

25 reaction products and ethyl chloroacetate esters were also identified. A comprehensive
26 mechanism of the processes happening inside electro-scrubber is proposed.

27

28 **Keywords**

29 VOCs removal; perchloroethylene; electro-absorption; oxidation electron mediator

30

31 **Highlights**

32 • Ta/BDD anode promoted higher conversion of Co(III) reaching 90% after 2
33 hours

34 • Electrolysis using Si/BDD anode attained 75.7% while Ta/BDD anode reached
35 90.5% of PCE removal

36 • Mediated electrooxidation with Co improved the PCE degradation rate

37 • Electrolysis with Si/BDD anode favors the generation of TCA as by-product

38

39

40

41

42

43

44

45

46 *Author to whom all correspondence should be addressed: manuel.rodrigo@uclm.es

47

48 **1. Introduction**

49 The harmful impacts of air pollution into the environment and human health have
50 increased the concern not only of the environmental agencies but also of the general
51 population (Landrigan et al., 2018; Caplin et al., 2019). There are many types of
52 gaseous pollutants, being a very important group the volatile organic compounds
53 (VOCs), whose main sources are combustion and evaporation processes associated to
54 the processing of fuels and solvents (Dhamodharan et al., 2019; Zhang et al., 2019).
55 Because of their hazardousness, several technologies have been proposed for the
56 degradation of VOCs. Among many others, it is worth to mention catalytic oxidation
57 (Zhang et al., 2016), biological process (Mudliar et al., 2010), adsorption (Zhang et al.,
58 2017) and plasma catalysis (Karatum and Deshusses, 2016). However, most of them
59 have important disadvantages such as low efficiency, excessive energy consumption,
60 secondary gaseous pollution, catalytic deactivation, etc. (Mudliar et al., 2010; Karatum
61 and Deshusses, 2016; Zhang et al., 2016; Zhang et al., 2017; Vikrant et al., 2019). In the
62 last years, coupled technologies have also been tested for the treatment of air pollution,
63 with the aim to highlight the possible synergies and create technologies more cost-
64 efficient.

65 In this line, electro-scrubbing technology has appeared as a promising methodology to
66 treat gaseous streams (Muthuraman and Moon, 2012; Chung and Moon, 2013;
67 Govindan and Moon, 2015). This process combines the absorption (which can be
68 carried out with different equipment such as columns or *jet scrubbers*) (Bal et al., 2019;
69 González-Pérez et al., 2020) with an electrochemical treatment that allows either
70 reduction (Govindan et al., 2017a; Muthuraman et al., 2018a, b; Adam Gopal et al.,
71 2019) or oxidation of the absorbed pollutants. In electrochemical cells used in electro-
72 scrubbing technology, different anodes have been tested such as aluminum (Govindan
73 et al., 2016), Pt/Ti (Chandrasekara Pillai et al., 2009; Govindan et al., 2012a), BDD

74 (Muthuraman et al., 2017; González-Pérez et al., 2020), and gas diffusion electrodes
75 (Yang et al., 2011).

76 The electrochemical systems have widely studied for the treatment of liquid current as
77 wastewater (Martínez-Huitle and Panizza, 2018) or for environmental applications using
78 renewable energy (Ganiyu and Martínez-Huitle, 2020) and these processes can be
79 developed by direct and indirect mechanisms. The first mechanism consists of the direct
80 exchange of electrons between the pollutants and the electrode surface. In the second,
81 the exchange of electrons occurs by mediation of electroactive species contained in the
82 electrolyte (in electro-scrubbers, the electrolyte also works as the absorbent which act as
83 mediators for the electrons shuttling between the electrode and the pollutants
84 (Scialdone, 2009).

85 Indirect processes can be promoted from oxygen or salts contained in the electrolyte
86 that lead to the formation of species such as hydrogen peroxide (Paz et al., 2019; Souza
87 et al., 2019), ozone (García-Morales et al., 2013), peroxosulphates (Balaji et al., 2015;
88 Waclawek et al., 2017; Wang and Wang, 2018), peroxophosphates (Muthuraman et al.,
89 2017) and active chlorine species (de Moura et al., 2015). Alternatively, indirect
90 processes can also be promoted with the addition of metal ions such as Ag, Ce, Co, Fe
91 and Mn to acid solutions, used as electrolytes (Govindan et al., 2012a; Govindan and
92 Moon, 2013; Muthuraman and Moon, 2017). In these cases, the process consists of the
93 anodic oxidation of the metal from its stable oxidation state (M^{Z+}) to a higher oxidation
94 state (M^{Z+1}), so that later this species reacts with the pollutants, regenerating its reduced
95 state (M^{Z+}).

96 These electro-scrubbing processes have been studied for the treatment of VOCs in the
97 recent years (Farmer, 1992; Matheswaran, 2008). Govindan et al., 2012b studied the

98 removal of CH₃CHO by combination of wet scrubber and electrolysis using Co(III) in 4
99 M H₂SO₄ medium and Pt/Ti as anodic electrode. Results showed that only 20% of
100 removal was attained without cobalt whereas 100% of removal was reached in the
101 presence of 0.01 M Co(III). Mediated electrolysis with Co(III) in a 5 M H₂SO₄ was
102 proposed for the removal of NO using a divided cell electro-scrubbing unit, with Pt/Ti
103 electrodes, reaching almost 28% of NO removal, while only 5% was attained in the
104 absence of cobalt. A combined mediated electro-oxidation and electroreduction also
105 was evaluated and revealed a great improvement in the NO removal and up to 97% of
106 removal efficiency (Govindan et al., 2016). A similar setup was used by the same group
107 using an electro-scrubber with Co(III) for the removal of H₂S with removal efficiency of
108 98% at 10°C (Govindan et al., 2012a).

109 Thus, among the indirect processes promoted with the addition of metal ions, good
110 results have been reported in cobalt (III)-mediated electrochemical oxidation treatments.
111 For example, this system has been applied for the destruction of contaminants in
112 solution such as volatile hydrocarbons and phenol (Farmer, 1992; Matheswaran, 2008).
113 On the other hand, using the technology of electro-scrubbing, (Govindan et al., 2012b).
114 studied the elimination of CH₃CHO through a combination of a wet scrubber and an
115 electrolysis system using Co(III) in H₂SO₄ 4M medium and Pt/Ti as anode.. Results
116 showed that in the absence of cobalt only 25% removal was achieved, while 100%
117 removal was achieved in the presence of 0.05 M Co (III). In another work they
118 proposed the electrolysis mediated with Co(III) in a 5 M H₂SO₄ electrolyte for the
119 removal of NO using a divided cell electro-scrubbing unit, with Pt/Ti anode, reaching
120 28% removal of NO in the presence of Co(III), while when the combination of
121 electrooxidation and mediated electroreduction was evaluated, a great improvement in
122 NO removal was revealed, reaching 97% removal efficiency (Govindan et al., 2016).

123 The same group used a similar configuration with a Co(III) electro-scrubber for H₂S
124 removal achieving a removal efficiency of 98% at 10°C (Govindan et al., 2012a). In
125 another investigation, the treatment of a mixture of gases (NH₃, (CH₃)₃N, CH₃SH, H₂S
126 and CH₃CHO was carried out using as absorbent electrolyte a 0.75 M Co(II) solution in
127 4 M H₂SO₄ Pt/Ti as anode, where, working at 10°C, removal efficiencies close to 100%
128 were obtained, except for CH₃SH, which exhibited an efficiency of 95% (Govindan and
129 Moon, 2013). In this line, chlorinated hydrocarbons have caused many environmental
130 and health problems (Bhatt et al., 2007; Huang et al., 2014) and lately, some studies
131 have carried out their removal in liquid phase (Semitsoglou-Tsiapou et al., 2016;
132 Dominguez et al., 2018) and soil polluted (Santos et al., 2019; Raimondo et al., 2020),
133 but also their transference to gaseous currents to avoid the widespread of persistent
134 pollution (Lopes et al., 2013; Muñoz-Morales et al., 2019; Munoz-Morales et al., 2020).
135 Additionally, some removal pathways have been proposed to shed light on the
136 recalcitrant properties (Ferreira et al., 2020).

137 With this background, the aim of the present work is to assess the efficiency of the
138 mediated electro-oxidation process using Co(II) acetate in acid solution as mediator in
139 the degradation of perchloroethylene. Perchloroethylene is a toxic compound, extremely
140 persistent in the environment and classified as a probable human carcinogen (Class B2)
141 (S.E. Manahan). This study is based on the differences found in a previous results
142 (Escalona-Durán et al., 2021), which two coatings of boron-doped diamond supported
143 on silicon substrate and tantalum substrate were used to promote the electrogeneration
144 of Co (III). to evaluate their efficiency on the direct and mediated degradation of the gas
145 pollutant. Results will highlight the importance of catalytic properties of the anode
146 substrate and feasibility of using electro-scrubbing technology for the removal of
147 gaseous PCE.

148 With this background, the objective of this work is to evaluate the efficiency of the
149 mediated electrooxidation process using Co(II) acetate in acid solution as mediator in
150 the degradation of perchloroethylene, which is a toxic compound, extremely persistent
151 in the environment and classified as a probable human carcinogen (Class B2) (S.E.
152 Manahan). This study is based on the differences found in previous results (Escalona-
153 Durán et al., 2021), in which boron doped diamond electrodes supported on silicon and
154 tantalum substrate were used to promote the electrogeneration of Co (III). Therefore, the
155 same electrodes were used to evaluate their effectiveness on direct and mediated
156 degradation of the contaminated gas stream. The results highlight the importance of the
157 catalytic properties of the anode substrate and the feasibility of using electro-scrubbing
158 technology for the removal of gaseous PCE.

159 **2. Materials and methods**

160 **Chemicals.** Cobalt (II) acetate 4-hydrate (99%) was purchased from Panreac
161 (Barcelona, Spain) and used as received. Perchloroethylene ($C_2Cl_4 > 99\%$) was
162 purchased from a.r. Sigma-Aldrich (Darmstadt, Germany). Sulfuric acid (98%) and
163 Hexane (HPLC Grade) were supplied by Scharlau (Barcelona, Spain). Helium and
164 nitrogen (Al Air Liquide España, S.A) were used in gas chromatography and helium
165 was filtered by a Hydrocarbon Cartridge Filter (Thermo Fisher Scientific) before its use.
166 Double deionized water (Millipore Milli-Q system, resistivity: 18.2 M Ω cm at 25°C)
167 was used to prepare all solutions. Perchloroethylene was then added in a closed
168 volumetric flask and the solution was softly stirred with a magnetic bar overnight to
169 achieve complete dissolution.

170 **Experimental system.** Four main components integrate the experimental system: a
171 glass column absorber, two storage tanks and an electrochemical cell as shown in
172 Figure SM1. More details can be found elsewhere (Castañeda-Juárez et al., 2020;

173 González-Pérez et al., 2020; Munoz-Morales et al., 2020) This setup is divided in two
174 interconnected circuits: a liquid circuit which mainly contains the electrolyte/absorbent
175 and a gaseous circuit. Firstly, 1.2 L of an aqueous solution of 150 mg L⁻¹ of PCE was
176 stored in the liquid waste desorption (LWD) tank and from here, the volatilization of
177 PCE was promoted by bubbling a carrier air stream generated with a 3.8 W air
178 compressor (Silent Pump (8) model SI6000, ICA SA, Toledo-Spain) with a flowrate of
179 360 L h⁻¹. This gas stream passes throughout of the LWD tank (1), favoring the
180 stripping of PCE and then it flows throughout of the absorption packed column (2),
181 where it is transferred to a liquid circuit. Gas and liquid phases flow countercurrent in
182 the column. Thus, the LWD tank promotes a realistic gaseous flow of PCE that
183 simulates the gaseous currents produced in real case studies.

184 Regarding to the absorbent-electrolyte storage (AES) tank (3), acidic solutions (1.0 M
185 H₂SO₄), with or without the addition of 0.01 M of Co(II) ions (1.5 L), were recirculated
186 using a centrifugal pump (4) to the electrochemical cell (5), which is connected to a
187 power supply (6). DiaCell[®] cells supplied by Adamant Technologies (La Chaux-de-
188 Fonds, Switzerland) consisting of boron-doped diamond (BDD) as anode and stainless
189 steel as cathode with an inter-electrode gap of 5 mm, were used during the electro-
190 absorption tests (EAB). Two types of BDD electrodes were evaluated. In the first case
191 the BDD coatings were supported on silicon and in the second on tantalum substrate.
192 All electrodes were circular (100 mm diameter) with an active surface of 78.6 cm². The
193 BDD coating have a thickness of 5.9 and 7.3 μm, respectively, for the Si and Ta
194 supports, and these diamond coatings were doped with 2500 ppm of boron
195 concentration. These electrodes were subjected to cleaning procedure during 10 min in a
196 1.0 M Na₂SO₄ solution at 15 mA cm⁻² prior to electrolysis assays. The absorbent-
197 electrolyte storage (AES) tank (3) is the auxiliary tank of the electrochemical cell. It

198 was made of glass with a thermoregulated water jacket and a capacity of 2.5 L with
199 sample point placed in the upper part. The AES tank provide residence time to the
200 electrochemical cell to promote chemical reactions mediated by oxidants or reductants
201 generated by the application of the electric current. Both tanks LWD and AES are also
202 connected to equilibrate the total pressure of the system. The centrifugal pump is a
203 Micropump[®] GB-P25 J F5 S (flow rate 160 L h⁻¹) supplied by Techma GPM s.l.r.
204 (Milan, Italy) connected to the electrochemical cell by a Tecalan[®] tube. Extreme care
205 was taken to avoid gaseous losses in all compartments by using tight-fitting ground
206 silicone stoppers and by sealing with Teflon tape. Experiments were performed for 120
207 min. Samples from liquid and gas phases were collected in duplicated at specified time
208 intervals.

209

210 **Analysis procedures.** Concentration of Co (III) during the reaction was monitored by
211 UV-Vis spectroscopy, using a Cary Series 300 UV-Vis spectrophotometer equipped
212 with a quartz cell with a 1 cm path length. For the Co (II) aqueous complex, the visible
213 absorbance at 510 nm was measured. Values obtained from absorption measurements at
214 610 nm were used to evaluate the conversion to a Co (III) complex. Samples of liquid
215 and gaseous phases were taken from sampling ports in the LWD and AES tanks. The
216 procedure to determine and quantify PCE concentration in gas and liquid phase was
217 described elsewhere (Castañeda-Juárez et al., 2020; González-Pérez et al., 2020),
218 obtaining a quantification limit of 0.1 mg L⁻¹. Oxidants species produced by the
219 electrodes and cobalt ions mediators were determined iodometrically according to
220 (Kolthoff and Carr, 1953) and standard methods (APHA-AWWA-WPCF, 1998). The
221 quantification of by-products generated in the absorption and electro-absorption
222 treatments was carried out using different chromatographic methods. To analyze carbon

223 tetrachloride a Jasco HPLC LC-2000 with a PDA MD-2018 Detector (Jasco, Tokio,
224 Japan) was used. The mobile phase consisted of an aqueous solution of 0.1% H₃PO₄ at a
225 flow rate of 1.0 mL min⁻¹. The detection wavelength used was 280 nm and the
226 temperature of the oven was maintained at 25°C. Volume injection was set to 20 µL.
227 Trichloroacetic acid and other by products (methyl chloroacetate, ethyl dichloroacetate,
228 ethyl trichloroacetate) were analyzed in liquid phase employing a HPLC Agilent 1100
229 series (Agilent Tech. Santa Clara, CA, USA) with a DAD detector set at 220 nm. An
230 ion exchange column-SupercogelTM H with 30 cm × 7.8 mm ID was used in the
231 temperature of 30°C. The mobile phase was 1% H₃PO₄ at a flow rate of 0.8 mL/min.
232 The injection volume was 20 µL. The limit of quantification obtained was less than 1
233 mg L⁻¹ in all intermediates detected.

234

235 **Results and discussion**

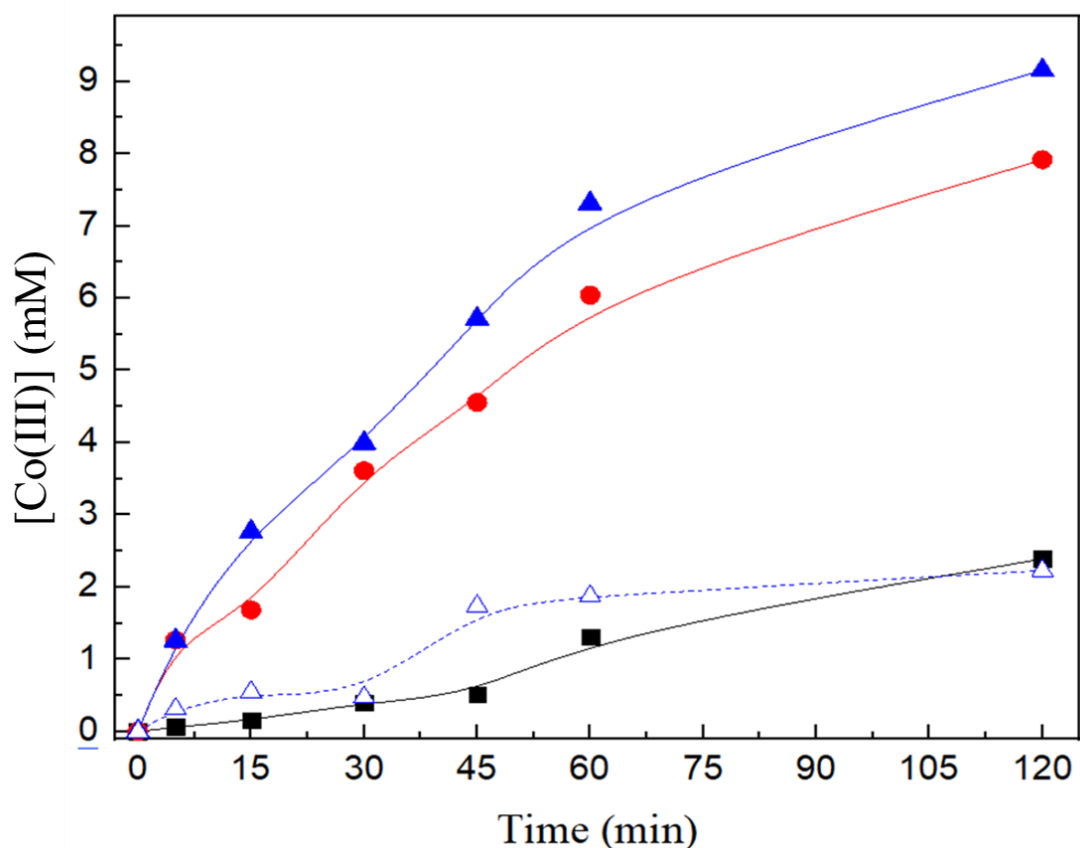
236

237 Figure 1 shows the results obtained during the electrolysis of a solution containing
238 Co(II) acetate using two different BDD anodes. This study was made to confirm the
239 production of the Co(III) electrochemical mediator in a sulfuric acid solution 1.0 M to
240 be used later as electrolyte/absorbent.

241 As can be seen, a very different behavior of the two anodes tested was obtained. The
242 electrooxidation was more efficient when the diamond anode deposited on a tantalum
243 substrate was used than in the case of the electrode on silicon substrate. Thus, the
244 conversion to Co (III) was very slow using Si/BDD, needing around 90 minutes of
245 oxidation reaction to produce only 0.8 mM Co(III) (which means only 8% of
246 conversion). Meanwhile, using Ta/BDD, the generation of Co(III) was faster with a
247 linear increase over the first 60 minutes, being one order of magnitude higher and

248 reaching a maximum of 8 mM after 90 minutes of electrolysis, (which means around
249 80% of conversion). These results confirm that not only the coating but also the
250 substrate is important in the selection of an anode material, as demonstrated in previous
251 published-works by our group (Escalona-Durán et al., 2021). In addition, it can be
252 observed an improvement in the generation of Co(III) (from 75% up to 90% of
253 conversion, see Fig. 1) with the increase in the current density from 10 until 100 mA
254 cm⁻². These results, obtained using an undivided cell equipped with BDD electrodes, are
255 very relevant and indicate the significance of the electrocatalytic properties of the
256 electrode's materials when mediated electro-oxidation processes are looked for.
257 Previous studies (Govindan et al., 2017b)- using a divided electrolytic flow cell and
258 Pt/Ti anode showed a generation efficiency of Co(III) of 41% at the anodic half-cell
259 (with Co(II)SO₄ in 5 M H₂SO₄) after 5.0 h operation. This production of mediator
260 allowed an electro-scrubbing with 90% of removal of CH₃CHO. The same group
261 previously also demonstrated that removal efficiency of CH₃CHO was better at higher
262 current densities and explained this observation in terms of the higher production of
263 Co(III) ions in the media (Govindan et al., 2012b).

264 Thus, results obtained in this work clearly demonstrate the excellent electrocatalytic
265 features of Ta/BDD surface for being used in mediated electro-scrubbers, promoting
266 higher conversions of the reversible mediators Co (II)/Co (III). Therefore, the highest
267 conversions of Co (II)/Co (III) obtained with the Ta/BDD anode, in this first test,
268 demonstrates its excellent electrocatalytic characteristics to be used in mediated electro-
269 scrubbing systems.



270

271 **Fig. 1.** Concentration evolution of Co(III) ions during electrolysis with Si/BDD at 100
 272 mA cm⁻² (Δ) and with Ta/BDD at 100 mA cm⁻² (\blacktriangle), 50 mA cm⁻² (\bullet) and 10 mA cm⁻²
 273 (\blacksquare). Experimental conditions: [H₂SO₄] = 1.0 M with 0.01 M of Co (II) acetate.

274 To evaluate the role of the cobalt as mediator during the electro-absorption treatment of
 275 perchloroethylene, three experiments were carried out with the two anodes: i) EAB in
 276 acid medium without Co mediator; ii) EAB in the presence of Co as mediator and iii)
 277 EAB with Co as mediator and with a pre-electrolysis time. The comparison of the first
 278 and the second experimental set-ups is important to understand if the addition of a
 279 mediator promotes an improvement in the degradation of PCE, considering the large
 280 efficiencies associated to the direct electrolytic processes with diamond anodes. The last
 281 set-up is also important to verify if it is worthy a previous time of electrolysis for Co (II)
 282 conversion before the start-up of the electro-absorption process (aiming to provide an

283 initial concentration of Co (III) mediator in the absorbent). Fig. 2 shows the evolution in
284 the PCE concentration during the six electro-absorption experiments in the liquid and
285 gas phases of the tank in which PCE is initially contained (part a and c) and in the
286 electro-absorber where it is treated (part b and d).

287 Thus, in parts a and c, the concentration evolution in the tank which contains the PCE
288 shows similar mass decay during all processes evaluated. This behavior was expected
289 considering that the evolution of the compound in the tank refers to a simple desorption
290 process, in which only a physical phenomenon is occurring. Hence, no significant
291 differences are observed, meaning that the PCE fed to the system absorption column-
292 electrochemical cell is provided with almost the same rate in the six tests, regardless of
293 the processes happening on the absorption column.

294 On the other hand, parts b and d shows the evolution of PCE in the electro-absorber
295 (system column absorption-electrochemical cell). A higher concentration of PCE is
296 found in the phase gas as compared to liquid phase for all processes and for both
297 electrodes evaluated. This indicates that physical absorption of PCE is a slow process.
298 The PCE concentration absorbed in liquid phase reached a maximum between 5 and 15
299 min, decreasing until the end of the treatment.

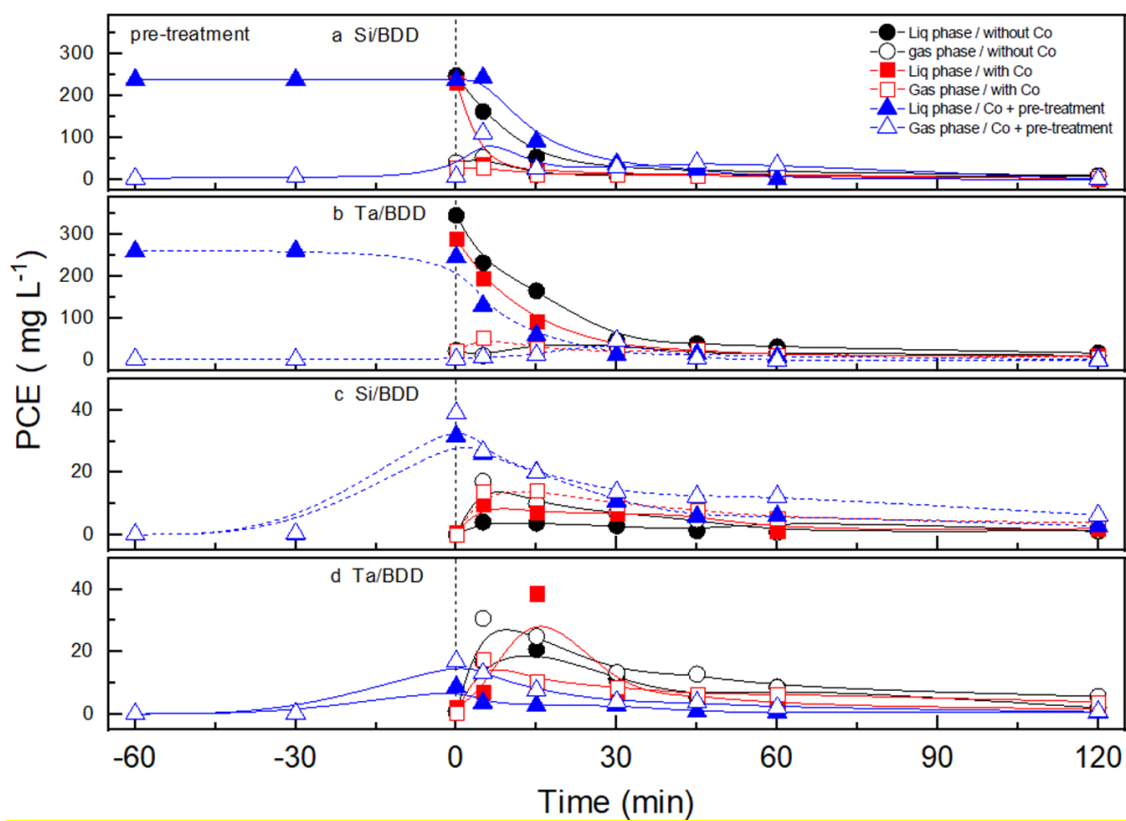
300 The removal percentages of PCE were 75.7, 79.0 and 91.2 % during the experiments
301 carried with Si/BDD and 90.5, 95.9 and 95.3 % during the experiments carried with
302 Ta/BDD, for experiments without Co, with Co, and with Co plus pre-electrolysis,
303 respectively. Therefore, formation of oxidation mediators improves the removal of PCE
304 and the Ta/BDD anode promotes the conversion of PCE, especially without addition of
305 metal catalysts precursors. A slight improvement was observed for both electrodes
306 when Co was added to the system, indicating the electrolysis with diamond can face the

307 removal of PCE by direct processes but that the formation of electro catalyzers can help
308 to improve results.

309 The removal percentages of PCE were 75.7, 79.0 and 91.2% in the experiments carried
310 out with Si/BDD and 90.5, 95.9 and 95.3% in the experiments carried out with Ta/BDD,
311 for systems without Co, with Co and with Co and pre-electrolysis, respectively. The
312 elimination of PCE is promoted with both anodes and a slight improvement is observed
313 with the addition of the metallic catalyst, which indicates that electrolysis with diamond
314 electrodes can efficiently remove PCE by direct reactions with the physiosorbed
315 hydroxyl radicals. This behavior is typical of these non-active anodes, but the
316 improvement obtained with the metallic electrocatalysts is not as relevant as expected
317 (just a 5% higher conversion) and this does not seem to support the application of these
318 more complex treatments. The production of Co (III) ions does not seem to be the more
319 important factor for the improving of PCE depletion but the generation of efficient
320 oxidants by the reactions in the electrode surface (which would be especially useful in
321 very dilute contaminated matrix).

322 However, when pre-electrolysis was carried out to promote the Co(III) generation in the
323 absorbent before the electro-absorption, an improvement in the PCE removal was only
324 obtained for Si/BDD (12%). This can be explained considering that the conversion of
325 Co(III) employing Si/BDD anodes was slower as compared to the obtained with the
326 Ta/BDD anodes and confirms that the effect of Co mediators has more influence with
327 Si-BDD that produce less powerful oxidants in their surface. In both cases, the previous
328 electrolysis contributed to promote the conversion of Co (III) ions and to improve the
329 degradation of PCE when the electro-absorption started, but as Ta-BDD anode
330 promotes the faster and more efficient generation of Co (III) mediators and oxidants, the
331 effect of this pretreatment is less important in the overall PCE removal. Besides, the

332 energy consumptions estimated were 80.7, 70.3, and 103.3 kWh·L⁻¹ using Si/BDD as
 333 anode, and 63.3, 63.0 and 91.6 kWh·L⁻¹ for Ta/BDD for electrolysis without Co, in
 334 presence of Co as mediator and in presence of Co and with a pre-electrolysis time,
 335 respectively. Thus, initially, from energy point of view, the improvement obtained for
 336 previous electrolysis for Si can worth the higher cost. However, for Ta, the increase in
 337 the energy demand of 28.6 kWh·L⁻¹ is not justified once, no improvement was obtained
 338 using a pre-electrolysis time.

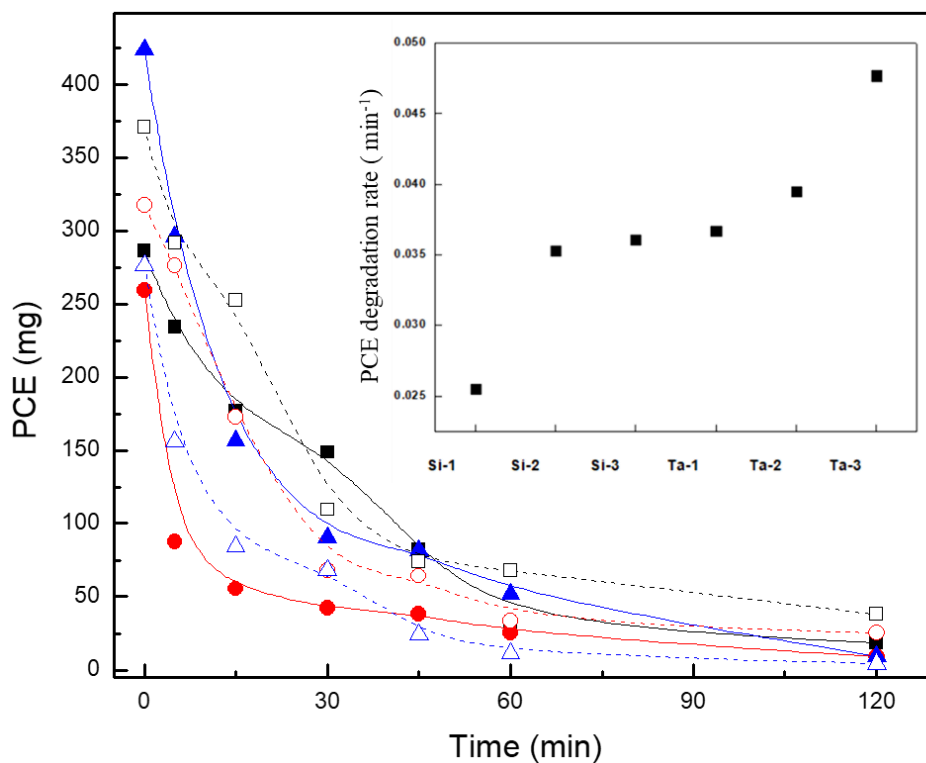


339

340 **Figure 2.** Mass evolution of PCE during the electro-absorption treatment over time
 341 being (■,□) EAB without Co, (●,○) EAB with Co and (▲,△) EAB with Co + pre-
 342 electrolysis time. (a) and (b) samples collected in the PCE tank and (c) and (d) samples
 343 collected in absorption column. The absorbent tank is equipped with Si/BDD (full
 344 points) and Ta/BDD (empty points) anode ($j=100 \text{ mA cm}^{-2}$) Full points: liquid phase,

345 and empty points: gas phase. Experimental conditions: $[H_2SO_4] = 1.0 \text{ M}$; experiments
346 with cobalt ions (0.01 M of Co (II) acetate).

347 Figure 3 shows the constant rates obtained after fitting the total removal of PCE in the
348 system (tank + absorption column + electrochemical reactor) to first order kinetic. As
349 can be observed the degradation rate increases in the presence of Co especially when
350 pre-electrolysis is carried before the electro-absorption process started. In addition,
351 values of the kinetic constants confirm that removal with Si/BDD is less efficient than
352 with Ta/BDD, which can be explained in terms of activation of oxidants with the
353 improved production of Co (III) mediators with the Ta/BDD anode. These observations
354 suggest an important role of the oxidant mediators in the system.



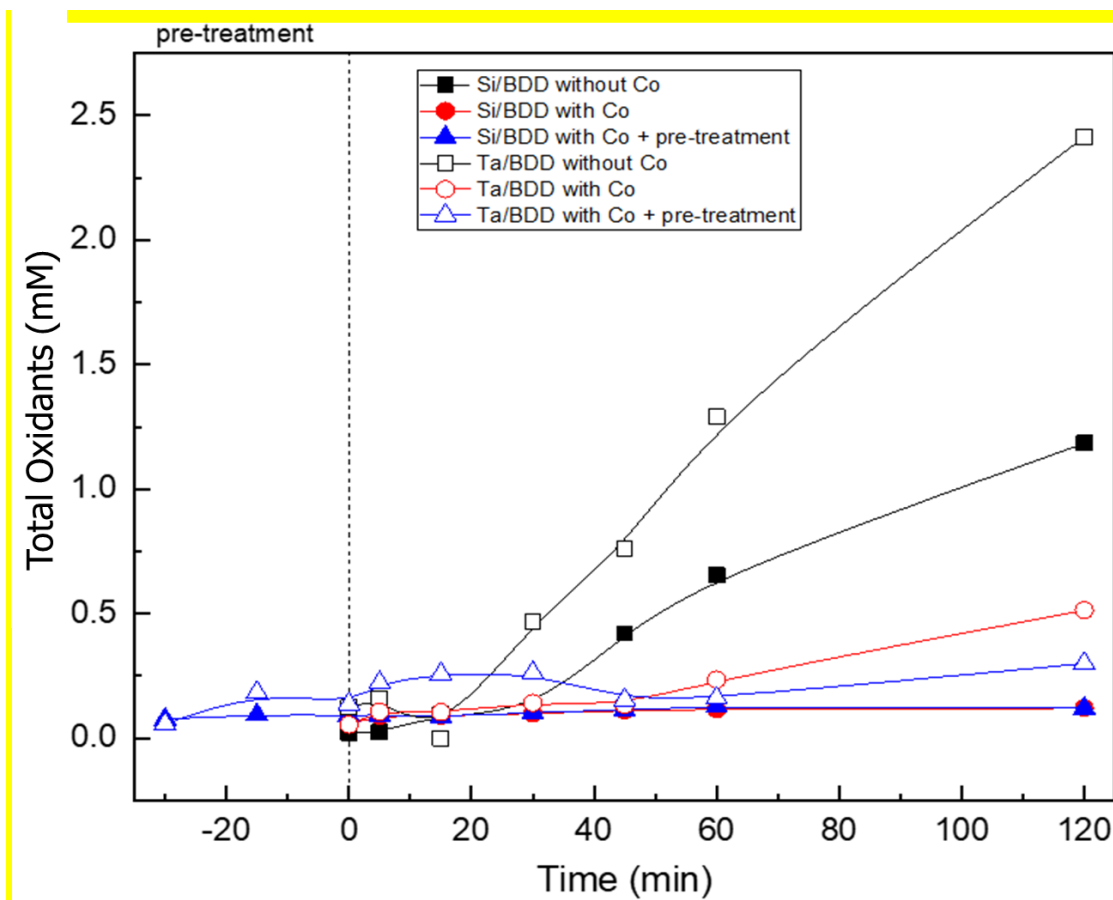
355

356 **Fig. 3.** Total removal of PCE from the system and kinetic constants obtained after
357 fitting experimental data to first order depletion model. (■,□) EAB without Co, (●,○)
358 EAB with Co and (▲,△) EAB with Co + pre-electrolysis time in an absorbent tank

359 with an electrochemical cell equipped with Si/BDD (full points) and Ta/BDD (empty
360 points) anodes. Onset: PCE degradation rate/ min^{-1} in Si and Ta substrates of 1) sulfuric
361 media 1.0 M, 2) sulfuric media 1.0 M with cobalt ions 0.01 M and 3) sulfuric media 1.0
362 M with 0.01 M of cobalt ions; and 30 min of pretreatment.

363 Thus, concurrently to PCE degradation and conversion to Co (III) mediator, other
364 oxidants can be electrogenerated on diamond surface. Among them, worth to mention
365 persulfates and ozone, which can be responsible of the low impact of the Co mediators,
366 because they act also as mediators in the degradation of PCE. Also, hydrogen peroxide,
367 whose occurrence cannot only be explained from the anodic oxidation of water but also,
368 and more importantly, from the cathodic reduction of oxygen. Fig. 4 shows the
369 evolution of total oxidants for each anode surface employed with time during the
370 different electro-absorption system applied in the treatment of PCE. As can be seen,
371 without cobalt in the medium, the presence of measured oxidants was higher during the
372 electro-absorption employing Ta/BDD as anode as compared to the process in which
373 the Si/BDD was used. After two hours, 2.5 mM was reached in the case of Ta/BDD and
374 less than 1.5 mM in the case of Si/BDD. However, in the presence of cobalt as
375 mediator, there is a huge decrease in the concentration of oxidants capable to oxidize
376 iodide to iodine, what initially seems to be astonishing. In the case of using Si/BDD
377 anodes there is a decrease of 89% while for Ta/BDD the decrease is 78%. This
378 observation is important and can be explained by the interaction of Co (III) with the
379 other oxidants formed. Unfortunately, the promotion of oxidants is not always positive
380 from the viewpoint of their accumulation in the electrolyte, because their interaction
381 may lead to the formation of other species with shorter lifetime. This is the case of
382 peroxone, an example well described in the literature (Martínez-Huitile et al., 2015),
383 when ozone and hydrogen peroxide are mixed, and which lead to the massive formation

384 of hydroxyl radicals. In that case, a measurement of oxidants leads to a lower
385 concentration than the dosed when the two oxidants are added, but the oxidation effects
386 during the treatment of an organic is improved, because of the more powerful oxidant
387 generated. However, sometimes, the radicals formed can be wasted and form non-useful
388 species such as oxygen (formed by the combination of hydroxyl radicals). Regarding
389 the changes observed in the electrolyte in this work, when pre-electrolysis was done in
390 order to promote the conversion of Co (II) to Co (III), in Si/BDD no differences were
391 observed when compared to the system without pre-electrolysis. However, when
392 Ta/BDD was employed, after 30 min of treatment, is possible to see around 30% of
393 decrease in the oxidants' concentration indicating that the conversion of these oxidants
394 to hydroxyl radicals is better.

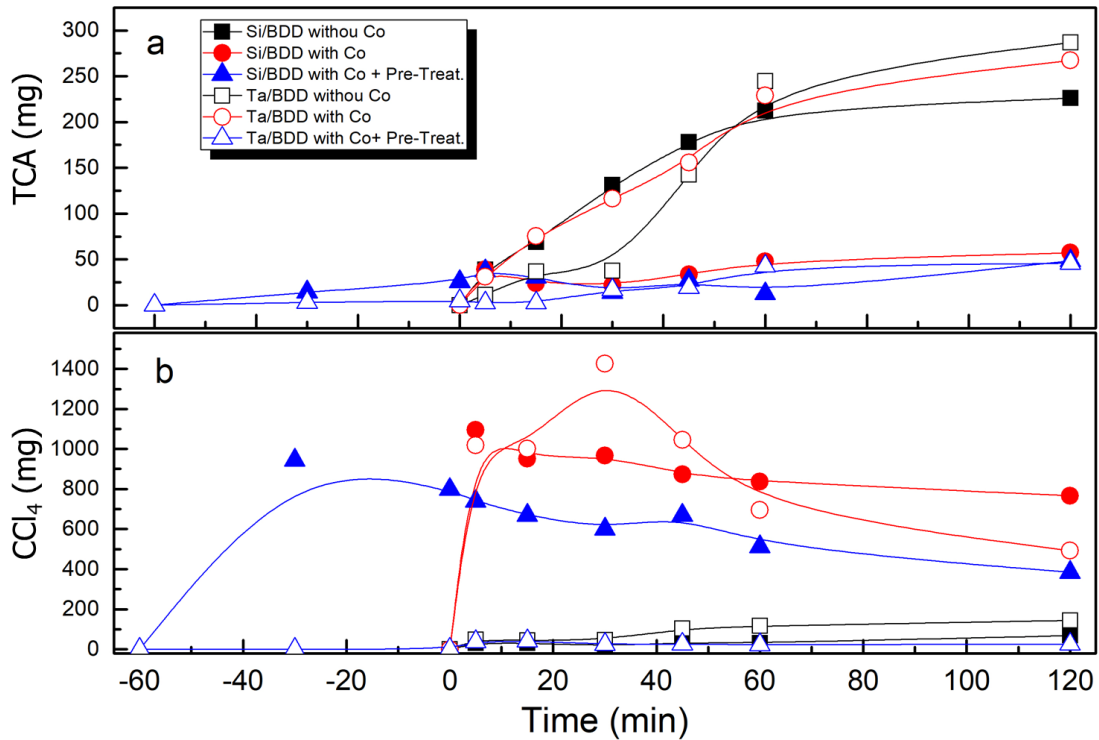


395

396 **Fig. 4.** Evolution in the production of oxidants during the electro-absorption treatment
397 over time being (■,□) EAB without Co, (●,○) EAB with Co and (▲,△) EAB with Co
398 + pre-electrolysis time in an absorbent tank with an electrochemical cell equipped with
399 Si/BDD (full points) and Ta/BDD (empty points) anode.

400 Another very important point in the treatment of the PCE is the speciation formed
401 during the treatment. Fig. 5 shows the evolution of the concentrations of trichloroacetic
402 acid-and carbon tetrachloride during the electro-absorption tests. A larger formation of
403 TCA is obtained for both anodes tested when EAB without cobalt (II) ions was applied.
404 In the presence of mediator Co, it is possible to observe a decrease in the concentration
405 of TCA for both anodes. However, this decrease is quite higher using Si/BDD.
406 Regarding to the application of pre-electrolysis before electro-absorption process, the
407 evolutions of acids were lower for both anodes, which means that the pre-electrolysis
408 generates compounds that promote other transformation mechanisms for the reaction
409 products. Regarding carbon tetrachloride, very low concentrations were obtained during
410 the treatments by EAB (without Co) for both anodes, being a little bit higher in the case
411 of Ta/BDD (reaching around 90 mg). When Co was added to the system, highest
412 concentrations of CCl₄ were attained employing Ta/BDD as anode, increasing over time
413 until 1500 mg and decreasing at the end of the process. When pre-electrolysis was used
414 to electro-generate Co (III), it does not have a high influence in the case of Ta/BDD
415 anode. However, using the Si/BDD anode, the highest quantity of CCl₄ is detected at the
416 beginning of the process, that would be related with the influence of gaseous evolution
417 from both electrodes during the electrooxidation. However, the total amount of this by-
418 product detected at the end was 25% lower than the value attained when Co was added
419 to the system without a pretreatment. For this by-product, the influence of the substrate

420 seems to be more limited than for trichloroacetic acid, although a minor quantity of
 421 carbon tetrachloride has been detected when Ta /BDD anode was employed with Co.

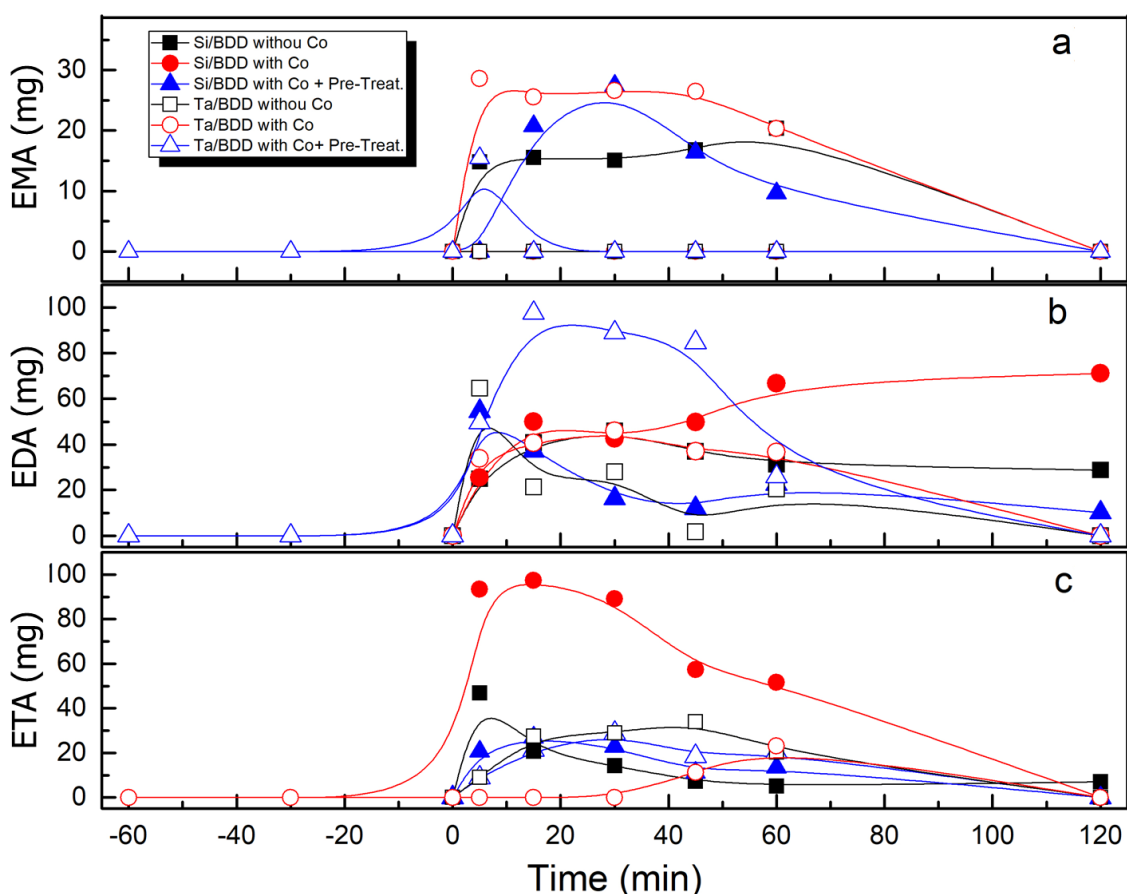


422

423 **Figure 5.** Mass Evolution of Trichloroacetic acid (a) and carbon tetrachloride (b)
 424 generated during the electro-absorption treatment over time being (■,□) EAB without
 425 Co, (●,○) EAB with Co and (▲,△) EAB with EAB with Co + pre-electrolysis time
 426 inside absorbent tank with an electrochemical cell equipped with Si/BDD-Si (full
 427 points) and Ta/BDD-Ta (empty points) anode.

428 In addition to TCA and CCl₄, three ethyl chloroacetates esters were detected during the
 429 experiments (by HPLC comparing peaks to standards), although the amount produced is
 430 much less significant than that of the two previously discussed species. Fig. 6 shows the
 431 evolution in the production of these minority intermediates. Part a show that the
 432 quantity detected of ethyl chloro-acetate (EMA) is under 50 mg. It is observed in all
 433 tests carried out, except for the EAB with Ta/BDD (without Co), indicating that in that
 434 case it is efficiently depleted as produced. Anyhow, this species was completely

435 removed in all cases at the end of the treatment tests, pointing out its role as reaction
436 intermediate. Part b focuses on the evolution of the concentration of ethyl dichloro-
437 acetate (EDA) in the electrooxidation process. As in the case of EMA, EDA is always
438 removed during the tests and, hence, it can be considered also as a reaction
439 intermediate. This compound is promoted in the EAB with Si/BDD anode and it
440 reached a maximum amount of 100 mg in the first samples taken during the tests in
441 which the pre-electrolysis with cobalt ions was carried out. Changes are very similar
442 during the EAB with Ta/BDD anodes. In this case, the maximum quantity detected was
443 30 mg, indicating a more efficient depletion. Part c shows the changes in the amount of
444 ethyl trichloro-acetate (ETA). In this case a different behavior appears, being totally
445 removed in the tests in which Ta/BDD was used as anode, but not in the tests with the
446 Si/BDD anode. With Si/BDD anode, an increasing trend appears at the early beginning
447 obtaining at the end the higher concentration when cobalt ions were used without pre-
448 electrolysis. This means that the presence of cobalt ions, and the lower efficiency of
449 Si/BDD in the production of powerful oxidants, can affect to the evolution of this
450 intermediate, promoting its accumulation in the absorbent. With the Ta/BDD anodes,
451 although high quantities were reached in the first stages especially when a pre-
452 electrolysis with cobalt ions was applied (around 100 mg), complete removal of these
453 by-products was attained at the end of all tests. As can be seen, the maximum
454 concentration peaks shift towards higher reaction times as the molecules is less
455 chlorinated, suggesting a sequential dechlorination of the esters, which in addition can
456 be formed by the reaction of TCA with other intermediates generated during the
457 decomposition of PCE. Anyhow, the great reactivity of chlorine in electrochemical
458 systems makes difficult to elucidate a precise tentative mechanism.



459

460 **Figure 6.** Evolution in the production of **acidic chlorinated esters intermediates (a)** ethyl
 461 chloro-acetate, **(b)** ethyl dichloro-acetate and **(c)** ethyl trichloro-acetate in the liquid
 462 phase during the electro-absorption treatment over time being (■,□) EAB without Co,
 463 (●,○) EAB with Co and (▲,△) EAB with EAB with Co + pre-electrolysis time inside
 464 absorbent tank with an electrochemical cell equipped with **Si/BDD-Si** (full points) and
 465 **Ta/BDD-Ta** (empty points) anode.

466 Thus, based on the by-products detected and reported in literature (Munoz-Morales et
 467 al., 2020), Fig. SM2 shows the possible mechanism for PCE degradation. The reaction
 468 may develop from different radicals such as $\text{Cl}\cdot$ and $\text{OH}\cdot$ radicals and by many oxidants,
 469 being very important the role of the cobalt, according to the results discussed. A first
 470 stage should be the formation of phosgene, which then transforms into carbon dioxide
 471 and CCl_4 . This reaction is not electrochemical but chemical, as it has been widely

472 reported in the literature, being favored in the wet gaseous phase (Yamazaki, 2004). On
473 the other hand, the anodic generation of oxidants leads to the formation of
474 trichloroacetic acid which combines with other intermediates to form ester halogenated
475 derivatives, that are sequentially dehalogenated. Finally, the non-halogenated
476 intermediates are fully destroyed as it is supposed because no other intermediates are
477 detected in the system in significant concentrations with the analytical techniques
478 applied. The harsh oxidation conditions generated in the electrolysis with diamond
479 electrodes behaves as an electrochemical cold combustion with respect to intermediates
480 and in the treatment of diluted wastes it is very common the non-detection of relevant
481 intermediates because once the molecule starts its degradation it is fully destroyed. This
482 affirmation seems consistent with the results obtained in this work.

483

484 **Conclusions**

485

486 From this work the following conclusions can be drawn:

- 487 • Perchloroethylene can be treated using electro-absorption processes, in which a
488 packed column is combined with an electrochemical cell equipped with diamond
489 electrodes.
- 490 • There is a great influence of the substrate, on which the diamond coating is
491 deposited, on the reactivity of the system when using cobalt ions as
492 electrochemical mediators. Ta/BDD anode allows to obtain higher
493 concentrations of Co (III) ions and to attain faster removals of PCE.
- 494 • Type of anode also influence on the presence of other oxidants which are also
495 relevant to explain the performance of the treatment.

- 496 • Three strategies can be successfully used for the treatment of PCE: absorbent
497 free of cobalt (III) precursors, absorbent containing Co (III) precursors, and
498 absorbent containing Co (III) precursors undergoing previous electrolysis. The
499 most successful was the last, confirming the important role of mediated
500 electrooxidation processes in the degradation of PCE.
- 501 • Carbon tetrachloride and trichloroacetic acid were found to be the main reaction
502 products. Chloroacetate esters were detected, and they allow to propose a
503 dehalogenation mechanism, which successfully complement previous
504 mechanisms proposed for this novel PCE treatment.

505

506

507 **Acknowledgements**

508 Financial support from the Spanish Agencia Estatal de Investigación and European
509 Union through project PID2019-107271RB-I00 (AEI/FEDER, UE) and the Spanish
510 Government (Grant N° FPU16/00067) are gratefully acknowledged. F. L. Souza is
511 gratefully acknowledged to Coordenação de Aperfeiçoamento de Pessoal de nível
512 Superior (CAPES) process 88881.171154/2018-01 for the scholarship awarded. F.
513 Escalona-Durán gratefully acknowledges CAPES by the scholarship given under the
514 CAPES-PRINT program (process 88887.363246/2019-00).

515

516 **References**

517 Adam Gopal, R., Govindan, M., Moon, I.S., 2019. Enhanced electro-reduction of NO to NH₃ on
518 Pt cathode at electro-scrubber. *Environ. Sci. Pollut. Res. Int* 26, 29517-29523.
519 American Public Health Association, American Water Works Association and Water
520 Environmental, 1998. 20th Edition. Standard methods for the Examination of water and
521 wastewater, . Washington, DC.

522 Bal, M., Reddy, T.T., Meikap, B.C., 2019. Removal of HCl gas from off gases using self-priming
523 venturi scrubber. *J. Hazard. Mater.* 364, 406-418.

524 Balaji, S., Muthuraman, G., Moon, I., 2015. Influence of cathode on the electro-generation of
525 peroxydisulfuric acid oxidant and its application for effective removal of SO₂ by room
526 temperature electro-scrubbing process. *J. Hazard. Mater.* 299, 437-443.

527 Bhatt, P., Kumar, M.S., Mudliar, S., Chakrabarti, T., 2007. Biodegradation of chlorinated
528 compounds—A Review. *Critical Reviews in Environ. Sci. Tech.* 37, 165-198.

529 Caplin, A., Ghandehari, M., Lim, C., Glimcher, P., Thurston, G., 2019. Advancing environmental
530 exposure assessment science to benefit society. *Nat. Commun.* 10, 1236.

531 Castañeda-Juárez, M., Muñoz-Morales, M., Souza, F.L., Sáez, C., Cañizares, P., Almazán-
532 Sánchez, P.T., Linares-Hernández, I., Rodrigo, M.A., 2020. Electro-absorbers: A comparison on
533 their performance with jet-absorbers and absorption columns. *Catalysts* 10, 653.

534 Chandrasekara Pillai, K., Chung, S.J., Raju, T., Moon, I.S., 2009. Experimental aspects of
535 combined NO_x and SO₂ removal from flue-gas mixture in an integrated wet scrubber-
536 electrochemical cell system. *Chemosphere* 76, 657-664.

537 Chung, S.J., Moon, I.S., 2013. An improved method of removal for high concentrations of NO
538 by electro-scrubbing process. *Process Saf. Env.* 91, 153-158.

539 de Moura, D.C., do Nascimento Brito, C., Quiroz, M.A., Pergher, S.B.C., Martinez-Huitle, C.A.,
540 2015. Cl-mediated electrochemical oxidation for treating an effluent using platinum and
541 diamond anodes. *J. of Wat. Process Eng.* 8, e31-e36.

542 Dhamodharan, K., Varma, V.S., Veluchamy, C., Pugazhendhi, A., Rajendran, K., 2019. Emission
543 of volatile organic compounds from composting: A review on assessment, treatment and
544 perspectives. *Sci. Total Environ.* 695, 133725.

545 Dominguez, C.M., Oturan, N., Romero, A., Santos, A., Oturan, M.A., 2018. Removal of lindane
546 wastes by advanced electrochemical oxidation. *Chemosphere* 202, 400-409.

547 Farmer, J.C., Wang, F. T.; Lewis, P. R.; Summers, L. J. , 1992. Destruction of chlorinated
548 organics by cobalt(III)-mediated electrochemical oxidation. *J. Electrochem. Soc.* 139 3025.

549 Ferreira, M.B., Souza, F.L., Muñoz-Morales, M., Sáez, C., Cañizares, P., Martínez-Huitle, C.A.,
550 Rodrigo, M.A., 2020. Clopyralid degradation by AOPs enhanced with zero valent iron. *J. Hazard.*
551 *Mater.*, 122282.

552 Ganiyu, S.O., Martínez-Huitle, C.A., 2020. The use of renewable energies driving
553 electrochemical technologies for environmental applications. *Curr. Opin. Electrochem.* 22, 211-
554 220.

555 García-Morales, M.A., Roa-Morales, G., Barrera-Díaz, C., Bilyeu, B., Rodrigo, M.A., 2013.
556 Synergy of electrochemical oxidation using boron-doped diamond (BDD) electrodes and ozone
557 (O₃) in industrial wastewater treatment. *Electrochem. Commun.* 27, 34-37.

558 González-Pérez, O., Muñoz-Morales, M., Souza, F.L., Saez, C., Cañizares, P., Rodrigo, M.A.,
559 2020. Jet electro-absorbers for the treatment of gaseous perchloroethylene wastes. *Chem.*
560 *Eng. J.*, 125096.

561 Govindan, M., Adam Gopal, R., Moon, I.S., 2017a. Efficient removal of gaseous
562 trichloroethylene by continuous feed electro-scrubbing using a new homogeneous
563 heterobimetallic electro-catalyst. *Chem.Eng. J.* 308, 1145-1153.

564 Govindan, M., Bond, A.M., Moon, I.S., 2017b. Implementation of concurrent electrolytic
565 generation of two homogeneous mediators under widened potential conditions to facilitate
566 removal of air-pollutants. *Sci. Rep.* 7, 29.

567 Govindan, M., Chung, S.-J., Jang, J.-W., Moon, I.-S., 2012a. Removal of hydrogen sulfide
568 through an electrochemically assisted scrubbing process using an active Co(III) catalyst at low
569 temperatures. *Chem.Eng. J.* 209, 601-606.

570 Govindan, M., Chung, S.J., Moon, I.S., 2012b. Mineralization of gaseous acetaldehyde by
571 electrochemically generated Co(III) in H₂SO₄ with wet scrubber combinatorial system. *ACS*
572 *Comb Sci* 14, 359-365.

573 Govindan, M., Gopal, R.A., Ahn, H.G., Moon, I.S., 2016. Synergistic effect of mediated
574 electrochemical reduction and mediated electrochemical oxidation on NO removal by electro-
575 scrubbing. *J. Electrochem. Soc.* 163, E390-E396.

576 Govindan, M., Moon, I.-S., 2015. Uncovering results in electro-scrubbing process toward green
577 methodology during environmental air pollutants removal. *Process Saf. Environm.* 93, 227-232.

578 Govindan, M., Moon, I.S., 2013. A single catalyst of aqueous CoIII for deodorization of mixture
579 odor gases: a development and reaction pathway study at electro-scrubbing process. *J. Hazard.*
580 *Mater.* 260, 1064-1072.

581 Huang, B., Lei, C., Wei, C., Zeng, G., 2014. Chlorinated volatile organic compounds (Cl-VOCs) in
582 environment - sources, potential human health impacts, and current remediation
583 technologies. *Environm. Inter.* 71, 118-138.

584 Karatum, O., Deshusses, M.A., 2016. A comparative study of dilute VOCs treatment in a non-
585 thermal plasma reactor. *Chem. Eng. J.* 294, 308-315.

586 Kolthoff, I.M., Carr, E.M., 1953. Volumetric determination of persulfate in presence of organic
587 substances. *Anal.Chem.* 25, 298-301.

588 Landrigan, P.J., Fuller, R., Acosta, N.J.R., Adeyi, O., Arnold, R., Basu, N., Baldé, A.B., Bertollini,
589 R., Bose-O'Reilly, S., Boufford, J.I., Breyse, P.N., Chiles, T., Mahidol, C., Coll-Seck, A.M.,
590 Cropper, M.L., Fobil, J., Fuster, V., Greenstone, M., Haines, A., Hanrahan, D., Hunter, D., Khare,
591 M., Krupnick, A., Lanphear, B., Lohani, B., Martin, K., Mathiasen, K.V., McTeer, M.A., Murray,
592 C.J.L., Ndahimananjara, J.D., Perera, F., Potočník, J., Preker, A.S., Ramesh, J., Rockström, J.,
593 Salinas, C., Samson, L.D., Sandilya, K., Sly, P.D., Smith, K.R., Steiner, A., Stewart, R.B., Suk, W.A.,
594 van Schayck, O.C.P., Yadama, G.N., Yumkella, K., Zhong, M., 2018. The Lancet Commission on
595 pollution and health. *The Lancet* 391, 462-512.

596 Lopes, F.V.S., Miranda, S.M., Monteiro, R.A.R., Martins, S.D.S., Silva, A.M.T., Faria, J.L.,
597 Boaventura, R.A.R., Vilar, V.J.P., 2013. Perchloroethylene gas-phase degradation over titania-
598 coated transparent monoliths. *Appl. Catal. B: Environm.* 140-141, 444-456.

599 Martínez-Huitle, C.A., Panizza, M., 2018. Electrochemical oxidation of organic pollutants for
600 wastewater treatment. *Curr. Opin. Electrochem.* 11, 62-71.

601 Martínez-Huitle, C.A., Rodrigo, M.A., Sirés, I., Scialdone, O., 2015. Single and coupled
602 electrochemical processes and reactors for the abatement of organic water pollutants: A
603 critical review. *Chemical Reviews* 115, 13362-13407.

604 Matheswaran, M.C., S. J. Moon, S., 2008. Cobalt(III)-mediated oxidative destruction of phenol
605 using divided electrochemical cell. *Korean J. Chem. Eng.*, 25, 1031-1035.

606 Mudliar, S., Giri, B., Padoley, K., Satpute, D., Dixit, R., Bhatt, P., Pandey, R., Juwarkar, A.,
607 Vaidya, A., 2010. Bioreactors for treatment of VOCs and odours - a review. *J. Environ. Manage.*
608 91, 1039-1054.

609 Munoz-Morales, M., Castaneda-Juarez, M., Souza, F.L., Saez, C., Canizares, P., Martinez-
610 Miranda, V., Linares-Hernandez, I., Rodrigo, M.A., 2020. Assessing the viability of electro-
611 absorption and photoelectro-absorption for the treatment of gaseous perchloroethylene.
612 *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-020-10811-2>

613 Muñoz-Morales, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2019. A new electrochemically-
614 based process for the removal of perchloroethylene from gaseous effluents. *Chem. Eng J.* 361,
615 609-614.

616 Muthuraman, G., Moon, I.-S., 2012. A review on an electrochemically assisted-scrubbing
617 process for environmental harmful pollutant's destruction. *J. Ind. Eng. Chem.* 18, 1540-1550.

618 Muthuraman, G., Moon, I.S., 2017. Innovative reductive remediation of carbon tetrafluoride at
619 room temperature by using electrogenerated Co(1). *J. Hazard. Mater.* 325, 157-162.

620 Muthuraman, G., Ramu, A.G., Cho, Y.H., McAdam, E.J., Moon, I.S., 2018a. Electrochemically
621 generated bimetallic reductive mediator Cu(1+)[Ni(2+)(CN)4](1-) for the degradation of CF4
622 ethanol by electro-scrubbing. *Waste Manag. Res.* 36, 1043-1048.

623 Muthuraman, G., Ramu, A.G., Cho, Y.H., McAdam, E.J., Moon, I.S., 2018b. Sustainable
624 degradation of carbon tetrafluoride to non-corrosive useful products by incorporating reduced
625 electron mediator within electro-scrubbing. *J. Ind. Eng. Chem* 63, 275-280.
626 Muthuraman, G., Thirumavalavan, M., Il Shik, M., 2017. In situ electrochemically generated
627 peroxyphosphoric acid as an oxidant for the effective removal of gaseous acetaldehyde.
628 *Chem. Eng J.* 325, 449-456.
629 Paz, E., Pinheiro, V., Aveiro, L., Souza, F., Lanza, M., Santos, M., 2019. Hydrogen peroxide
630 electrogeneration by gas diffusion electrode modified with tungsten oxide nanoparticles for
631 degradation of orange II and sunset yellow FCF azo dyes. *J. Braz. Chem.Soc.* 30(9)
632 <http://dx.doi.org/10.21577/0103-5053.20190111>
633 Raimondo, E.E., Aparicio, J.D., Bigliardo, A.L., Fuentes, M.S., Benimeli, C.S., 2020. Enhanced
634 bioremediation of lindane-contaminated soils through microbial bioaugmentation assisted by
635 biostimulation with sugarcane filter cake. *Ecotoxicol. Environ. Saf.* 190, 110143.
636 S.E. Manahan, *Environmental.Chemistry*, fifth ed., Lewis Publishers, Michigan, 1991.
637 Santos, A., Domínguez, C.M., Lorenzo, D., García-Cervilla, R., Lominchar, M.A., Fernández, J.,
638 Gómez, J., Guadaño, J., 2019. Soil flushing pilot test in a landfill polluted with liquid organic
639 wastes from lindane production. *Heliyon* 5, e02875.
640 Scialdone, O., 2009. Electrochemical oxidation of organic pollutants in water at metal oxide
641 electrodes: A simple theoretical model including direct and indirect oxidation processes at the
642 anodic surface. *Electrochim. Acta* 54, 6140-6147.
643 Semitsoglou-Tsiapou, S., Templeton, M.R., Graham, N.J.D., Hernández Leal, L., Martijn, B.J.,
644 Royce, A., Kruithof, J.C., 2016. Low pressure UV/H₂O₂ treatment for the degradation of the
645 pesticides metaldehyde, clopyralid and mecoprop – Kinetics and reaction product formation.
646 *Water Research* 91, 285-294.
647 Souza, F.L., Rocha, R.S., Ferreira, N.G., Rodrigo, M.A., Lanza, M.R.V., 2019. Effects of coupling
648 hybrid processes on the treatment of wastewater containing a commercial mixture of diuron
649 and hexazinone herbicides. *Electrochim. Acta* 328, 135013.
650 Vikrant, K., Park, C.M., Kim, K.-H., Kumar, S., Jeon, E.-C., 2019. Recent advancements in
651 photocatalyst-based platforms for the destruction of gaseous benzene: Performance
652 evaluation of different modes of photocatalytic operations and against adsorption techniques.
653 *J. Photochem. Photobiol. C: Photochem. Reviews* 41, 100316.
654 Wacławek, S., Lutze, H.V., Grübel, K., Padil, V.V.T., Černík, M., Dionysiou, D.D., 2017. Chemistry
655 of persulfates in water and wastewater treatment: A review. *Chem. Eng J.* 330, 44-62.
656 Wang, J., Wang, S., 2018. Activation of persulfate (PS) and peroxymonosulfate (PMS) and
657 application for the degradation of emerging contaminants. *Chem. Eng J.* 334, 1502-1517.
658 Yamazaki, S.T., T.; Yoshida, A., 2004. Reaction Mechanism of Photocatalytic Degradation of
659 chlorinated ethylenes on Porous TiO₂ Pellets: Cl radical-initiated mechanism. *J. Phys. Chem. A*
660 108, 5183-5188.
661 Yang, J., Liu, K., Jia, J., Cao, L., 2011. Electro-scrubbing volatile organic carbons in the air stream
662 with a gas diffusion electrode. *J. Hazard. Mater.* 188, 125-131.
663 Zhang, X., Gao, B., Creamer, A.E., Cao, C., Li, Y., 2017. Adsorption of VOCs onto engineered
664 carbon materials: A review. *J. Hazard. Mater.* 338, 102-123.
665 Zhang, Y., Wei, C., Yan, B., 2019. Emission characteristics and associated health risk assessment
666 of volatile organic compounds from a typical coking wastewater treatment plant. *Sci. Total*
667 *Environ.* 693, 133417.
668 Zhang, Z., Jiang, Z., Shanguan, W., 2016. Low-temperature catalysis for VOCs removal in
669 technology and application: A state-of-the-art review. *Catalysis Today* 264, 270-278.

670

671