1   **Treatment of toluene gaseous streams using packed column electro-**

2   **scrubbers and cobalt mediators**

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9

10   **Abstract**

11   An absorption system has been combined with an electrochemical cell to treat a gaseous

12   stream polluted with toluene. Toluene retention in 3 hours operation tests was higher

13   than 87.0% in the case of treating the gaseous stream with single scrubbing, 97.0% in

14   the case of using electro-scrubbing and over 99.0% in using cobalt-mediated electro-

15   scrubbing. It was found that the amount of toluene that escapes from the electro-

16   scrubber does not only depend on the flow rate but also on the current density and the

17   presence of the metallic mediator. The higher are the current densities, the greater are

18   the amount of electrochemically degraded toluene. In addition to the mediating effect

19   of the metal, the results also suggest an important participation of the redox

20   sulfate/persulfate pair in the degradation of toluene. Only methyl-cyclohexane (at very

21   low concentrations) is observed as intermediate, despite carboxylic acids were also

22   initially expected. The formation of this compound can be explained in terms of the

hydrogenation of toluene. The very low concentrations absorbed and the very high current densities support the occurrence of an electrochemical cold combustion in the electro-scrubber.

Graphical abstract
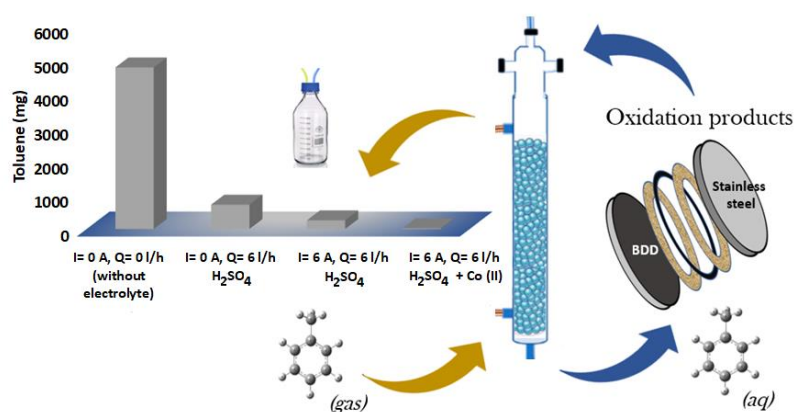
Keywords

Electro-absorption; polluted air stream; toluene; VOCs removal; metallic mediators

Highlights

- Toluene was efficiently removed from gases using the electro-scrubbers.

- Low faradaic efficiencies because of low solubility of toluene in the absorbent.

- Mediated electro-oxidation mechanisms promoted by the presence of cobalt.

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Introduction

The accelerated growth of the industrial and transport sector has importantly increased air pollution, not only with atmospheric pollutants but also with their associated massive emissions of volatile organic compounds (VOCs) [1]. Because of that, in recent decades, removal of VOCs from air has been of greatest concern to the scientific community and although important technological advances have been made, there are still many challenges to be overcome in the near future. Thus, improvements in the efficiency of already existing technologies and development of new promising technologies are becoming a challenge for researchers all around the world. In this context, the main in-use technologies for the abatement of VOCs emissions, exhaustively researched in recent years, include:

- Destruction techniques such as thermal oxidation [2], catalytic oxidation [3], and biological treatment [4] and

- Recovery techniques such as condensation [5], adsorption [6], membrane separation [7] and absorption [8, 9].

Among all technologies, it is worth to focus on absorption. This technology can also be classified as destruction technique if it is properly combined with a suitable destruction technology, where absorption behaves as a concentrator of pollutants. It is based on the contact of the polluted gas stream with a liquid solvent in a device designed to provide suitable contact surface areas between phases, to facilitate mass transfer from the gas to the absorbent liquid [8]. However, this absorbent liquid becomes a secondary wastewater and needs to be regenerated [10] either by recovering the pollutant in case this recovery is cost-effective, or by destroying it when recovery is not economically

61 viable. Among the destruction technologies, electrochemical advanced oxidation

62 processes (EAOPs) are gaining attention, because of the high efficiencies and

63 adaptability to the removal of many types of pollutants, including not only VOCs but also

64 odor substances and atmospheric pollutants ([11-13]).

65 These EAOPs have been exhaustively evaluated for the treatment of wastewater during

66 the last two decades, with thousands of scientific works pointing out their advantages

67 over other advanced oxidation processes regarding the avoidance in the formation of

68 refractory species and the much lower operation and investment cost. It has also been

69 highlighted the suitability of their combination with other technologies such as light

70 irradiation [14] or ultrasound applications [15], which often gives chance to remove

71 pollutants more efficiently. Use of special coatings for the anode and the cathode, such

72 as the very efficient conductive diamond anodes and Vulcan carbon doped with

73 platinum cathodes, are key to obtain high efficiencies in the production of oxidants [16-

74 18]. Mechanical design of the cell is also a key to improving mass transport and

75 consequently the kinetics of the process.

76 Recently, the combined application of electrochemical treatment with absorption

77 (electro-scrubbing) has been found to be a very interesting and appropriate application

78 ([19-36]). The low concentration of pollutant transferred from the gas to the liquid

79 (limited not only by the transfer rate but also by the equilibrium solubility) is a real

80 handicap that forces to look not only for the most efficient reactor design and electrodes

81 composition but also for a suitable formulation of the absorbent which maximizes the

82 dissolution and promotes the formation of oxidants (when acting as electrolyte in the

83 electrochemical process) [22, 29, 31, 34]. In this context, the addition of precursors of

4

84 mediators (like ions Ag(I) or Co(II) [24, 28, 36, 37] has demonstrated to be crucial and to

85 have a huge impact on the efficiency of the removal of pollutants. The role of the

86 mediators seems to be outstanding, but there are many inputs to be considered for a

87 proper performance, being one of the speciation of the metallic ion in solution, which

88 as indicated in Pourbaix diagram of cobalt species reported in the literature is rather

89 complex [38].

90 Considering this background, in this work, it is going to be evaluated the operation of a

91 process that combines absorption, one of the main technologies for removal of gaseous

92 pollutants, with anodic oxidation, one of the most popular electrochemical techniques

93 for effluent decontamination, with the purpose of removing toluene from a gaseous

94 stream. This electro-absorption technology will be compared in terms of the absence

95 and presence of cobalt mediator precursor in the electrolyte/absorbent, Toluene was

96 used as a contaminant because this compound is one of the most common volatile

97 organic compounds, which is used as a solvent and fuel additive and is listed as a strong

98 carcinogen by the World Health Organization [39], so many recent studies [40-55] have

99 focused on its degradation.

100 **Materials & methods**

101 **Reagents.** Toluene was purchased from Servier Laboratories S.A. (Toledo, Spain).

102 Sulfuric acid (98%) and Hexane (HPLC Grade) were supplied by Scharlab (Barcelona,

103 Spain). Cobalt (II) sulphate 7-hydrate (99%) was purchased from Panreac (Barcelona,

104 Spain). Double deionized water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at 25º

105 C) was used to prepare the solutions, all reagents were used as received.

106   **Experimental setup.** The experimental system is shown in Figure 1. For each experiment

107   0.1 L of toluene were placed in a glass bottle (1) and its volatilization to generate a

108   stream of contaminated gas was induced by bubbling with an aquarium aerator (2) at

109   different flow rates (6.0, 12.0, 18.0 and 30.0 L h^{-1}). On the other hand, the liquid stream

110   with the electrolyte/absorbent was recirculated with a peristaltic pump model Percom

111   N-M II (5) with a flow rate to 6.0 L h^{-1}. The promoted stream of gas contaminated with

112   toluene flows through the packed column (6), fill up with glass spheres (diameter 5 mm),

113   which provide a wide contact surface to favor the mass transfer of the contaminant to

114   the liquid phase. Simultaneously, this electrolyte/absorbent (0.05 M of sulfuric acid,

115   with or without the addition of 500 mg L^{-1} of Co (II) ions) stored in the

116   electrolyte/absorbent tank (4) passes through the packed column in a descending and

117   countercurrent manner to the gas flow, dragging the pollutant transferred from the gas

118   phase. Then, it is recirculated through the electrochemical cell (3) where it is degraded.

119   Finally, the residual gas stream passed through two hexane tanks (placed in series) (7)

120   to be trapped the remaining toluene.
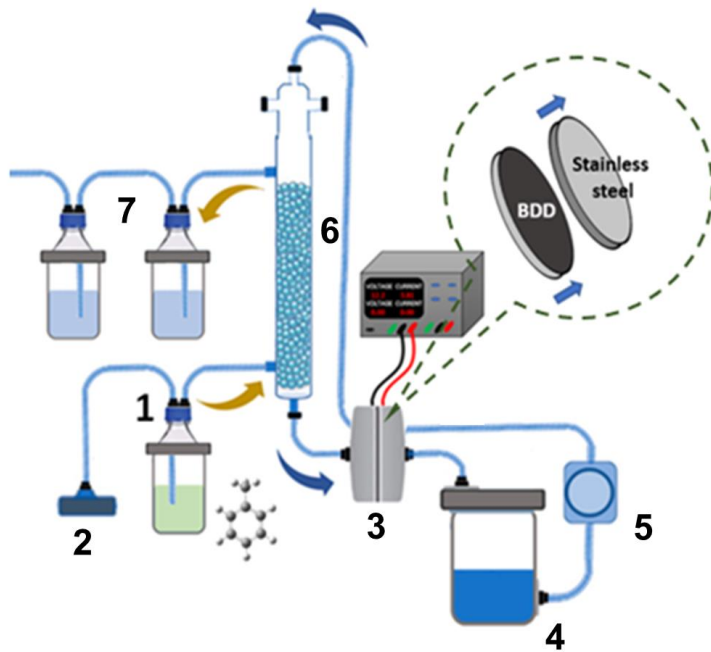
Figure 1. Experimental setup (1) Contaminant solution tank, (2) aquarium aerator, (3) electrochemical cell, (4) electrolyte/absorbent tank, (5) peristaltic pump, (6) glass packed column and (7) storage tank to collect residual toluene that escapes from the electro-scrubbing process

The electrochemical cell employing during the electro-scrubbing treatments was a DiaCell® (Adamant Technologies, Switzerland), with an Si/BDD anode (effective area of and stainless steel as a cathode (78.6 cm^2). The separation between the electrodes was 10 mm and the boron content in the anodic coatings was 500 ppm[20].

Experimental procedure. Experiments were performed for 180 min and liquid and gaseous samples (1.0 and 5.0 cm^3 respectively) are taken for chromatographic analysis. These samples are placed in 10 cm^3 flasks to be diluted in water and/or hexane (2.0 cm^3).

133   The flasks are shaken vigorously using a vortex shaker and then the organic phase is

134   separated for analysis by GC. For their part, aqueous samples are analyzed by liquid

135   chromatography (HPLC). The concentrations of toluene in the gas phase and residual

136   toluene collected in hexane were analyzed by gas chromatography with a flame

137   ionization detector (GC-FID). Helium and nitrogen were purchased from Al Air Liquide

138   España, S.A. An SPB-5 fused silica capillary column (30m x 0.25mm x 0.25μm film

139   thickness) was used, the carrier gas flow rate (helium) was 1 mL min^{-1}. The make-up gas

140   was nitrogen (35 mL min^{-1}) and the operating temperatures were: injector, 250 °C;

141   detector, 300 °C; and oven, with a temperature program of 40 °C (5 min), 10 ºC min^{-1}

142   (120 ºC) and 5 min. To construct the calibration curves, different amounts of toluene

143   were added in hexane and the samples were analyzed by GC/FID, evaluating the signal

144   obtained with a retention time of 6.5 minutes. The intermediates and the toluene in the

145   electrolyte-absorber were determined by liquid chromatography using an Agilent 1100

146   series (Agilent Tech. Santa Clara, CA, USA) chromatograph with a UV-Vis detector set at

147   210 nm. A Gemini 5U C18 110A column was used in the temperature of 25ºC. The mobile

148   phase was 70/30 water-acetonitrile at a flow rate of 0.8 mL min^{-1} and the injection

149   volume was 20 μL. To determine the total oxidants concentration, it was used the

150   Method I^-/I_2., which consists of a colorimetric titration. By means of this technique, it is

151   possible to determine all the oxidant species that are in the solution that oxidize the

152   iodide ion to molecular iodine. Experimental procedures and reagents were described

153   by [56]. Potassium iodide (1.0 g) is added to a fixed volume of sample (10 ml) which,

154   when reacting with the oxidizing species, generates free iodine. The solution is then

155   acidified with 20% sulfuric acid and the free iodine is titrated with a solution of sodium

156   thiosulfate (0.001 N), using starch as an indicator.

Results & Discussion

Figure 2 compares the toluene retained in the two sequential hexane absorber traps, placed at the outlet of the experimental device, after passing an air flow of 6.0 L h^{-1} throughout a toluene solution for 3 hours to strip toluene and simulate a gaseous stream of this pollutant.
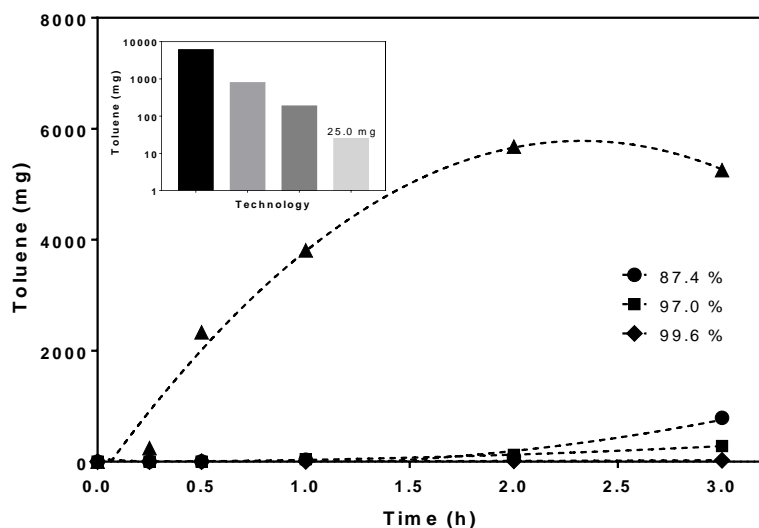
Figure 2. Toluene escaping from the experimental device after 3 hours of passing 6 L h^{-1} of air through contaminant solution tank. (▲) no absorption; (●) absorption; (■) electro-absorption at 6A; (◆) Co mediated electro-absorption at 6A. Inset: comparison of final concentrations in semi log plot.

As it can be seen, retention of toluene in the electrolyte/absorbent is higher than 87.0%. In addition, comparing bare absorption with electrochemically assisted scrubbing at 6.0

170 A, the effect of the electrochemical treatment can be clearly observed with a reduction

171 in the concentration of 97.0 % in the electrolyte containing only sulfate and 99.6% in the

172 case of the electrolyte containing cobalt mediators. For the sake of clarity, final values

173 reached at the end of the tests are compared in semilogarithmic plot in the inset of the

174 Figure, where it can be highlighted the efficiency of the electrochemically assisted

175 absorption treatment for this gas for which only 25 mg escapes.

176 The amount of toluene that escapes from the electro-scrubber does not only depend on

177 the flow rate but also on the current density and presence of cobalt mediators, as shown

178 in the next figures 3 and 4, respectively.

179 Figure 3 informs that, for an operation current intensity of 6.0 A, the system is very

180 efficient in the removal of the toluene up to 6.0 L h^{-1} (equivalent to the smallest amounts

181 of toluene escaping from the system shown in the figure), but the quantities of toluene

182 removal at higher flow rates are much lower (large amounts of toluene escaping from

183 the installation). It is important to take in mind that 6.0 A is equivalent, for a 100%

184 current efficiency, to the production of 671.5 mmol of electrons in 3 hours (considering

185 Eq. 1).

186

187 $$n = \frac{It}{F} \hspace{4cm} (Eq. 1)$$

188

189 where n is the amount of substance released (moles of electrons), I is the intensity of

190 electric current (in Amper), t is the time (in seconds) and F is the Faraday constant

191 (96500 C mol^{-1}).

10

192

The amount of toluene which enters the system during the 3 hours at 6.0 L/h is 68.17 mmol (data obtained by chromatographic method), which needs 2454.4 mmol of electrons (considering 36 mol e$^-$/mol toluene) for total oxidation (considering Eqs. 2-4). This means that if only a direct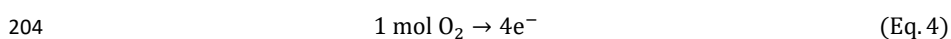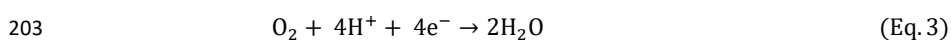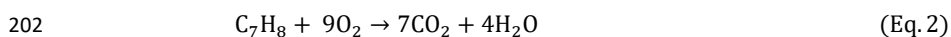 electronic transfer were carried out, the limiting reagents are electrons generated. Thus, a good adjustment of the operating conditions of the process is required in terms of promoting oxidant species that act as mediators in the removal of the contaminant and it is also important to relate the influence of the inflow gas flow on the toluene that escapes from the device with the removal of toluene from the gas stream.

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \qquad (Eq. 2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (Eq. 3)$$

$$1 \text{ mol } O_2 \rightarrow 4e^- \qquad (Eq. 4)$$

Thus, with 3.0 L h^{-1} the removal is almost complete (99.6% with a release of only 25.35 mg) and at 6.0 L h^{-1} seems to be in the admissible operation limit, with an exhaustion of 97.0%. This value falls to 84.4% a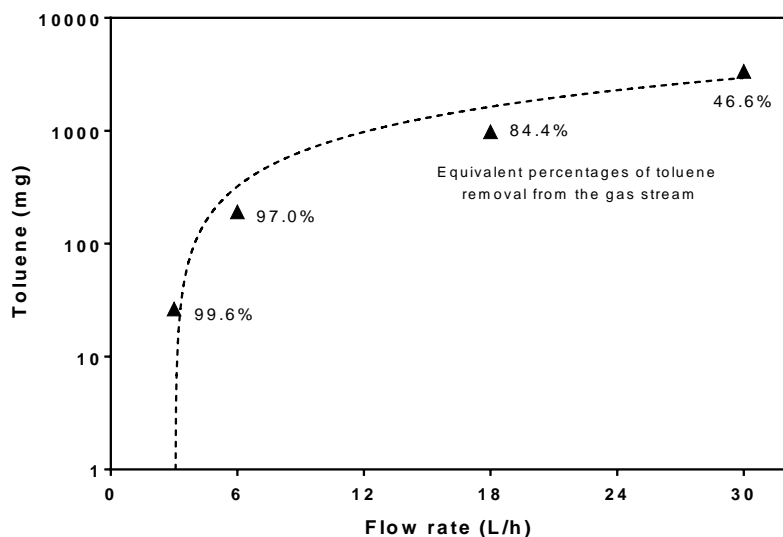t 18.0 L h^{-1}. Because of that, the flow rate of 6.0 L h^{-1} is going to be used for comparing the effect of current intensity applied and presence of cobalt mediators.

211

Figure 3. Influence of influent gas flow rate on the toluene escaping from the electro-scrubber device after 3.0 hours of operation at 6.0 A.

in Figure 4, where it can be seen that the higher is the current applied, the higher is the amount of toluene degraded electrochemically with faradaic current efficiencies (if considering one electron transfer) ranging from 0.6 to 4.0%. Low values of the faradaic efficiencies can be explained in terms of the very low concentrations of toluene dissolved into the electrolyte/absorbent, which made the direct transfer processes very inefficient. It is important to indicate that efficiency is much higher under the addition of Co ions, especially at the highest current density. This highlights the relevance of the mediated electrooxidation mechanisms in the performance of electro-scrubbers, because in non-mediated controlled electrochemical processes, efficiencies do not increase but decrease with the increase in the applied current intensity. So, it is marked both by the catalytic activity of the metal itself in the degradation of organic matter [57]

Comentado [FE2]: Cálculo

12

226 and by its contribution to the generation of sulfate radicals ($SO_4^{\bullet-}$), allowing a permanent

227 regeneration of oxidizing species [58, 59]. In the case of homogeneous metal activators,

228 the cobalt ion is specified as effective for the activation of peroxymonosulfate, since

229 these species can act as electron donors for the formation of the $SO_4^{\bullet-}$[59]. On the other

230 hand, the increases in the amount of toluene removed, observed in the absence of

231 cobalt ions indicates that the redox pair sulfate/persulfate may also be playing a very

232 important role in the degradation of toluene. Anyhow, this increase is much lower than

233 that observed with cobalt ions, indicating that the addition of this oxidant precursor has

234 a positive effect associated to the promotion in the mediated electrooxidation

235 mechanisms [58].

236 Advanced oxidation processes based on ($SO_4^{\bullet-}$) are known to offer efficient results due

237 to their comparable oxidation potential (2.5–3.1 V versus NHE) with respect to $^{\bullet}OH$

238 radicals and their selectivity and efficiency to react with aromatic organic compounds.

239 In addition, the sulfate radical has a half-life period higher than the hydroxyl radical,

240 which makes it highly competitive for the degradation of toluene absorbed in the

241 electrolyte [58, 60].

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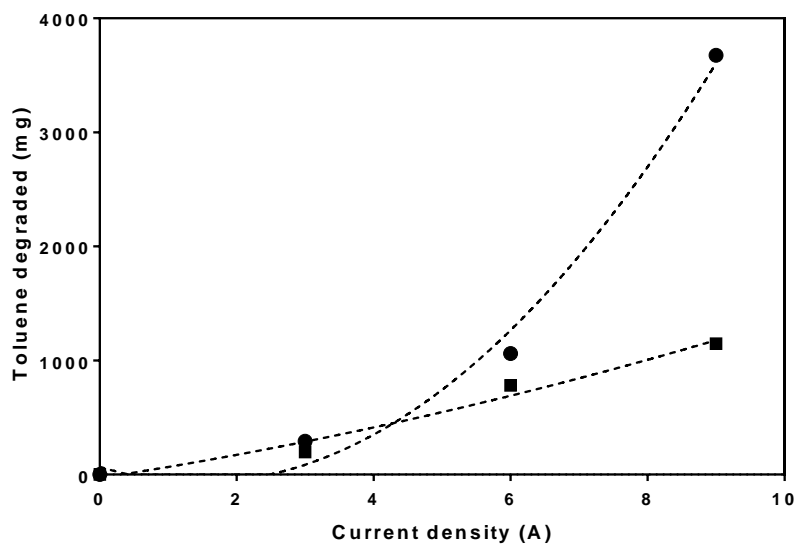
Figure 4. Influence of the current intensity applied on the amount of toluene degraded

electrochemically after 3.0 h in an electro-scrubber fed with 6.0 L h^{-1} (■) no Co mediator

(●) Co mediator. Inset: faradaic current efficiency for an electron transfer of 1.

Comentado [FE3]: No tengo estos datos para graficar

The low concentrations of toluene dissolved in the electrolyte/absorbent are confirmed

in Figure 5, which shows that even at the highest flow rate, this value is below 120 mg

L^{-1}. Theoretical solubility of toluene in distilled water is 562.9 ± 9.6 mg L^{-1} at 20ºC and it

is known to decrease with the presence of salts (as it is the case in the present study),

where it falls down to values as low as 144 mg L^{-1} in solution with a salt concentration

of 3 M in NaCl or to 257.3 mg L^{-1} in solutions of 0.6 M in K$_2$SO$_4$ [61].

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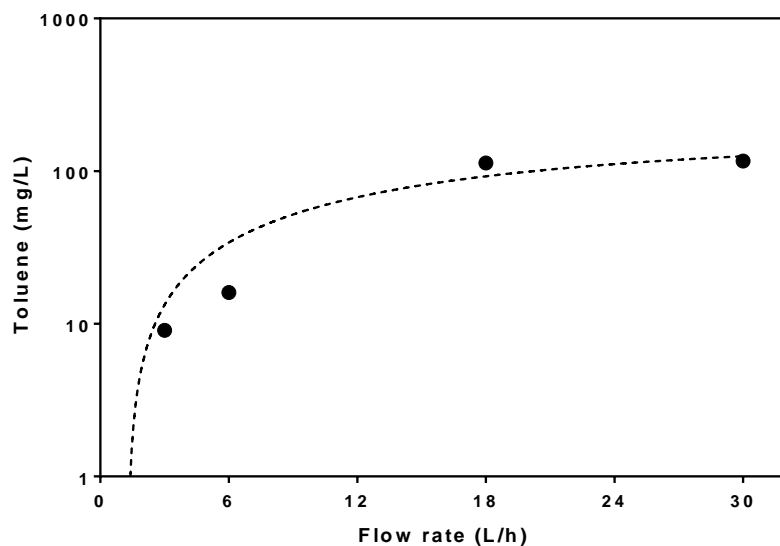
Figure 5. Influence of influent gas flow rate on the dissolution of toluene in the electrolyte of the electro-scrubber during operation at 6.0 A (steady state value reached).

In addition, in those studies in which the solubility was tested, liquid toluene was mixed with liquid water, which is a much easier way to dissolve toluene than from the absorption of gas in which toluene is carried by air. Considering that the cells used in the electro-scrubber are DiaCell®, with a COD limit around 53.0 mmol L^{-1} [62, 63] and the assumption of linear decrease in the efficiency [64, 65] according to the ratio concentration/concentration limit, values obtained are as expected in the case of the sulfate containing electrolyte. In this case, a maximum efficiency of 2.4 % (1.3 mmol Toluene/53.12 mmol) is expected for a direct oxidation process. The higher values obtained, when cobalt salts are added to the electrolyte/absorbent, can be explained because of the improvement associated to the Co (III) mediators [24, 25, 36, 37].

Comentado [FE4]: cálculos

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Figure 6 shows the oxidants generated in the system capable to oxidize the iodide as a function of the current intensity applied after three hours of treatment. As seen, the higher is the current the higher is the production of oxidants. However, opposite to what it could be expected, the concentration of oxidants formed in the system with cobalt seems to be much lower, according with the method used to detect them. Initially, it is important to note that in an acidic environment, the effect of oxygen is enhanced. Thus, the oxygen dissolved in the electrolyte (the carrier of toluene is air) can explain the high value detected when no current is applied and with the course of electrolysis in the system in the absence of cobalt, the persulfate species electrogenerated from the electrolyte may be the main responsible for the linear evolution observed with increasing the current density; on the other hand, the air (carrier gas) causes the oxygen to continue to dissolve in the electrolyte/absorbent, also contributing to the increase in the concentration of oxidants. However, in the case of the cobalt-containing electrolyte, there is no production of oxidants in time zero and with electrolysis, the increase in the production of oxidants over the current density is much smaller. In solution, cobalt (II) ions generate a stable aqueous compound $Co[H_2O]_6^{2+}$ that can reduce the effect of dissolved oxygen, which would explain the absence of oxidants without electrolysis. On the other hand, with the application of current it is suggested that Co (III) mediators participate in the oxidation of toluene as well as in the improved production of other oxidizing species, not accounted for with this analytical technique due to their shorter useful life (such as hydroxyl radicals or sulfate radicals), which justifies the low results obtained and would be agree with the best toluene removals reflected in figure 2 (knowing that the oxidizing power of hydroxyl radicals and sulfate radicals is higher than

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290 that of persulfate anion) hydroxyl radicals, it is known that they are generated, but their

291 high reactivity in the media make their detection a process rather complex [66, 67].

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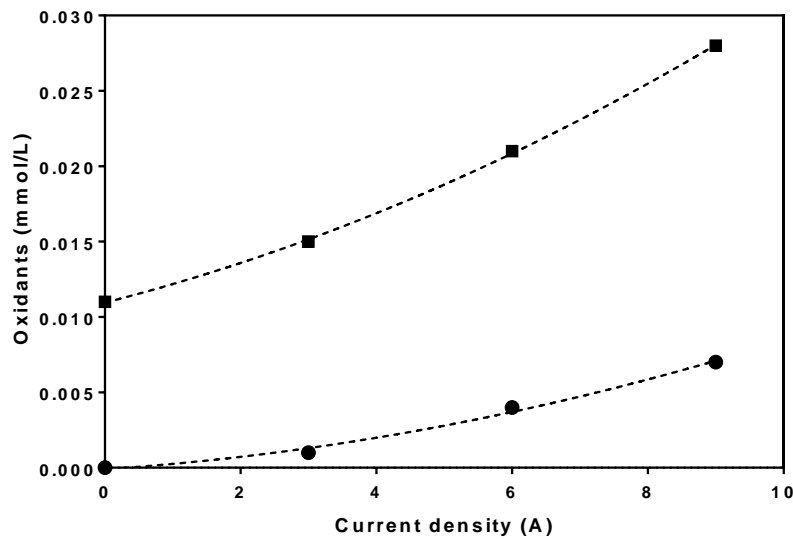
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294 Figure 6. Influence of the current intensity applied in the concentration of oxidants

295 produced in an electro-scrubber operated at 6.0 L h^{-1} (■) no Co mediator (●) Co

296 mediator.

297 Regarding intermediates, as shown in Figure 7, by GC-MS, only o-methylphenol p-

298 methylphenol and methyl-cyclohexane are observed in the electrolyte/absorbent of the

299 electro-scrubber. The two isomers are observed in higher concentrations during the

300 absorption tests than in the electro-absorption tests, indicating that they are not

301 reaction intermediates, but they are also coming from the raw industrial toluene solvent

302 stripped. As seen a similar degradation is obtained in the presence and in the absence

303 of Co, which is around 50% for the orto-isomer and 21% for the para isomer. However,

304 the evaluation of organics along the process indicate that are refractory compounds

305 because once these compounds are generated, their removal is very complex (the

306 concentration is rather constant along the treatment). Thus, further works related with

307 the improvements of these installations should be consider the novel design of electro-

308 scrubbers to obtain higher efficient absorption equilibrium and electrochemical

309 processes. Regarding the other organic detected, the methyl-cyclohexane, it is

310 important to remark that it is not observed in the bare absorption (indicating that it is

311 not a component dragged from the industrial solvent stripped) but a reaction

312 intermediate that is proposed to result from the hydrogenation of toluene [68, 69]. This

313 compound could be decomposed to cyclohexane and methyl acetate which are also

314 dangerous to human and the environment. Also, it was confirmed that was successfully

315 removed using Biotrickling Filters [70] and some metal catalytic experiments with

316 manganese(III) porphyrins [71]. In addition, it is important to notice that it only appears

317 in the degradation with cobalt ions, so that its generation is related to the mediated

318 reactions promoted By HPLC no carboxylic acids were detected. Although C4 and C2

319 carboxylic acids are expected from the degradation of aromatics, especially oxalic acid,

320 the same observation has been made in previous works [72-75] and it can be explained

321 in terms of the very low concentrations of toluene dissolved and the very high current

322 densities applied. Thus, the electrochemical oxidation with diamond coatings of low

323 concentrated pollutant behaves as a cold combustion and almost no intermediates are

324 observed because they are rapidly degraded after their formation.

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Con formato: Fuente: (Predeterminada) +Cuerpo (Calibri)

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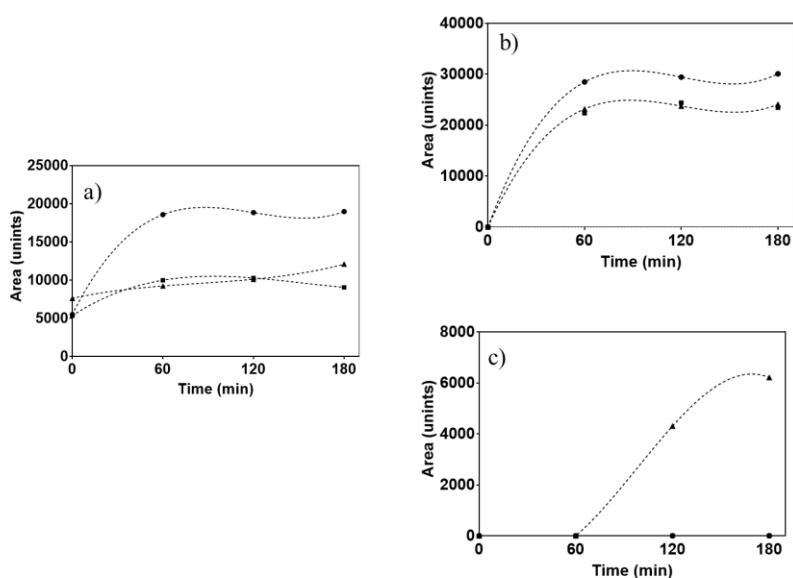
Figure 7. Chromatographic area of the main intermediates detected during the operation of the scrubber (●) electro-scrubber (■) and Co mediated electro-scrubber (▲) fed with 6.0 L h^{-1} and at 6.0. A. a) 2-methylphenol b) 4 methyl-phenol and c) methyl-cyclohexane.

Conclusions

From this work the following conclusions can be drawn:

- Toluene can be efficiently removed using packed column absorbers combined with an electrochemical cell (packed column electro-scrubber).

- Current efficiencies are low but within the range expected using DiaCell ® equipped with diamond coatings, because of the low concentration of toluene dissolved in the electrolyte/absorbent. Adding Co(II) salts into the formulation of

338 the electrolyte/absorbent. allow to increase the efficiency in the removal of

339 toluene.

340 • Increasing current density improves the current efficiency as expected for a

341 mediated electrochemical process. This is observed in the presence and absence

342 of cobalt, which supports that the sulfate/persulfate pair also behaves as

343 mediator in the degradation of toluene.

344 • Only methyl-cyclohexane (at very low concentrations) is observed as

345 intermediate, despite carboxylic acids were also initially expected. The formation

346 of this compound can be explained in terms of the hydrogenation of toluene. The

347 very low concentrations and the very high current densities support the

348 occurrence of an electrochemical cold combustion in the electro-scrubber.

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