

1 Continuous electro-scrubbers for the removal of perchloroethylene: 2 keys for selection

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11 Abstract

12 In this work, the removal of perchloroethylene (PCE) using continuous-operation electro-
13 scrubbers is evaluated. Two types of electro-scrubbers were made by combining a jet
14 mixer or a packed absorption column with a single flow-cell. The absorbent/electrolyte is
15 recirculated between both devices, being electrolyzed in the cell and retaining the
16 pollutant in the scrubber. In both scrubber's system, an important amount of PCE was
17 absorbed into the electrolyte and the application of electric current significantly improved
18 the results, highlighting the efficiency of the integration of technologies. Tests in the
19 absence of absorbent/electrolyte confirmed the reactivity of the PCE in the wet gas phase.
20 The jet-mixer system turned out to be more efficient than the packed column, yielding
21 better results both in absorption and electro-absorption modes, and reaching a PCE
22 removal greater than 90%. Meanwhile, the addition of cobalt mediators did not improve
23 the electro-scrubbing efficiency as initially expected: in the case of the packed column

24 electro-scrubber there were no changes while in the case of the jet mixer surprisingly it is
25 generated a negative effect.

26

27 **Keywords**

28 Perchloroethylene; electro-scrubber; scrubber; continuous operation mode; cobalt
29 mediator

30

31 **Highlights**

- 32 • PCE removed continuously using packed column and jet-mixer electro-scrubbers.
- 33 • Important chemical reactivity of PCE
- 34 • No significant improvement with the addition of cobalt mediators.
- 35 • Better performance of jet-mixers electro-scrubbers.

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40 **1. Introduction**

41 Removal of gaseous pollutants from the atmosphere is becoming a topic of major interest.
42 There are many technologies available, but the promising results obtained by
43 electrochemically-assisted scrubbing processes enhance the continuous research on this
44 topic [1, 2]. The production of oxidants species through electrochemical technology in
45 the liquid that acts as electrolyte/absorber helps to improve the absorption capacity of this
46 liquid, and the simultaneous degradation of the pollutant absorbed has increased the
47 capacity of treatment in comparison with single absorption process. Because of that, the
48 selection of a proper absorbent / electrolyte becomes a key parameter for the design of
49 electro-scrubbers.

50 Electrolysis is known to efficiently produce ~~efficiency~~ many types of oxidants from the
51 oxidation of ions typically contained in water [3-5]. Thus, it is known the formation of
52 many different species from the oxidation of chloride anions [6, 7] and also the production
53 of peroxy-species from the oxidation of carbonate, sulfate, phosphate or even acetate
54 anions [8-12]. Cations are less involved in the production of oxidants, but iron cations are
55 used in the production of ferrates [13, 14]. Besides, the production of other oxidants such
56 as ozone or hydrogen peroxide, not directly related with the presence of ions in the
57 electrolyte, has been found as relevant [15, 16]. These oxidants may have a direct effect
58 on the removal of pollutants absorbed, as it has been shown recently for acetaldehyde and
59 SO₂, which were effectively removed with in situ electrochemically generated oxidants
60 from the salts contained in the absorbent/electrolyte [17, 18]. However, it has been found
61 that the efficiency of the process can be improved by adding in the formulation of the
62 absorbent/electrolyte metal redox pairs that behave as catalyst, being continuously
63 regenerated in the electrochemical cell. Thus, silver (throughout the Ag(I)/Ag(II) redox
64 mediator pair) has been used for the removal of nitrogen oxides [19] [20], mixtures of

65 NO_x and SO₂ [21] and odorous substances such as CH₃SH and H₂S [22]. Nickel has been
66 used as electro-catalyst for the removal of halogenated substances such as C₂HCl₃ [23],
67 CF₄ [24] and CCl₄ [25] and for atmospheric pollutants such as NO [26] and N₂O [27].
68 Iron (as Fe (IV)/Fe (III) redox mediator pair) was used for the efficient removal of N₂O
69 [13]. Despite the significant results obtained with these metals, cobalt has become the
70 most promising precursor of oxidants within this category, and the Co(II)/Co(III) redox
71 pair has been highlighted in many recent publications [28, 29]. Thus, the generation of
72 aqueous Co(III) active catalyst favored the deodorizing of gases mixtures containing
73 CH₃SH, H₂S, NH₃, (CH₃)₃N and CH₃CHO [30, 31] or gaseous streams with a single
74 pollutant as H₂S [32]. On the other hand, the Co(II)/Co(I) redox mediator pair has been
75 used for the removal of C₂HCl₃ [33].

76 Besides the composition of the liquid used as absorbent/electrolyte, the transfer of the
77 pollutants from the gas phase to the absorbent/electrolyte is other of the most critical
78 aspects in this treatment technology, and the device used to optimize the contact between
79 the gas and liquid plays a fundamental role in reaching high pollutant removal rates.
80 Pioneers in this field have focused on the use of packed columns, where absorption is
81 promoted through the direct contact of moving gas and liquid streams (preferably in
82 countercurrent flow). The packed column works with the basic idea of providing a long
83 residence time (through a larger contact surface) between pollutants and the
84 electrolyte/absorbent and can be easily coupled with electrolyzers by recirculating
85 continuously the absorbent/electrolyte between both units. Obviously, there are many
86 other absorption technologies that can be integrated with electrochemical cells, such as
87 the spray columns and the centrifugal absorbers. Among them, jet mixers have shown
88 outstanding efficiencies throughout the production of tiny bubbles of the polluted gases
89 into the absorbent/electrolyte. In this case, venturi effect is used to promote the interaction

90 between the gaseous contaminant and the absorbent/ electrolyte and it has demonstrated
91 high efficiencies in the operation in discontinuous mode [34]. A recent comparison
92 between the jet absorber and the packed absorption column for the electro-scrubbing in
93 discontinuous mode of PCE from gas streams, confirmed the high dependence of process
94 efficiency on the absorption technology used [35].

95 In this work, we are going further by developing two electro-scrubbing installations that
96 operate in continuous mode, aiming to determine in more realistic conditions which of
97 the two absorption technologies fits better with the electrochemical technology. Another
98 important insight is to understand the effects of the addition of the mediator pair Co
99 (II)/Co (III) on the performance of the electro-scrubber devices when PCE is fed to the
100 treatment in continuous mode.

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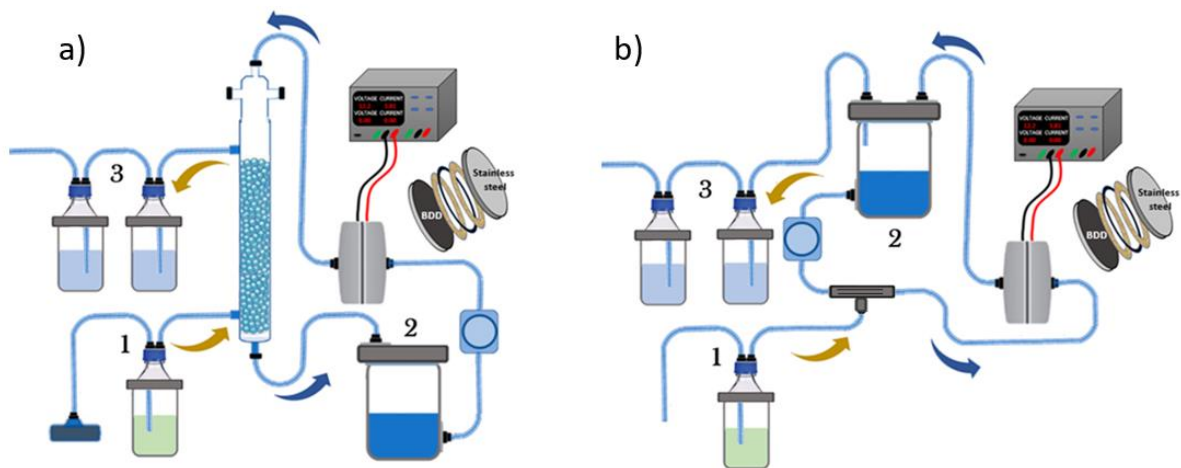
102 **2. Materials & Methods**

103 **2.1. Chemicals**

104 Cobalt (II) acetate 4-hydrate (99%) was purchased from Panreac (Barcelona, Spain) and
105 used as received. Perchloroethylene (C_2Cl_4 > 99%) was purchased from a.r. Sigma-Aldrich
106 (Darmstadt, Germany). Sulfuric acid (98%) and Hexane (HPLC Grade) were supplied by
107 Scharlau (Barcelona, Spain). Helium and nitrogen (Al Air Liquide España, S.A) were
108 used in gas chromatography and helium was filtered by a Hydrocarbon Cartridge Filter
109 (Thermo Fisher Scientific) before its use. Double deionized water (Millipore Milli-Q
110 system, resistivity: 18.2 M Ω cm at 25°C) was used to prepare all solutions.
111 Perchloroethylene solutions were obtained in a closed volumetric flask after a softly
112 stirring with a magnetic bar overnight.

113 **2.2. Experimental setup**

114 The experimental lab scale set-ups (shown in Figure 1) consisted of two installations
115 working in continuous mode with different absorber devices: a) packed column electro-
116 scrubber and b) jet mixer electro-scrubber. Both systems consist of three fundamental
117 sections: 1- Perchloroethylene solution tank, where the gaseous polluted flow is produced
118 by stripping with air 2- Absorber system: consisting of an electrolyte-absorbent storage
119 tank (glass tank with a thermoregulated water jacket) and an undivided flow
120 electrochemical cell, where the pollutant is retained in the absorbent/electrolyte and
121 destroyed electrochemically directly on surface of electrodes or mediated by oxidants
122 produced on these surfaces and 3- Absorption tanks with hexane to collect residual PCE
123 escaping from the electro-scrubbers.



124

125 Figure 1. Experimental setup: a) packed column electro-scrubber; b) jet mixer electro-
126 scrubber. (1) pollutant solution tank, (2) electro-scrubbing system and (3) collection
127 tank of pollutants escaping from the electro-scrubbing.

128 An aqueous solution with 150 mg L^{-1} of PCE was placed in a glass bottle and its
129 volatilization was induced to generate a stream of contaminated gas (flow rate of 6.0 L
130 h^{-1}) by two different configurations: in the installation a) bubbling with an aquarium
131 aerator, and in the installation b) bubbling with a venturi system. On the other hand, the

132 liquid stream was generated with a peristaltic pump model Percom N-M II with a flow
133 rate of 6.0 L h^{-1} in the installation a) and with a Rover Pompe BE-M10 bidirectional self-
134 priming electric pump (maximum flow 250 L min^{-1}) in the installation b). In the first
135 case the stream of gas contaminated with PCE flows through the absorption column, made
136 of glass with 0.5 m length and an inner diameter of 500 mm, where 0.4 m were packed
137 with high-quality borosilicate glass spheres ($8 \text{ mm} \pm 0.75$). The absorber-electrolyte (0.05
138 M of sulfuric acid with or without the addition of 8.49 mM of Co (II) sulfate passes
139 through the absorption column in a descending and countercurrent manner to the gas flow,
140 dragging the pollutant transferred from the gas phase, that is recirculated through the
141 electrochemical cell where it is degraded. In the second case, the jet-mixer scrubber
142 (venturi made of PVC with a throat diameter of the jet 4.23 mm) operating in horizontal
143 position, generates air bubbles capable of favoring the contact surface area (and hence the
144 mass transfer kinetics) of the contaminant to the liquid phase. Finally, in both installations
145 the residual gas stream is passed through hexane tanks to trap the perchloroethylene that
146 was not retained or destroyed in the electro-scrubber. All the processes were carried out
147 at 25° C and atmospheric pressure conditions. The commercial electrochemical cell
148 (DiaCell®) used was supplied by Adamant Technologies (La Chaux-de-Fonds,
149 Switzerland), equipped with boron-doped diamond (Si/BDD) as anode and stainless steel
150 as cathode. Additional details can be found in a previous work [34].

151 **2.3. Experimental procedure**

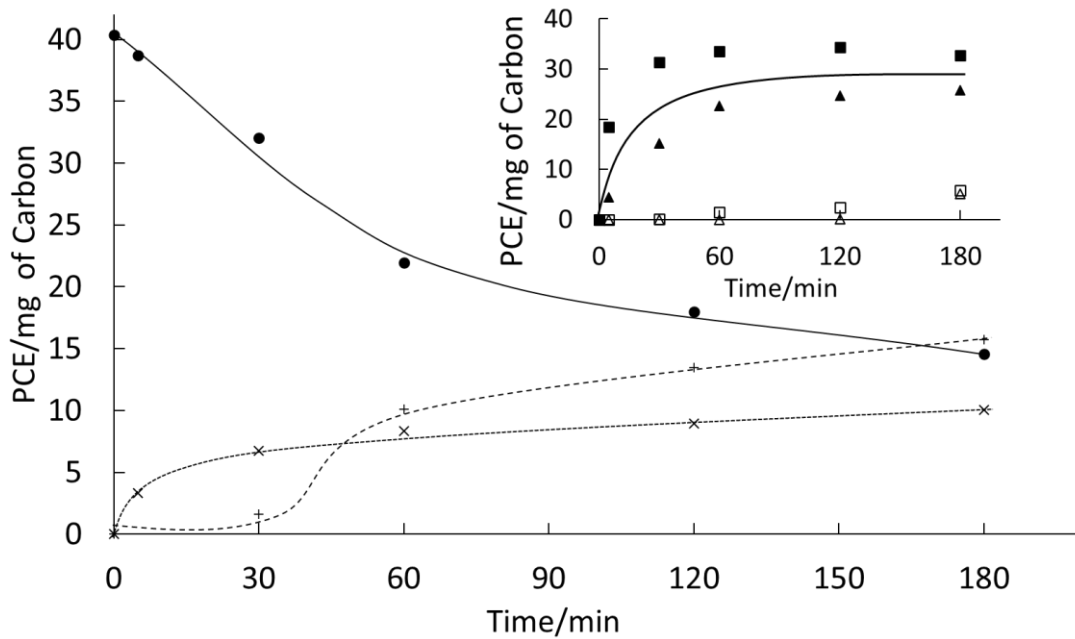
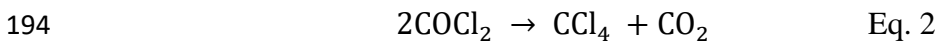
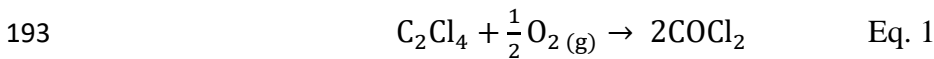
152 Experiments were performed for 180 min and samples from liquid and gas phase were
153 collected at specified time intervals. Gas chromatography (GC) and High-Performance
154 Liquid Chromatography (HPLC) were used to monitor the evolution of PCE degradation
155 and intermediates. The concentrations of PCE in the gas phase and residual PCE collected
156 in hexane were analyzed by Gas Chromatography Electron Capture Detector (GC-ECD)

157 (Thermo Fisher Scientific) using an TG-5MS capillary column (30 m × 0.25 mm). Liquid
158 and gas samples were taken from sampling ports located in the three tanks shown in the
159 figure 1. Liquid aqueous samples were transferred to a glass vials and for gaseous samples
160 a volume of 5 mL was dissolved in 3 mL of hexane using glass vials with cap and PTFE
161 Septa to guarantee that no losses of gas occur during the gas bubbling. Next, to separate
162 the organic phase, a vortex stirrer was used to promote the mass transference of pollutants
163 to the hexane, then a centrifugal pump was used to separate aqueous and organic phases
164 (3 min at 4000 rpm) and finally, samples were filtered with 0.22 μm nylon filters and
165 transferred to appropriate vials for each GC analysis. Organic samples taken from the
166 hexane tanks, after filtering were directly transferred to a 2 mL for the analysis into GC.
167 To analyze carbon tetrachloride in aqueous solvent a Jasco HPLC LC-2000 with a PDA
168 MD-2018 Detector (Jasco, Tokio, Japan) was used and measured without extraction
169 procedure. The mobile phase consisted of 100% of 0.1% phosphoric acid (flow rate of 1
170 mL min⁻¹). The detection wavelength used was 280 nm and the temperature of the oven
171 was maintained at 25 °C. Volume injection was set to 20 μL. Regarding to the analysis
172 of trichloroacetic acid and other by products (methyl chloracetate, ethyl dichloracetate,
173 ethyl trichloroacetate) was determined using a HPLC Agilent 1100 series (Agilent Tech.
174 Santa Clara, CA, USA) with a DAD detector set at 220 nm and 200 nm for the different
175 chloracetates. The ion exchange column used was Supercogel™ H Column with 30 cm ×
176 7.8 mm ID. Other operating conditions are as follows: the mobile phase, 1% phosphoric
177 acid (H₃PO₄); column temperature, 30 °C; flow rate, 0.8 mL min⁻¹; injection volume, 20
178 μL. More details can be found in previous works [34-36].

179 **3. Results & Discussion**

180 To start with, some experiments to confirm the volatilization rate of PCE was carried out.
181 In the figure 2, it is shown the changes in the concentration of PCE when no

182 electrolyte/absorbent was contained in the experimental electro-scrubber devices.
 183 Previously to any test, it was checked for sealing the system by operating at higher
 184 pressures than those used in this work. However, as seen, the amount of PCE released
 185 from the initial tank is not fully collected in the two sequential hexane tanks placed as
 186 absorption traps. In addition, also worth to notice that no PCE is flowing out of this trap,
 187 as it was measured in the inset of the figure 2 where it is shown the quantity in liquid and
 188 gaseous phase of PCE that it is recovered in the system. In the second tank, PCE detected
 189 is nil (except for the last point). Hence, there is a decrease in the total amount of PCE
 190 monitored and this must be explained in terms of the reactivity of PCE in wet gaseous
 191 phase, where it is known to be transformed into phosgene in a first step (Eq 1) and then,
 192 into carbon tetrachloride (Eq 2).



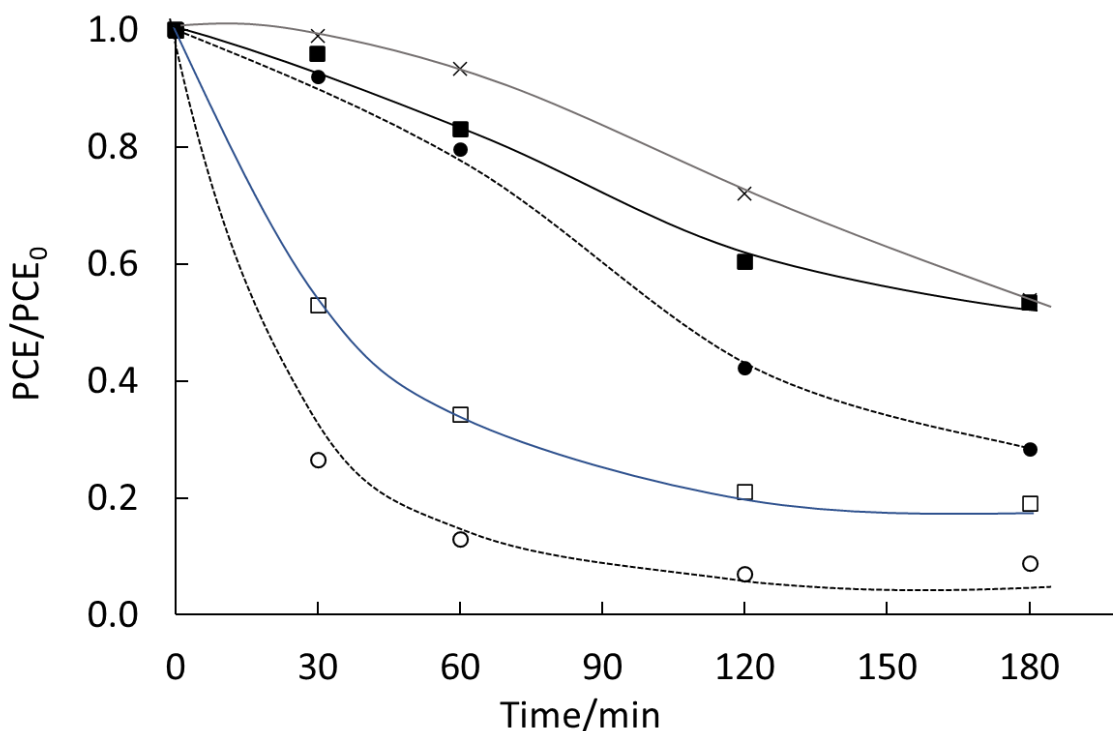
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196 Figure 2. PCE evolution in a preliminary test in absence of electrolyte/absorbent,
 197 circulating in the experimental electro-scrubber devices (gas phase PCE chemical

198 reactivity test), absorption tank (only gas phase) (●), hexane traps (x) and undetected
199 compounds (mass balance) (+). Inset: changes in the PCE with time in first (■) and second
200 (▲) hexane traps. Full points: liquid samples and empty points: gaseous samples. Influent
201 flow rate = 6 L h⁻¹. T= 20°C.

202 Based on the literature [37], this is a typical set of reactions occurring in wet gaseous
203 phase, being one of the hazards associated to the occurrence of PCE pollution in the gas
204 phase, because phosgene is even more hazardous than PCE and, in addition, it is well-
205 known its decomposition into carbon tetrachloride [38]. Hence, under the operation
206 conditions tested, PCE is not expected to be reduced and this trend must be considered in
207 the discussion of the effect of the different electro-scrubbers evaluated in this work.

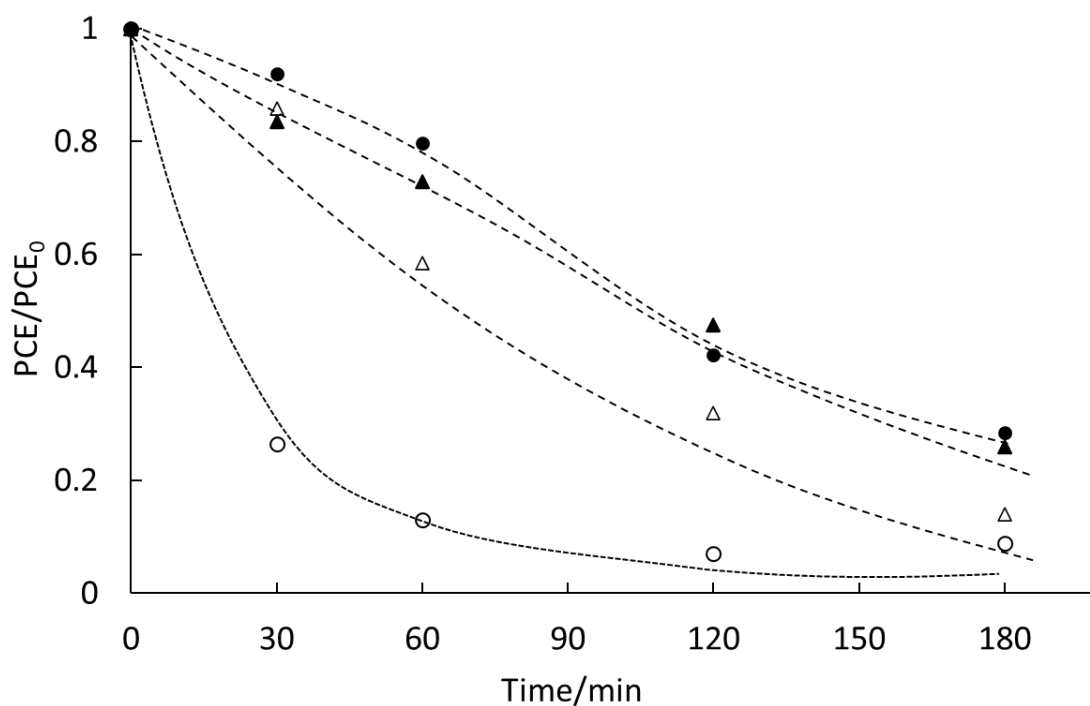
208 Figure 3 compares the reactivity of PCE during 3-hours experiments by scrubbing and
209 electro-scrubbing using a packed column and a jet mixer scrubber (considering the
210 amount of PCE in all the tanks available in the installation and the transformation of PCE
211 into phosgene). As seen, absorption into the absorbent/electrolyte allows to retain an
212 important amount of PCE contained in the influent and this amount is increased
213 importantly when electric current is applied, and the ~~scrubbers~~ scrubbing process
214 becomes into electro-scrubbing. Regarding absorption technologies, the jet-mixer system
215 overcomes the packed column, both in scrubbing and in electro-scrubbing modes,
216 allowing to remove more than 90% of the influent PCE with the jet electro-scrubber. This
217 confirms that the absorption process is promoted by jet-mixer and this could be related to
218 the production of tiny bubbles of the polluted gases into the absorbent/electrolyte because
219 of the high velocity in the throat of the jet-mixer. Another important point to be
220 highlighted from the operation of scrubber and electro-scrubber in continuous mode is
221 the stabilization of the total pollutant amounts in less than two hours.



222

223 Figure 3. PCE evolution *vs* time during the scrubbing (■,□) and electro-scrubbing (●,○)
 224 process with 0.05 M H₂SO₄ electrolyte, using the packed column (full points) and jet-
 225 mixer (empty points) scrubbers. (x) blank experiment with no electrolyte and no electric
 226 current. Operation conditions: $j=100 \text{ mA cm}^{-2}$; 6.0 L h^{-1} PCE/air flow.

227 In literature [30-32], it is reported a very positive effect in the efficiency of the electro-
 228 scrubbers by adding into the absorbent/electrolyte Co(II) salts, because they become
 229 precursors or electrochemical mediators of Co(III) [33]. As the generation of this
 230 mediator was previously confirmed [39], to verify this potential improvement in novel
 231 systems developed, Figure 4 focused on the effect of the addition of cobalt mediators with
 232 both electro-scrubbers. As observed, and opposite to what initially expected, the effect is
 233 not positive, but negative in the case of the jet-mixer and almost neutral in the case of the
 234 packed column electro-scrubber. The evolution of PCE during these experiments might
 235 be related to their reactivity in these physical conditions and the generation of
 236 intermediates could reduce the oxidation rate of this initial compound.

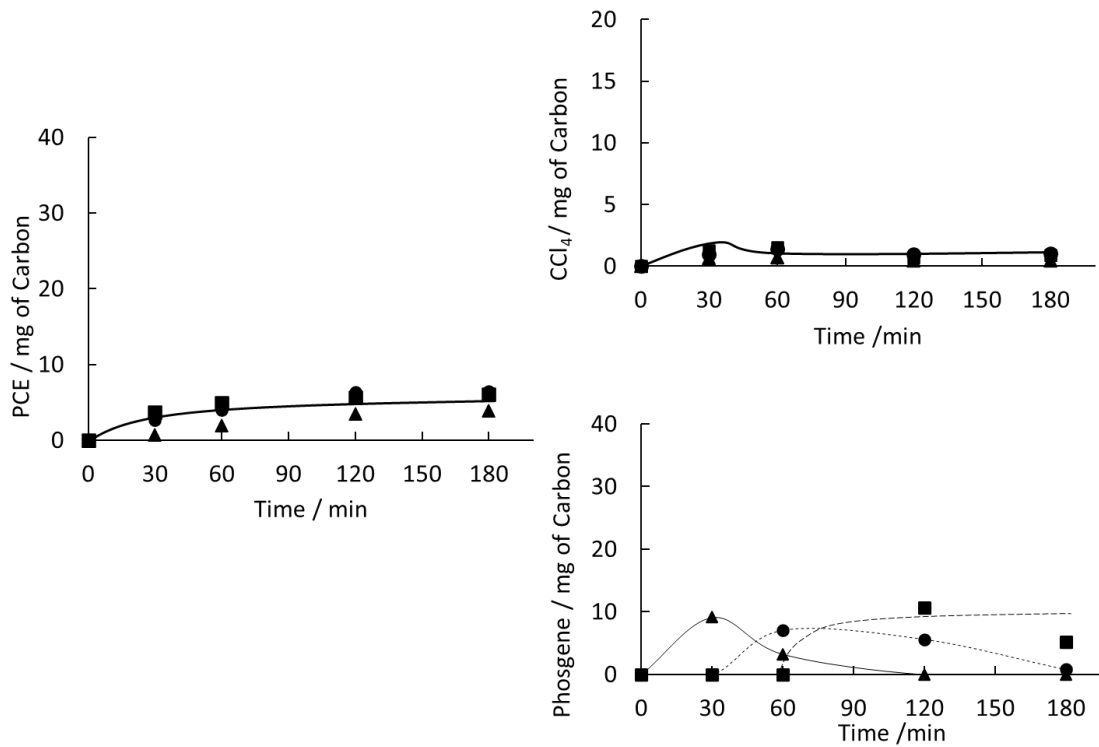


237

238 Figure 4. PCE evolution *vs* time during the electro-scrubbing with 0.05 M H₂SO₄
 239 electrolyte (●,○) and 0.05 M H₂SO₄ and 8.49 mM Cobalt (II) ions (▲,△) using the packed
 240 column (full points) and the jet-mixer (empty points) scrubber. Operation conditions:
 241 $j=100 \text{ mA cm}^{-2}$; 6.0 L h^{-1} PCE/air flow.

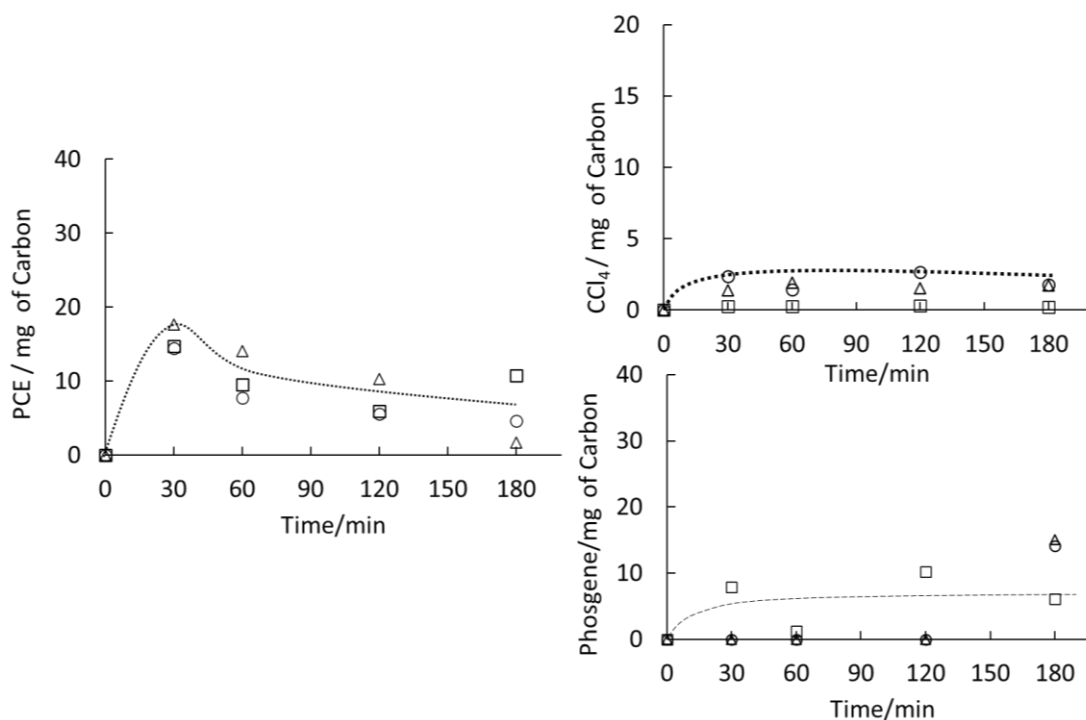
242 Figures 5 and 6 show the speciation measured (in mg of carbon equivalents) in the
 243 absorbent-electrolyte of the two electro-scrubbers tested in this work when operating as
 244 scrubbers and with the two absorbent/electrolyte formulations (with or without cobalt
 245 mediator precursors). Figure SM-1 shows some examples of an HPLC chromatogram to
 246 analyse CCl₄ and a GC-ECD chromatogram to analyse PCE from a liquid sample obtained
 247 during the experiments carried out with the jet mixer electro-scrubber using an acidic
 248 electrolyte with 8.49 mM Cobalt ions at 30 minutes. In comparing speciation, very
 249 different behavior can be noticed between both absorption technologies. Higher amounts
 250 of PCE are retained in the electrolyte when the jet mixer technology is used, which an
 251 initial increase followed by a decrease in the amount retained, that highlights the opposite

252 effects of a fast dissolution and the sequential degradation. This confirms again that jet-
253 mixer favors absorption process and that PCE is also electrochemically degraded.



254

255 Figure 5. Changes in the quantities of PCE, carbon tetrachloride and phosgene in the
256 absorbent-electrolyte during the scrubbing (■), electro-scrubbing with 0.05 M H₂SO₄
257 electrolyte (●) and electro-scrubbing with 0.05 M H₂SO₄ and 50 mM Cobalt (II) ions (▲)
258 using the packed column scrubber. Operation conditions: $j=100 \text{ mA cm}^{-2}$; 6.0 L h^{-1}
259 PCE/air flow.



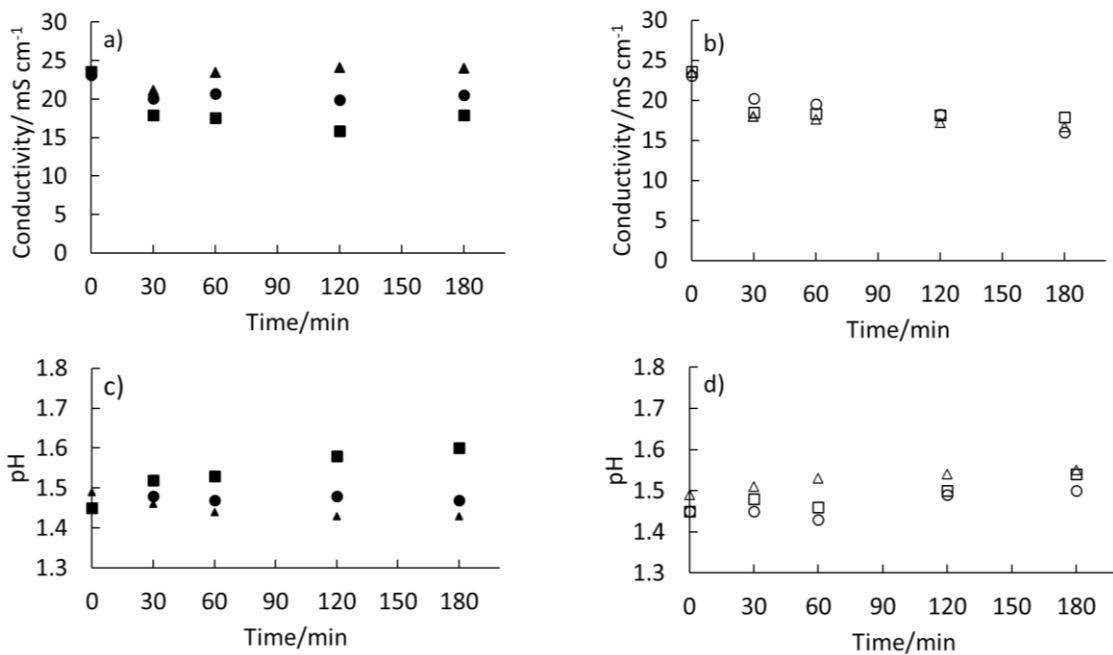
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261 Figure 6. Changes in the quantities of PCE, carbon tetrachloride and phosgene in the
 262 absorbent-electrolyte during the scrubbing (□), electro-scrubbing with 0.05 M H₂SO₄
 263 electrolyte (○) and electro-scrubbing with 0.05 M H₂SO₄ and 8.49 mM Cobalt (II) ions
 264 (△) using the jet-mixer scrubbers. Operation conditions: $j=100 \text{ mA cm}^{-2}$; 6 L h^{-1} PCE/air
 265 flow.

266 Regarding the formation of phosgene and carbon tetrachloride during the PCE treatment,
 267 this is in agreement with the reactivity of PCE observed in previous works [35, 36, 40] in
 268 which the system was operated in discontinuous mode: in wet conditions PCE is
 269 converted into phosgene (non-electrochemical process) which is very unstable and it is
 270 transformed into CCl₄ and TCA during electrolysis. Depending on the electrolysis
 271 conditions, they can be further oxidized to form carbon dioxide and chlorohydric acid as
 272 final products which indicates that pollution would be totally removed at the end of the
 273 process. It is important to notice that carbon tetrachloride is only relevant in the jet
 274 electro-scrubber (both with and without cobalt mediator precursors in the formulation of

275 the absorbent/electrolyte) where the amount of PCE absorbed is higher and a higher
276 reactivity is expected. Contrary, concentrations are negligible in the case of the packed
277 column scrubber and electro-scrubber and, also, in the case of the jet-mixer scrubber
278 (when no electric current is applied). Regarding phosgene, it is formed in the jet scrubber
279 and in the column scrubbers as well as electro-scrubbers. But it is important to notice that
280 it only appears in the two jet-mixer electro-scrubbers in the very last moment (its
281 formation seems to be prevented during most of the experimental time). In this later case,
282 it behaves as intermediate with a maximum in the time course of the amount contained in
283 solution.

284 Figure 7 shows a decrease in the ionic conductivity and an increase in the pH during the
285 operation of the tests, down and up, respectively, to a steady state value. Thus, regarding
286 pH, a slight increase can be observed in all cases from the initial value of 1.45, except for
287 the case of the Co-mediated packed column electro-scrubbers. This variation of the pH
288 may be related with the electrochemical reactivity of the system and it seems to have a
289 direct impact on conductivity, by reducing it, because of the lower quantity of protons.
290 The high conductivity (with initial values of 25 mS cm^{-1}) are associated to the
291 composition of the absorbent/electrolyte with 0.05 M of sulfuric acid.

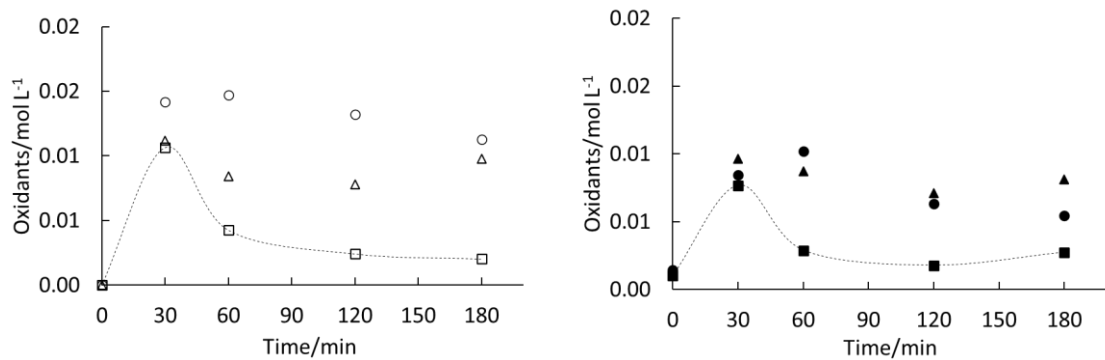


292

293 Figure 7. Evolution of pH conductivity in the electrolyte tank during the absorption (■,□),
 294 electro-scrubbing with 0.05 M H₂SO₄ electrolyte (●,○) and electro-scrubbing with 0.05
 295 M H₂SO₄ and 8.49 mM Cobalt (II) ions (▲,△) using a a) column absorber (full points)
 296 and b) jet-Venturi (empty points) with the time. Operation conditions: $j=100 \text{ mA cm}^{-2}$;
 297 $6.0 \text{ L h}^{-1} \text{ PCE / air flow}$.

298 Figure 8 shows how the production of oxidants is much higher with the jet mixer than
 299 with the packed column absorption system. With no electrochemical reaction (no current
 300 applied), the oxidants measured should be related to oxygen dissolved. As seen, it is
 301 produced a high generation at first which is then progressively reduced. In the case of the
 302 packed column, the initial generation of oxidants is lower and then, it is reduced faster
 303 down to a residual value. It was expected that the use of glass spheres to increase the
 304 contact surface would improve the oxidant production but according with results obtained
 305 this effect seems to be negligible. When electric current is applied, there is no decrease
 306 but stabilization in the concentration of oxidants and the highest production is observed
 307 for the jet-mixer electro-scrubber in solutions containing cobalt salts. In the case of the

308 packed column electro-scrubber, there are no differences between the oxidant
 309 concentrations monitored with the presence of the Co (II)/Co (III) in the acid electrolyte.
 310 Taking into account that the efficiency of the process in the removal of PCE does not
 311 seem to be related to the concentration of oxidants detected but neither the possible mass
 312 transfer limitations of the systems, these results may suggest that these oxidants have low
 313 influence on the degradation of PCE and indicates that degradation by other oxidants not
 314 accounted with this analytical technique because of their shorter lifetime (hydroxyl or
 315 sulfate radicals) should have higher influence to explain the results obtained.



316

317 Figure 8. Evolution of oxidant concentration (mol L⁻¹) vs time in the electrolyte tank
 318 during the scrubbing (■), electro-scrubbing with 0.05 M H₂SO₄ electrolyte (●) and
 319 electro-scrubbing with 0.05 M H₂SO₄ and 8.49 mM Cobalt (II) ions (▲) using a packed
 320 column absorber (full points) and jet-mixer (empty points). Operation conditions: $j=100$
 321 mA cm⁻²; 6.0 L h⁻¹ PCE/air flow.

322

323 4. Conclusions

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

- 325 • PCE can be removed from air streams using electro-scrubbers. Removal is
 326 efficient and higher than 90% within the experimental conditions applied.

- 327 • Under the continuous mode electro-scrubbing conditions studied in this work, the
328 addition of the mediator metal pair does not improve the PCE removal efficiency
329 in neither of the two scrubbers used. In fact, a negative effect is observed when
330 working with the packed column.
- 331 • Retention of PCE by absorbents is important; uncontrolled reactivity to phosgene
332 is also relevant.

333

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340

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