the dehalogenation of the chlorinated
286 hydrocarbons) into chlorine and hypochlorite, while in the electrolysis with the diamond
287 anode the oxidation does not stop at this point and hypochlorite is transformed into
288 chlorates and perchlorates. Because of the very low kinetic rate of the oxidation carried
289 out by these two oxoanions, they should result in a negative impact in terms of the
290 oxidation of I^- to I_2 as it can be observed in the Fig. SM-2. Thus, after passing 1.05 Ah,
291 the concentrations of perchlorate obtained in the diamond electrolysis were 96.6, 28.5 and
292 $9.0 \text{ mg dm}^{-3} \text{ Cl-ClO}_4^-$, respectively for clopyralid, lindane and perchloroethylene. These
293 values are important, taking into account that the initial concentration of chloride was
294 close to 160 mg L^{-1} and the variability among the different tests demonstrates the
295 complexity of the processes happening in the cell with many competing reactions. With
296 platinum anode, perchlorate was only detected in the electrolysis of the SWF obtained
297 with clopyralid and the concentration was less than four times lower than in the case of
298 using diamond. However, this difference does not reflect on a major point with respect to
299 the oxidative capacity of both electrodes as observed in the figures.

300

301 The other important parameter compared in Fig. SM-3 is the pH. Initial pH was 6.5 in the
302 SWF with lindane and PCE and 7.1 in the case of the SWF with clopyralid. In comparing
303 the values reached after passing an arbitrary current charge, it can be noticed a very
304 important difference: in the case of diamond anodes it decreases very significantly, while
305 in the case of the platinum electrolysis it does not undergo such a severe change, in fact,
306 it increases during the electrolysis.

307 Initially this may inform about different mechanisms in the oxidation of the pollutants.
308 The change in the pH is observed from the first moments, indicating that it should not be
309 related to the oxidation of organics to carboxylic acid but to other simpler processes. In
310 order to know more about this change, a voltammetric study was carried out where the
311 response of both electrodes were compared for the three polluted SWF (obtained by
312 washing soil with and without the pollutant). Results shown in Fig. 4, are surprising. The
313 higher intensities obtained for the platinum electrolysis indicate that there is a higher
314 direct oxidation rate on the surface of these electrodes as compared with changes observed
315 on the diamond electrode. Initially, it can be thought of the simple effect of the lower
316 resistance of the platinum electrode as compared to the BDD. However, it is not only the
317 lower electric conductivity of the platinum but also the oxidation process occurring on
318 the surface as the shape of the voltammograms is not linear but exponential. In addition,
319 in comparing the responses for the platinum, it can be observed that there are no
320 differences between the electrolysis of the SWF with PCE or lindane. This may suggest
321 that, in this case, the oxidation of SDS on the surface of the electrode is more important
322 than the oxidation of the pollutant (which in fact is negligible in terms of direct oxidation
323 according to the voltammetry because both curves are fully overlapped). Initially, this can
324 be predictable because the pollutant is expected to be present as micelles. On the other

325 hand, this response can also be due to the oxidation of chloride and/or any other inorganic
 326 compound. In the case of clopyralid (Fig. 4c), in which there is no SDS in the SWF, the
 327 presence of the organic pollutant leads to a very significant increase in the intensities
 328 recorded confirming that there is a direct oxidation pathway for these species. In addition,
 329 the base curve (obtain with SWF without clopyralid) also match with the base curve of
 330 the lindane and PCE experiments, indicating (because with clopyralid there is no SDS)
 331 that it should due to the oxidation of chloride or any other organic compound but not of
 332 the surfactant.



333
 334 **Fig. 4.** Voltammeteries of the SWF with lindane (a), perchloroethylene (b) and clopyralid
 335 (c) using boron doped diamond (black line) or platinum (discontinuous line) as working
 336 electrodes. Grey line: soil washing waste without pollutant.

337 The lower voltammetric response of the electrolysis with BDD indicates a lower direct
 338 electrochemical reactivity, which is not seen in the bulk results and should be more related
 339 to the production of hydroxyl radicals. In fact, the intensities recorded at very high
 340 overpotentials are considerably much slower. This may indicate a higher extension in the
 341 oxidation of water, which is also consistent with the higher decrease in the pH value (Eq.
 342 1) explaining the changes observed in the pH when using both electrodes.

343



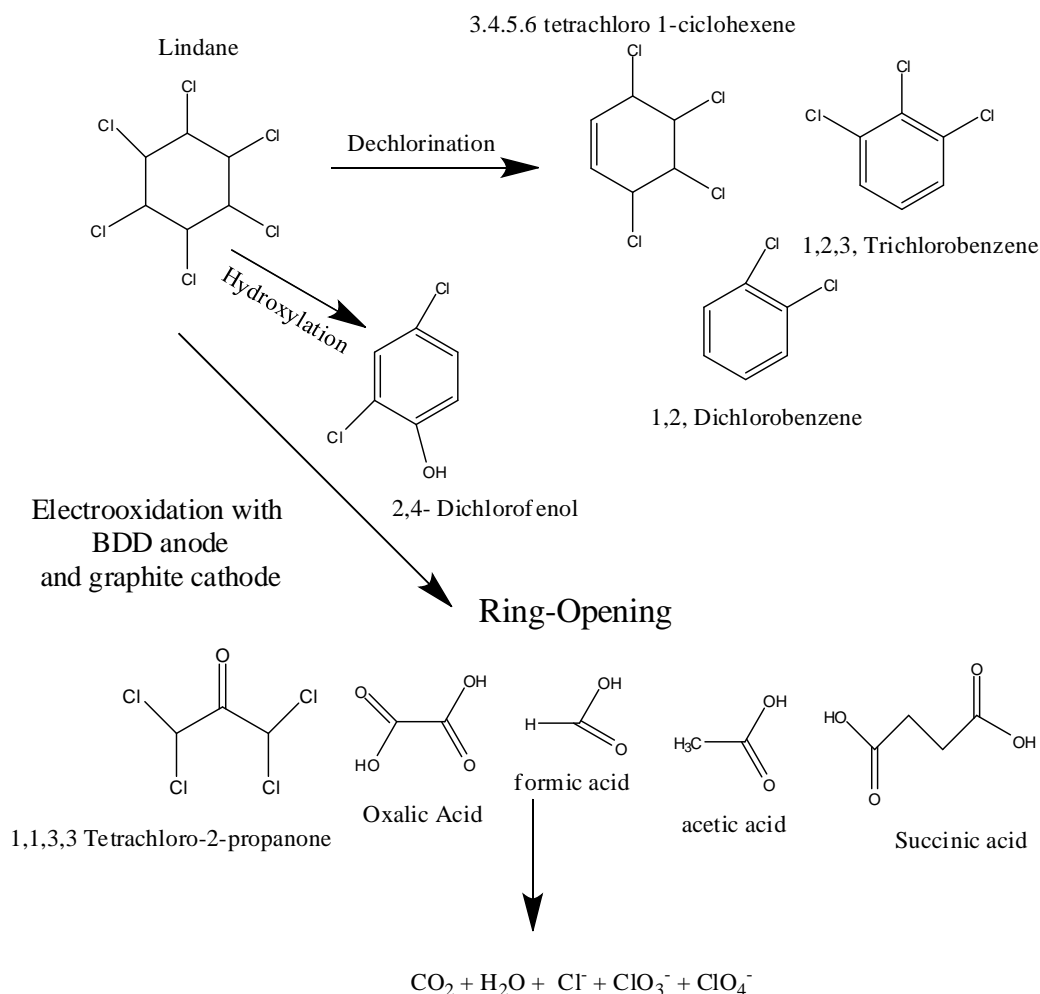


346

347 In addition, there is an important difference between the presence of lindane and PCE in
348 the SWF, with an important increase in the intensities obtained, which clearly indicates
349 that these species are also undergoing a direct oxidation on the surface of the electrode.
350 This is not as clear as in the case of the clopyralid in which the difference is extremely
351 low and which indicates that these species should be primarily removed by mediated
352 oxidation processes.

353 However, these differences are not observed in terms of speciation. In the case of lindane,
354 by GC-MS, it was confirmed almost the same intermediates in the electrolysis (Table
355 SM-1), which fits well to the oxidation mechanisms proposed in the literature (Nitoi et
356 al., 2013; Dominguez et al., 2018) and shown in Fig. 5. Additionally, it can be observed
357 similar speciation obtained with both electrodes. However, during the electrolysis with
358 BDD anodes the maximum concentration of intermediates is higher than during the
359 electrolysis with platinum.

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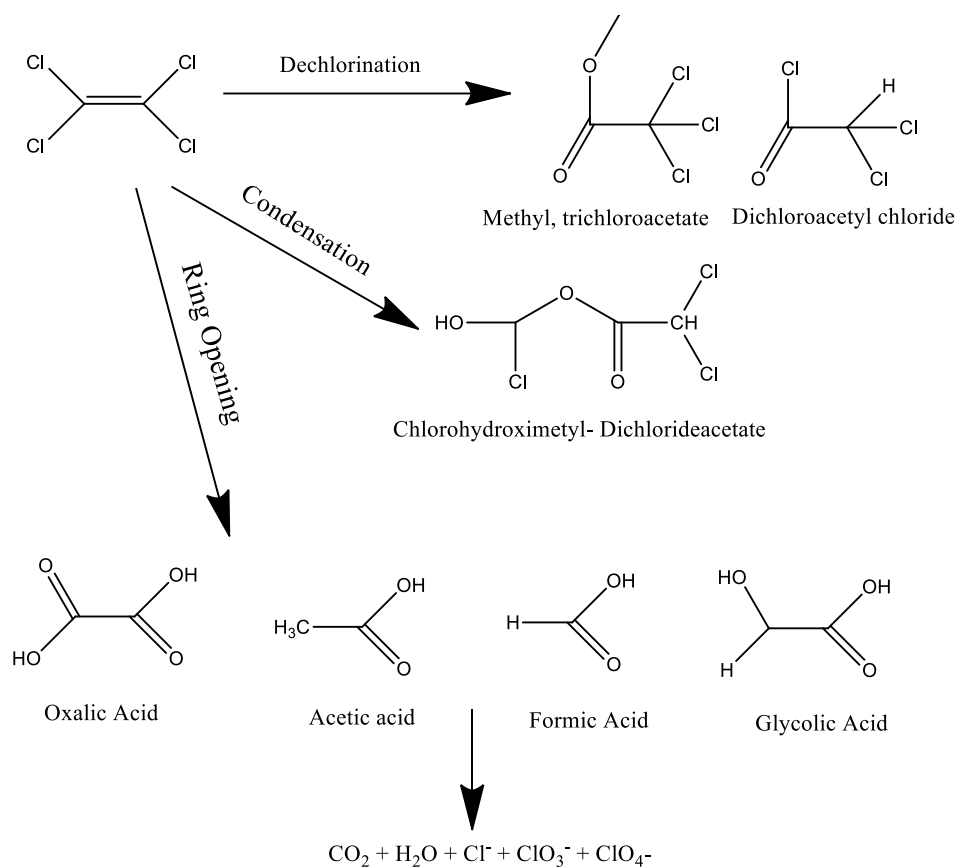


361

362

363 Fig. 5. Mechanisms of the electrochemical oxidation of lindane contained in the SWW
 364 using platinum and BDD anodes.

365 In the case of perchloroethylene, again nearly the same intermediates are found in the
 366 electrolysis with diamond and platinum. They are summarized in Table SM-2 and they
 367 follow the oxidation mechanisms suggested in bibliography (Miao et al., 2015; Karimaei
 368 et al., 2017), which is shown in Fig. 6. In this case, there are acids that are detected using
 369 BDD and other using platinum, however dechlorinated compounds are mainly detected
 370 in platinum anodes. These results are in concomitance with the experiments that showed
 371 higher efficiency in the removal of PCE with BDD anodes because the higher
 372 mineralization degree and less intermediates obtained.



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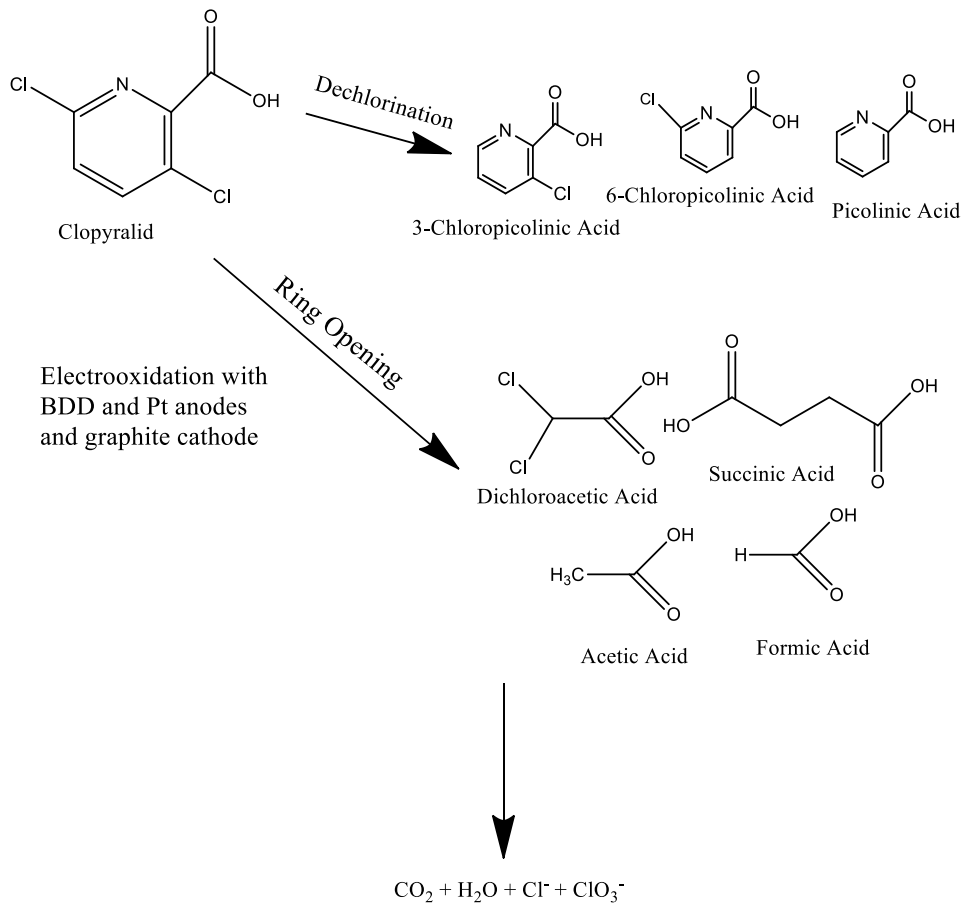
374 **Fig. 6.** Mechanisms for the electrochemical oxidation of perchloroethylene contained in
 375 the SWW using platinum and BDD anodes.

376 In the case of the clopyralid no GC-MS but HPLC was used to characterize intermediates
 377 because of the high solubility in water of this pollutant that makes difficult the extraction
 378 of clopyralid with organics solvents to analyze by gas chromatography(Ahmad et al.,
 379 2003). Results of Table SM-3 again pointed out that the oxidation route fits well with
 380 those proposed in the literature(Carvalho de Almeida et al., 2019) (**Fig. 7**). Again,
 381 intermediates detected during the electrolysis of SWF of clopyralid are nearly the same
 382 with platinum and BDD anodes that it fits well with results of depletion efficiency and
 383 kinetic studies with just slightly better results using diamond than platinum electrodes.

384

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386



388

389 **Fig. 7.** Mechanisms of the electrolysis of clopyralid (Carvalho de Almeida et al., 2019)

390 contained in the SWW using platinum and BDD anodes.

391 Hence, despite the very important differences observed in the rates of removal of the three

392 chlorinated organics and in the voltammetries, the oxidation mechanisms should be nearly

393 the same, at least in terms of the intermediates formed although the concentration of

394 intermediates differs significantly indicating the different oxidizability in both cases.

395 All these results confirm that electrolysis can be a good technology to remove chlorinated

396 hydrocarbons and that although platinum has a greater electrochemical reactivity, the

397 choice of diamond as anode material has important advantages because of the much

398 higher efficiency.

399

400

401 **Conclusions**

402 From this work, the following conclusions can be drawn:

- 403 • Polar organochlorinated compounds are easily extracted in the SWF with low
404 ratio SWF soil⁻¹ and without surfactant, however doses of surfactants as 0.1 g SDS
405 g⁻¹ soil are needed to obtain over 60% of extraction efficiency of non-polar
406 compounds.
- 407 • First order kinetics are observed in each compound with higher removal at the
408 early stages and generally better results are obtained using BDD as anode than
409 platinum.
- 410 • Higher oxidants are produced with platinum because BDD anodes promotes very
411 oxidized species with less oxidant capacity, however it does not reflect on a major
412 point with respect to the overall oxidative capacity.
- 413 • The evolution of pH and a voltammetry study indicate that higher oxidation rate
414 in the surface is observed with platinum anodes and a direct oxidation pathway is
415 promoted for other additional compounds (as surfactant or chlorine ions).
- 416 • Similar intermediates species are obtained during the electrooxidation using BDD
417 and platinum electrodes from the main mechanisms as dechlorination and ring-
418 opening which are detected with GC-MS and HPLC.

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