Assessing the viability of electro-absorption and photoelectro-absorption for the treatment of gaseous perchloroethylene

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Abstract

This work focuses on the development of electro-absorption and photoelectro-absorption technologies to treat gases produced by a synthetic waste containing the highly volatile perchloroethylene (PCE). To do this, a packed absorption column coupled with a UV lamp and an undivided electrooxidation cell was used. Firstly, it was confirmed that the absorption in a packed column is a viable method to achieve retention of PCE into an absorbent-electrolyte liquid. It was observed that PCE does not only absorb but it was also transformed into phosgene and other by-products. Later, it was confirmed that the electro-absorption process influenced the PCE degradation, favoring the transformation of phosgene into final products. Opposite to what expected, carbon dioxide is not the main product obtained, but carbon tetrachloride and trichloroacetic acid. Both species are also hazardous but their higher solubility in water opens possibilities for successful and more environmental-friendly removal. The coupling with UV-irradiation has a negative impact on the degradation of phosgene. Finally, a reaction mechanism was proposed for the degradation of PCE based on the experimental observations. Results were not as expected during the planning of the experimental work but it is important to take in mind that PCE decomposition occurs in wet conditions, regardless of the applied technology, and this work is a first approach to try to solve the treatment problems associated to PCE gaseous waste flows in a realistic way.

Keywords

VOCs removal; Perchloroethylene; Electro-absorption; UV irradiation

Highlights

- Absorption into electrolytes can help to retain PCE from gas effluents.
- Phosgene is produced by wet decomposition of PCE
- Electro-absorption favors transformation of phosgene into CCl_4 and TCA
- Almost no mineralization of gaseous streams was attained
- UV-irradiation does not have a significant influence.
- Reaction pathways with main liquid and gaseous by-products were proposed.

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Introduction

Over the last decades, electrochemical environmentalists have faced massively the development of technologies for the remediation of liquids wastes and polluted soils, sometimes developing applications with great interest (Abou Dalle et al., 2017; Moreira FC 2017; Muñoz-Morales et al., 2019; Rodrigo et al., 2014; Sirés et al., 2014); others only promising technologies with low TRLs (technology readiness level). However, the treatment of gaseous pollutants has only been tackled rarely and, in this point (G et al., 2016; Muthuraman and Moon, 2012) , there is a huge unexplored research field with hundreds of applications still needed to be developed. In this line, some studies have evaluated the degradation of volatile organic compounds (VOCs)(Liu et al., 2001; Lugaresi et al., 2014;), degradation of environmental odor gases (Govindan and Moon, 2013) and hospital indoor air (Zadi et al., 2018).

Additionally treatment of gases can be carried out directly in gas phase using electrochemical cells equipped with solids electrolytes (Barge and Vaidya, 2019; Muthuraman et al., 2018), either polymer exchange membranes or solid oxides (Monteiro et al., 2015; Yamazaki et al., 2001). Alternatively, it can be carried out in liquid phase (Miao et al., 2015; Sáez et al., 2010; Sáez et al., 2009), following the absorption (ABS) of the gas into a liquid, which is not only an absorbent of the separation unit but also the electrolyte of the electrochemical cell (Muthuraman and Moon, 2012). Hence, its formulation is a topic of the major importance, because it can help to retain more efficiently the gas into the liquid or it can promote the electrochemical generation of oxidants, which later are going to increase the efficiency of the process (Chung and Moon, 2013; Muthuraman et al., 2017). In addition, the combination of the absorber with the electrochemical cell is also a topic of great significance.

Chlorinated hydrocarbons are extensively used, not only as solvents or degreasers but also as pesticides, wood preservatives and in many other applications (Huang et al., 2014; Mrema et al., 2014). Pollution associated to these molecules is typically persistent and hazardous. High volatility of various of these pollutants brings up a case of special interest, typically associated not only to environmental concerns but also, and more importantly, directly related to health of humans(Basu et al., 1998). This is the case of perchloroethylene, a product with many applications in industry and laundries, nowadays with a decreasing use because of the problems associated to its volatility (Nijhuis N, 2010). Anyway, it is still massively applied, and it is a topic of major interest the search of a successful technology which can treat it. In the past, some studies were carried out showing the removal of PCE from aqueous solutions using ferrous ion catalyzed sodium percarbonate (Miao et al., 2015), Fenton process (Jho et al., 2010) and/or applying different electrochemical (Sáez et al., 2009) and sono-electrochemical degradation strategies (Sáez et al., 2010). In addition, previous works in our research group evaluated the removal of PCE from spiked soils (Muñoz-Morales et al., 2019), where it was found the importance of the amount of PCE that was partially volatilized during the treatment, a key aspect that it is not considered in many other works seem in the literature. Regarding to the removal of gaseous pollutants, electro-reductive hydro-dehalogenation has been successful used to remove some volatile organic halides (VOCs) (Lugaresi et al., 2014), following the promising results obtained in the treatment of other gases (Govindan and Moon, 2013).

Considering this background, this work aims to use electro-absorption (EABS) technology to treat gases produced in a synthetic waste containing perchloroethylene. To do this, a packed absorption column, an undivided electrochemical cell and UV lamps are going to be coupled in order to evaluate the retention and reactivity of the pollutant by ABS, EABS and photoelectro-absorption technologies and to elucidate the mechanisms involved in this process.

Materials and methods

Chemicals. All chemicals, including perchoroethylene (C_2Cl_4 > 99%) (a.r., Sigma-Aldrich), anhydrous sodium sulfate, phosphoric acid (85 %), sulfuric acid (98%), sodium carbonate (a.r., Fluka, Spain), were analytical grade and they were used as received. Hexane HPLC grade (a.r., Sigma-Aldrich, Spain) was used as mobile phase. Helium and nitrogen (Al Air Liquide España, S.A) were used in gas chromatography and helium was filtered by a Hydrocarbon Cartridge Filter (Thermo Fisher Scientific) before its use. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 ºC) was used to prepare all solutions. Na_2SO_4 at 0.04 M was previously dissolved in Milli-Q water and perchloroethylene (PCE) was then added in a closed volumetric flask and the solution was softly stirred with a magnetic bar overnight to achieve complete dissolution.

Experimental setup. The experimental set-up consisted of a wet absorption coupled with an electrochemical cell. The system has four components as shown in Fig. 1: two tanks, a packed absorption column and an electrochemical cell. The absorption column (0.5 m long, inner diameter of 50 mm) was made of glass. A length of 0.4 m of the column was packed with glass spheres (diameter 8mm). The gas liquid contact in the packed column was continuous. The liquid flowed down the column over the packing surface and the gas flowed up counter-currently. The first tank, which stored the absorbent-electrolyte, was made of methacrylate and had a capacity of 2.5 dm^3. It was filled with a solution consisting of 0.1 mol dm^{-3} Na_2SO_4 used as supporting electrolyte. A centrifugal pump was connected between the electrolyte storage tank and the top of the absorption column. The second tank, that contains the synthetic waste polluted with PCE (use to simulate in realistic conditions the generation of an PCE waste stream), was a jacketed glass tank connected to a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain). This tank had a capacity of 1.2 dm^3 and it was filled in with a solution containing 150 mg dm^{-3} of PCE. To favor transfer of this pollutant to the gas phase, the stripping was promoted by connecting an air-compressor Silent Pump model SI6000 (ICA SA, Spain) with 3.8 W, flow 360 dm^3 h^{-1}. Gas generated was flowed to absorption column. To couple UV photolysis to the treatments, an UVC lamp of 11 W (light path-length = 245 mm d_{ext} = 19 mm) was installed in the center of the absorption-column. The photo-absorption column was covered with aluminum foil to avoid exposure to UVC rays and during the collection of samples, the accumulation tank was covered with ice gel packs. Then, temperature was monitored to make sure it keeps practically constant during all processes (20±2 ºC). Extreme care was taken to avoid gaseous losses in all compartments by using tight-fitting ground-silicone stoppers and by sealing with Teflon tape. Electrolyses were carried out in a single compartment electrochemical flow cell DiaCell®, supplied by Adamant Technologies (Switzerland). Conductive–Diamond Electrodes (p-Si–boron-doped diamond) were used as anode and cathode. The BDD electrodes were subjected to cleaning procedure during 10 min in a 1 M Na_2SO_4 solution at 15 mA cm^{-2} prior to electrolysis assays. All the processes were conducted at atmospheric pressure conditions.

Analysis procedures. Liquid and gas samples were taken from the sampling ports of the absorption column and from the PCE glass tank. To determine perchloroethylene concentration in both gas and liquid phase, an L–L extraction process was employed before the analysis: 1.0 mL of samples were taken using a syringe/ gas-tight (Hamilton, Switzerland) following extraction with 3.0 mL of hexane using a glass vials with Cap and PTFE Septa. Then, it was shaken in a vortex stirrer for 3 min at 4000 rpm for the separation of the phases. Next organic phase was transferred to a GC vial. For by-products analysis, different techniques such as HPLC, ionic chromatography, and inorganic carbon analysis were used. Liquid samples were directly transferred to an adequate vial to measure the parameters and for gaseous sample, 5 mL was drawn and dissolved into 10 mL of Milli-Q water using a glass vials with cap and PTFE Septa to guarantee that no losses of gas occur during the gas bubbling. Then, a vortex stirrer was used during 3 min and the resulting samples were transferred to appropriate vials for each analysis. All samples extracted from electrolyzed solution were filtered with 0.22 µm nylon filters before analysis.

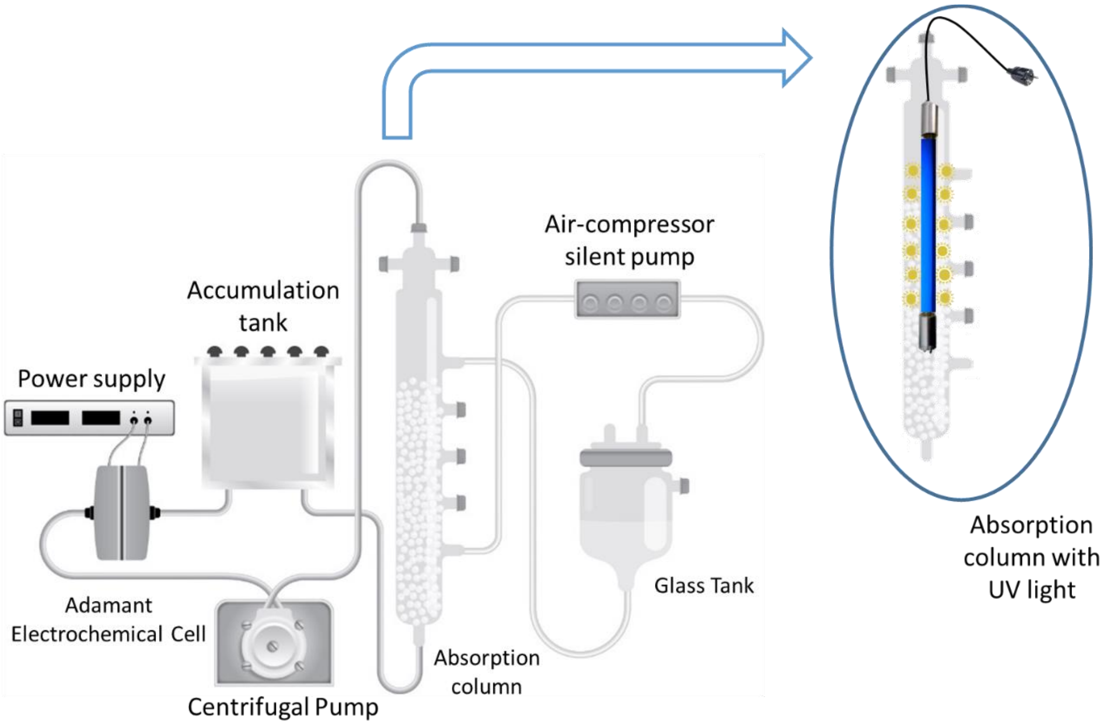

Figure 1. Experimental setup for the EABS process couple to the UV irradiation column.

The removal of perchloroethylene was quantified by Gas Chromatography Electron Capture Detector (GC-ECD) (Thermo Fisher Scientific) using analytical column using a

TG-5MS capillary column (30m×0.25mm×0.25mm), Ni micro-electron capture detector, a split/ splitless injector and ChromCard Software. Under the conditions used, the quantification limit of the GC- ECD was 0.1 mg dm^{-3}. The flow rate of gas He was 1.0 mL min^{-1}. The temperature of the oven was programmed as follows: kept at 60 °C for 1 min increased to 140 °C at 10 °C min^{-1} followed by another ramp at 10 °C min^{-1} to reach 260 °C followed by 2 min hold. The temperature of the injector was 260 °C.

For the determination of degradation by-products originated in the ABS and EABS treatments, two chromatographic methods were employed. The first was employed to analyze tetrachloromethane by means of a Jasco HPLC LC-2000 with a PDA MD-2018 Detector (Jasco, Japan). The mobile phase consisted of 100 % of 0.1% phosphoric acid (flow rate of 1 cm^3 min^{-1}). The detection wavelength used was 280 nm and the temperature oven was maintained at 25 ºC. Volume injection was set to 20 μL

Trichloroacetic acid (TCA) was determined using a HPLC Agilent 1100 series (Agilent Tech. USA) with a detection wavelength of 220 nm. The ion exchange column used was Supercogel^{TM} H Column with 30cm x 7.8mm ID. The mobile Phase was 1% phosphoric acid (H_3PO_4), the column temperature was 30°C, the flow rate was 0.8 cm^3 min^{-1} and the injection volume was 20 μL.

Chloride concentration was determined by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used to determine the anions using a eluent consisting of 85:15 v/v 3.6 mM Na_2CO_3/acetone at a flow rate of 0.8 cm^3 min^{-1}. Suppressor regeneration solution was 500 mmol dm^{-3} of sulfuric acid. The Inorganic Carbon concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Measurements of pH were carried out with GLP 20 Crison pH-meter.

Results and discussion

Absorption (ABS) and electro-absorption (EABS) of gases containing PCE. Fig. 2 shows the changes in the amount of PCE as a function of the treatment time, measured at the gas and liquid phases, in the tank containing the PCE liquid waste (PCE stripping tank) and in the tank that stores the electrolyte that flows throughout the absorption column, respectively, during the ABS and EABS treatments. Electrochemical technology was coupled to the ABS system in order to increase the removal efficiency of the PCE and its by-products by enhancing its reactivity, either by direct electrochemical oxidation or reduction, or by mediated processes generated by the oxidants and reductants produced on the electrode surfaces during the electrolytic process (such as those shown in eqs (1-4)). The experiment shown in the Figure was carried out at 8.0 A (102 mA cm^{-2}) and at initial pH of 6.5.

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e^- \quad (1)$$

$$SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (2)$$

$$SO_4^{2-} + \bullet OH \rightarrow (SO_4^{2-})^{\bullet} + OH^- \quad (3)$$

$$(SO_4^{2-})^{\bullet} + (SO_4^{2-})^{\bullet} \rightarrow S_2O_8^{2-} \quad (4)$$

As expected, there are no important differences between the single ABS and the EABS in the decay of PCE in the stripping tank containing the raw liquid waste (for both phases). PCE contained in liquid phase decreased rapidly for both technologies during the treatment time, reaching values lower than 50 mg within 15 min and attaining 95.8 % removal during the time span of 120 min (Henry's constant 0.02 atm m^3 mol^{-1}) . This rapid removal indicates the importance of volatilization processes during the treatment of liquid wastes containing PCE and the need of developing gas treatment technologies or operate in non-opened to atmosphere systems.

In the gas phase, the quantity of PCE increased at the beginning of the tests, attaining its maximum concentration just after 5 minutes of operation. This gas phase contacts with the absorbent-electrolyte in the absorption column and this explains the transfer of the PCE to the other circuit. The similar values obtained for the system with and without the electrochemical cell indicates that volatilization of the PCE contained in the liquid waste is almost not influenced by type of ABS treatment carried out (with or without electrochemical reaction).

Part b shows the increase in the amounts of PCE in the absorption column/tank circuit during the first 10 minutes in both liquid and gas phases. As seen, it reaches around 50 mg in the liquid phase and 20 mg in the vapor phase for both technologies, indicating the success in the absorption of the gas generated into the stripping tank which simulated the production of this gaseous stream. It also indicates that the ABS process is very fast, meaning that the packing material used is very effective for the absorption of PCE, which it can be related to the high specific area (which, in turn, provides intimate contact between the gas and absorbing liquid).

After 10 min, it is observed that PCE decreased in both phases remaining around 20 mg after 120 minutes for ABS process and only 8 mg in the liquid phase for the electrochemically assisted process. This means that 97 % PCE is removed at 120 min in the EABS technology which shows a higher mass-transfer coefficient (11.5 % higher in the EABS process). Then, less gaseous PCE is observed in EABS, because of their faster removal in liquid phase promoted by the electrochemical process. In addition, the rate of PCE decay after 5 min (calculated fitting experimental data to a first-order kinetic reaction model) in the column for EABS technology is three times faster than in the ABS process (3.85 x10^{-4} mol s^{-1} for the EABS compared to 1.39 10^{-4} mol s^{-1} for ABS process). This difference is indicative of the influence of the electrochemical processes and it can be explained in terms of the high production of hydroxyl radicals and mediated electro-reagents, such as peroxosulfates generated by oxidation of the sulfate anions contained in the absorbent-electrolyte and also chlorine produced from the dehalogenation of the PCE. Other important remark is that at 5 min only 33% of PCE remains unreacted. This behavior can be explained in terms of the high PCE reactivity, which is not only electrochemical but also, and very importantly, chemical, as it can be suggested from the generation of by-products of reactions shown in Figure 3.

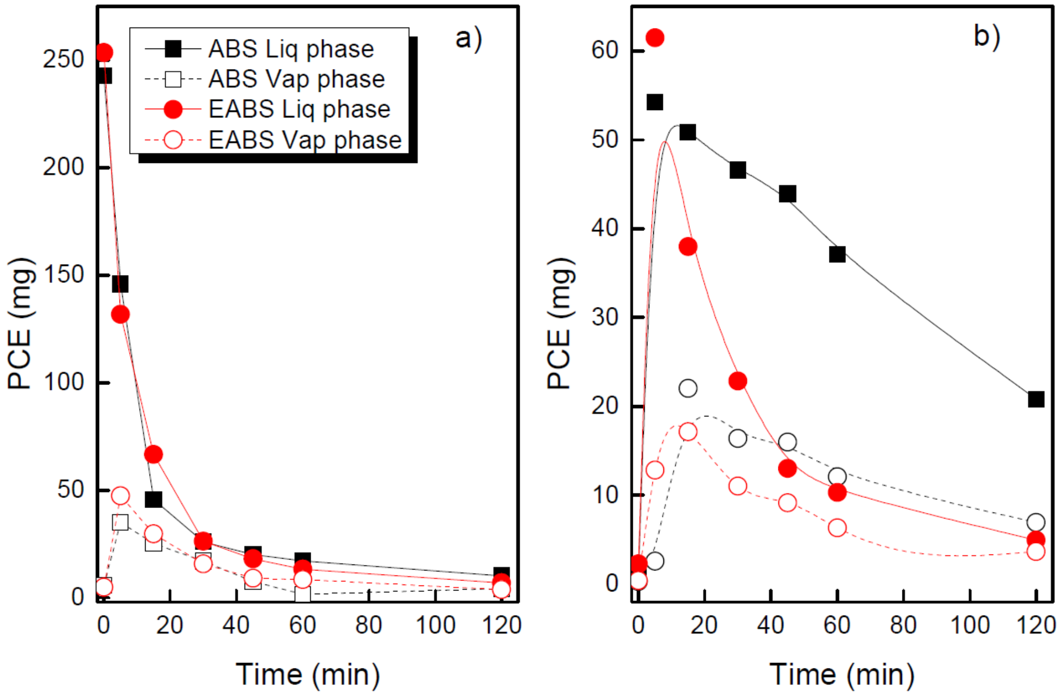

Figure 2. Mass decay of Perchloroethylene during the scrubbing operation (■) and electro-absorption treatment (EABS) (●) as a function of the time. Samples analyzed in the a) PCE tank and b) Absorption (ABS) column. Full points: liquid phase and empty point: gas phase.

Thus, two important by-products were identified during the ABS and EABS in rather high amounts by High Performance Liquid Chromatography (HPLC): carbon tetrachloride (CCl_4) and trichloroacetic acid (TCA). An important observation is that both compounds are not only observed in the absorbent but also in the gases monitored in both circuits. Thus, it can be seen the slight increase of the trichloroacetic acid and carbon tetrachloride in the PCE stripping tank, especially in the vapor phase. These by-products are not observed when the solution contained in the PCE stripping tank is not stripped and passed throughout the column and this observation may indicate that their production is carried out in the gas phase by wet decomposition of the PCE and, then, it is transferred to the liquid phases. In addition, as both compounds are observed in the system without the electrolyzer, their formation must be explained not by electrochemical but by chemical processes. Anyhow, it is important to point out that the amounts are very low in the single ABS process. However, they are very important in the EABS and this observation indicates that decomposition of the PCE is accelerated by the electrolytic processes produced in the electrochemical cell. In fact, it is important to point out the very high concentration of both products in the liquid phase, which suggest their generation by the electrochemical reaction of PCE in this phase. Anyway, both compounds are also contained in the gas phase, which can be explained by the liquid-gas transfer or by the previously commented wet chemical formation of both species. CCl_4 seems to be the primary final product of degradation in the EABS process and TCA is also a very important final product. This is not what it was initially expected, because there is no mineralization but simply transformation into other products with the only advantage of their lower volatility in the case of the TCA and the higher solubility in water in the case of the CCl_4 and TCA respect to PCE (1160 mg/L (CCl_4) and 54000 mg/L (TCA) vs 206 mg/L at 25ºC (He, 2003; Schneider, 1983; Verschueren, 2008). Moreover, it was observed an increase of pH in the column during the EABS from 6.0 to 11.3 in the phase liquid. In the PCE stripping tank, no important changes were observed, remaining around pH 6.0.

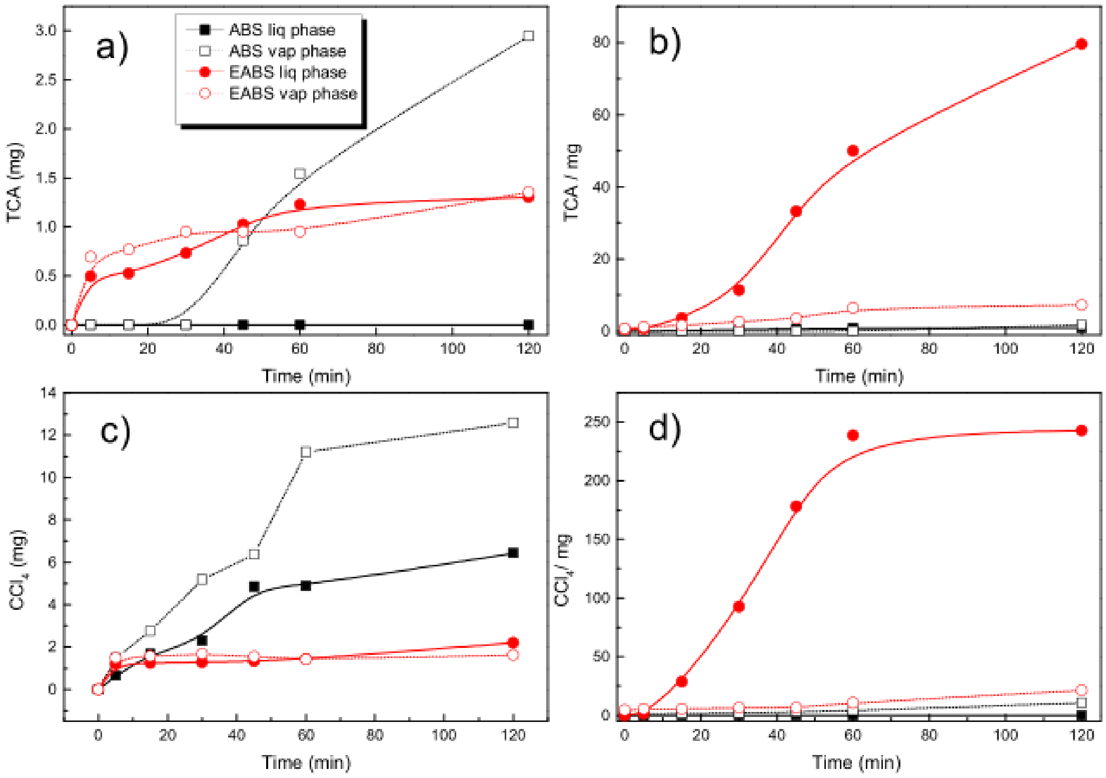

Figure 3. Mass decay of by-products generated during the (■) ABS process and EABS treatment (●) as a function of the time. a) TCA mass in PCE tank b) TCA mass in ABS column; c) CCl_4 mass in PCE tank; d) CCl_4 mass in ABS column. Full symbols represent liquid samples and empty symbols are gas samples.

Another important point to be highlighted is that mass balances informs about the formation of a third intermediate which is not detected by either HPLC or GC-ECD chromatography. However, according to UV spectrum it absorbs light a 365 nm (Xie et al., 2017), which is consistent with its identification as phosgene, a very volatile product whose formation is promoted during the wet decomposition of PCE. Phosgene have been related in literature as by-product of PCE promoted by hydrolysis reaction that occur at humid medium. In this case, phosgene could not be detected as by-product due to its decomposition during the gas chromatography processing. Thus, this compound is known to easily decompose to TCA and carbon tetrachloride. Amounts of phosgene produced are shown in Figure 4, where it can be seen that it has a behavior of intermediate during EABS processes while it behaves almost as final product in the case of the bare ABS. Anyway, the detection to TCA and CCl_4 indicates the partial hydrolysis of these species, which is not favored when the current is not applied in the electrolyzer.

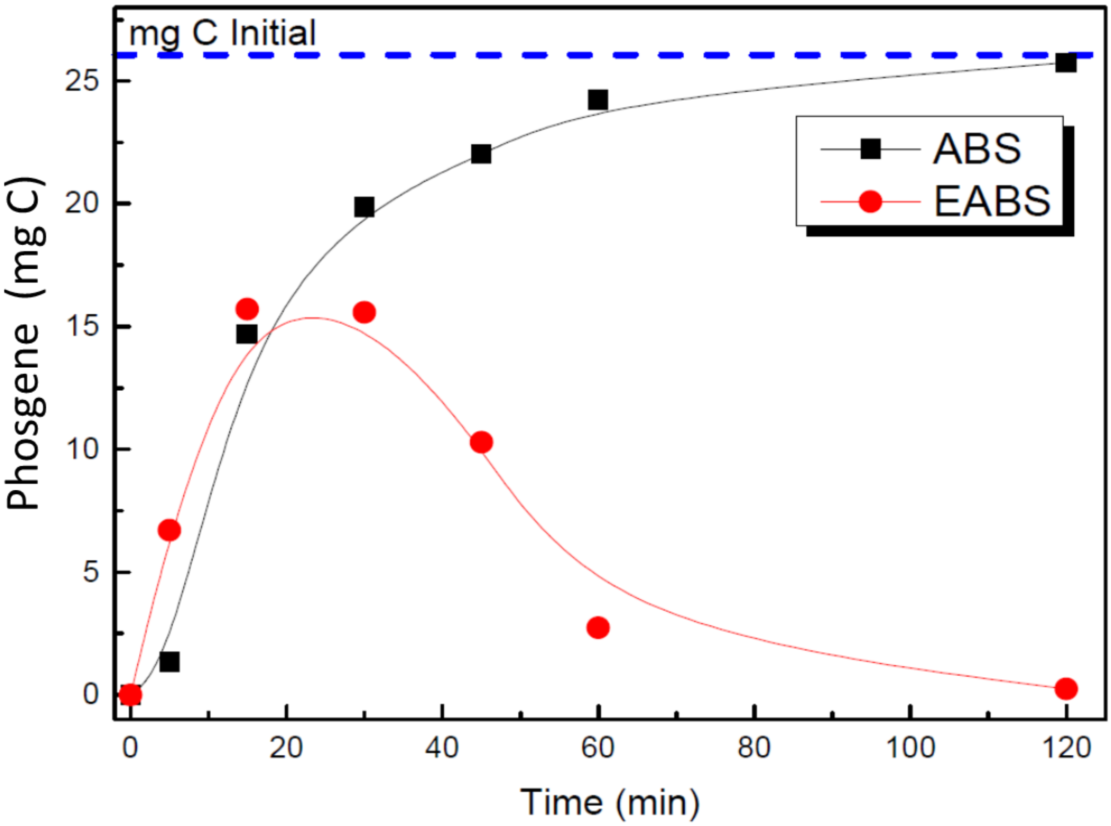

Figure 4. Phosgene mass generated during the (■)ABS process and EABS treatment (●) as a function of the time.

Photo-electroabsorption. It is known in the literature that PCE is capable to absorb light especially with short UV wavelengths. Thus, direct photolysis of PCE with UVC can leads to ionization resulting in removal of chlorine radicals from PCE molecules. In addition, it is well-known the formation of oxidants during electrolysis, such as hydrogen peroxide, ozone and peroxosulfates, which can be activated by UVC light irradiation, generating hydroxyl and sulfate radicals. Consequently, these radicals can promote the oxidation of organics. In this way, in order to enhance the removal efficiency of PCE and mainly its by-products removal, UV light was coupled to EABS (no significant changes were observed with just ABS).

Part A of Fig. 5 shows that the PCE in the tank presents the same behavior for the non-irradiated ABS and EABS processes. However, in the absorption column circuit (Fig. 5b) the maximum PCE found was 30 mg, almost the half of that obtained by non-irradiated processes (first-order kinetic constant was $5.87 \cdot 10^{-4}$ mol s^{-1}). This indicates the positive influence of the UVC light on the transformation of PCE. Additionally, to compare the degradation carried out when two or more processes are combined, the synergetic index was calculated from kinetics according to eq 5 obtaining a value of 1.12 ($k_{ABS} = k_{photo-ABS}$).

$$Sinergistic\ index\ = \frac{k_{PHOTO-EABS}}{K_{photo-ABS} +\ k_{EABS}} = \frac{5.87 \cdot 10^{-4}}{3.85 \cdot 10^{-4} + 1.39 \cdot 10^{-4}} = 1.12 \qquad (5)$$

This value indicates that there is just a slight positive synergetic effect for the PCE removal in the coupled process.

Regards to parts c and d of Fig 5., the main products generated shown by the HPLC are, again, CCl_4 and TCA. Phosgene occurrence was also confirmed by UV spectra and amounts formed are shown in Figure 6, where it can be seen a typical intermediated profile, although the decomposition to final products is less favored than in the case of the non-irradiated EABS process.

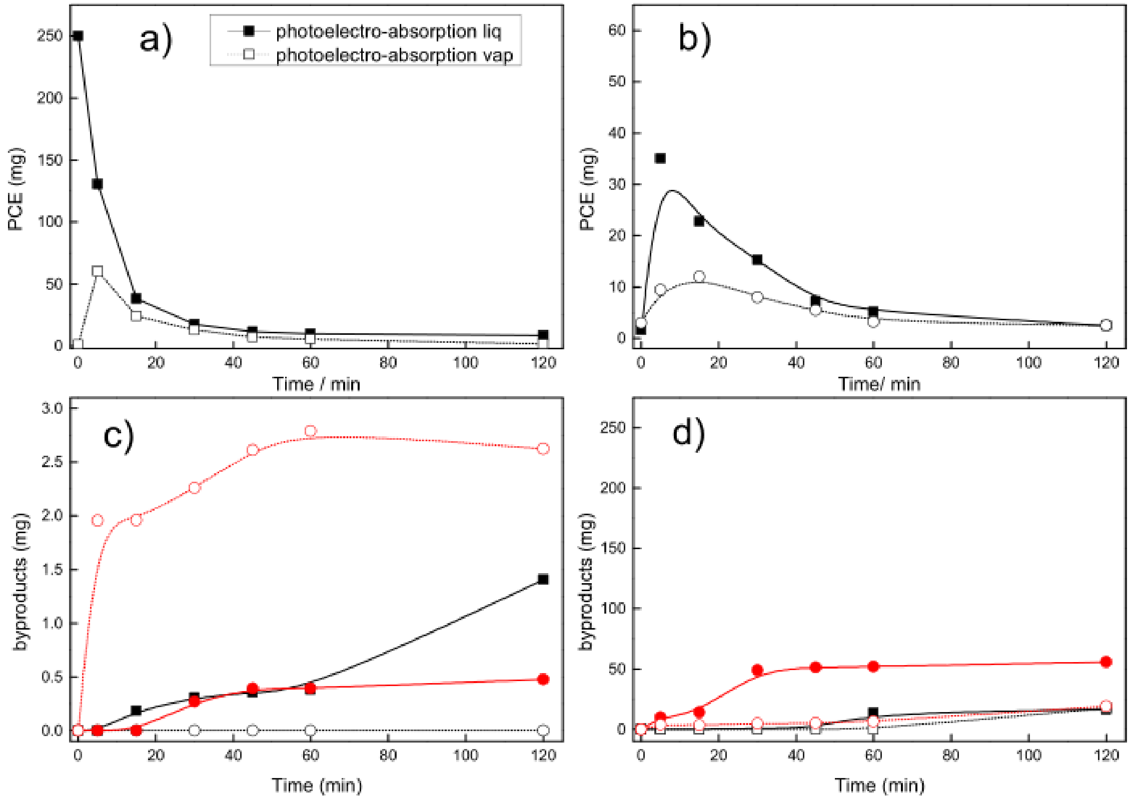

Figure 5. Changes in the amounts of PCE and intermediates in the photo-electroabsorption. a) and b) represents the mass decay of PCE; c) and d) by-products generated during the electro-scrubbing couple to UV treatment as a function of the time. a) and c) represents the samples analyzed in the PCE tank and b) and d) in the ABS column (■) TCA, (●) CCl_4;. Full symbols represent liquid samples and empty symbols are gaseous samples.

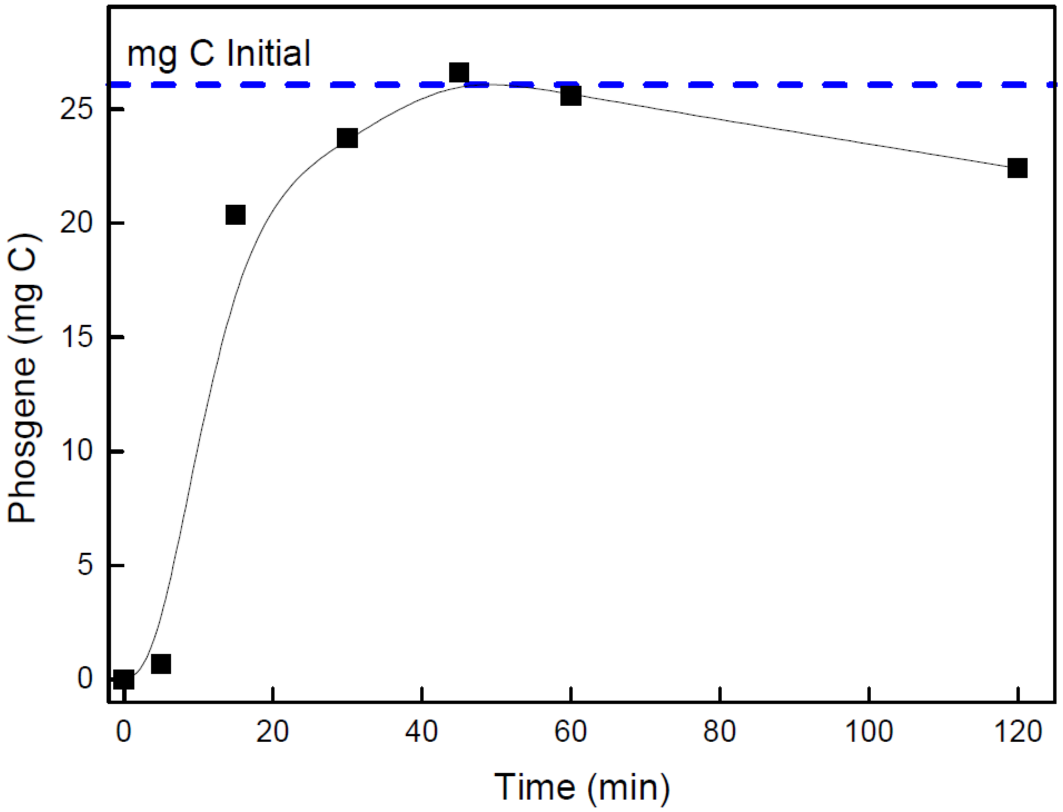

Figure 6. Phosgene mass generated during the photoelectro-absorption process.

Hence, the decomposition of oxidants into radical promoted by the UV irradiation does not seem to benefit the degradation of phosgene but to make it slower, indicating that the short lifetime of these radicals is negative in this case and pointing out that light irradiation does not have in this case a positive effect.

Reaction mechanisms in the electro-absorption (EABS) of PCE. The influence of current density and pH were studied by carrying out additional EABS tests at 0.8 A and 8A at pH 6 (natural PCE solution) and pH 3.0. Fig. 7 shows the carbon mass balance for each compound in the end of the treatments. As can be observed, during the ABS process, only around 10 % in mass of PCE remains in solution being almost converted into phosgene, which is a bad news from the environmental point of view as this species is even more volatile than the PCE (vapor pressures of $1.6\ 10^5$ vs $1.9\ 10^3$ Pa at 20ºC) and even, it is considered more hazardous. It was reported that the production of phosgene was inhibited when it is an increasing concentration of oxygen that does not appear at single ABS process. However, this negative view has not been discussed in previous works shown in the literature and it is a very important handicap to be overcome, because the formation of these species does not depend on the treatment technology proposed but it seems to occur naturally.

Comparing the EABS process at 0.8 A and 8.0 A, it is observed that at lower current density the progress of the reaction of phosgene into CCl_4 and TCA is lower, and the ratio of TCA formed seems to be higher. On the other hand, when higher current is applied, it is promoted the destruction of phosgene because of the massive production of hydroxyl radical and the local alkalization of the solution because of the hydroxyl anions generated (eqs 6-7).

$$M + H_2O \rightarrow M(OH)^* + H^+ + e^* \tag{6}$$

$$2\,H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \tag{7}$$

. Regarding to pH, it can be observed that acid medium contributed to PCE oxidation and promote the increase of the phosgene generation at lower j. However, at higher current densities, no significant differences were observed in terms of pH. Comparing both current densities, when UV irradiation is coupled to the EABS, it is observed that UVC light promotes the PCE photolysis decreasing its content in the end of the process and favoring the phosgene generation. However, it does not favor the decomposition of this compound.

These reaction products found in this work agree to those described in the literature and, based on that, a mechanism can be proposed. So that, in Figure 8 it is proposed a double pathway for the transformation of perchloroethylene. Thus, several studies have demonstrated that the photochemical or photocatalytic conversion of PCE can occur through two initiation steps: hydroxyl radical (HO•) and chlorine radical (Cl•) pathways (Petit et al., 2007; Son-Jong Hwang, 1998; Yamazaki, 2001; Yamazaki, 2004). Regarding the actions of these radicals, theoretical calculations indicates that HO• addition to PCE is more exothermic than the addition of Cl• (43.8 and 9.2 kcal mol^{-1}, respectively) (Yamazaki, 2001). Kinetic data point out that the reaction rate coefficient for Cl• addition to PCE can be from 2.5 to several hundred times faster than the reaction rate coefficient for addition of HO• to PCE (Nicovich, 1996; Petit et al., 2007; Thuner, 1999). This means that the addition of HO• to PCE can be expected to be negligible as compared to the addition of Cl• (eq 8-9).

$$PCE + OH^{*} \rightarrow HOCCl_2C \cdot Cl_2 \rightarrow \; HOCClCCl_2 + Cl \cdot \qquad (8)$$

$$PCE + Cl \cdot + H_2O \rightarrow HOCCl_2CCl_3^{*} \qquad (9)$$

Thus, according to literature, PCE can suffer a reductive dechlorination under UV radiation leading to the formation of trichloroethenyl radical, that reacts with water generating trichloroethylene (C_2HCl_3). PCE can also react with Cl•, leading to the formation of pentachloroethyl radical which, in turn, can react with O_2 generating pentachloroethaneperoxyl radical, followed by its dimerization, decomposing into pentachloroethoxyl radical and oxygen. The cleavage of the C–C bond of the pentachloroethoxyl radical yields to trichloromethyl radical and phosgene (CCl_2O) formation (Feiyan, 2002; Yamazaki, 2004). The trichloromethyl radicals can react with $Cl^{\bullet}$ as well as with water, yielding to the by-products carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$), respectively.

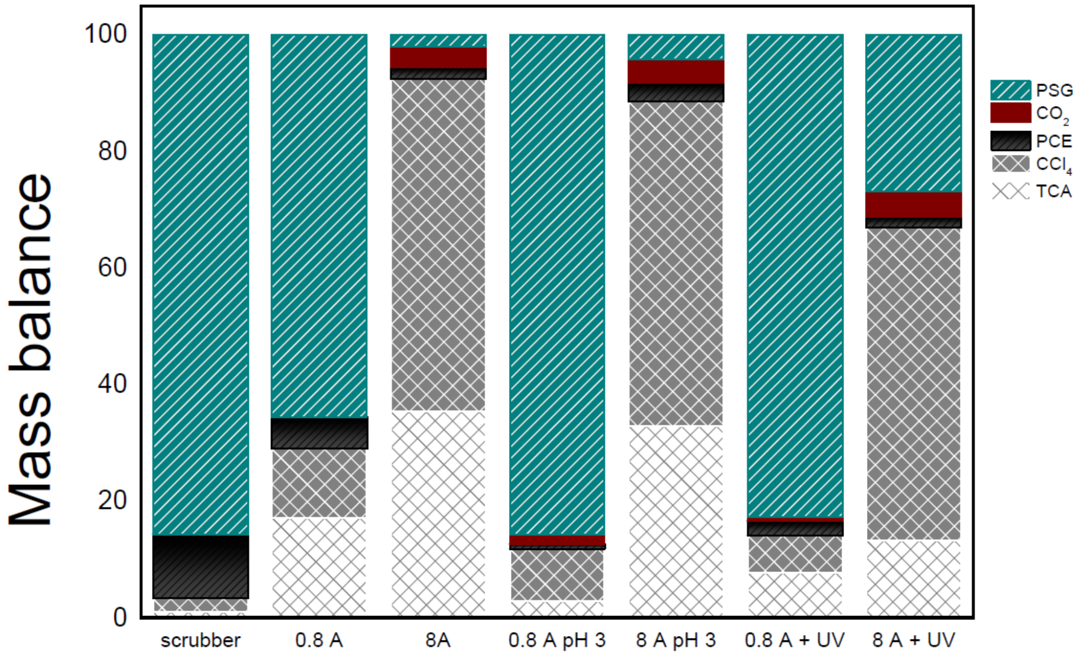

Figure 7. Carbon mass balance calculated for PCE and its degradation subproducts generated during all process investigated (▨) TCA, (▩) CCl$_4$, (▨) Phosgene, (■) PCE, (🟥) CO$_2$.

On the other hand, the attack of chlorine radicals and the higher absorption efficiency promotes the generation of intermediates in the liquid phase with the formation of trichloroacetyl chloride that reacts very fast and synthesize with chloride and hydroxyl radicals the trichloroacetic acid that mainly appears in the liquid phase where it is more stable. This route also was stimulated using an electrochemical process according with higher concentration observed in those experiments.

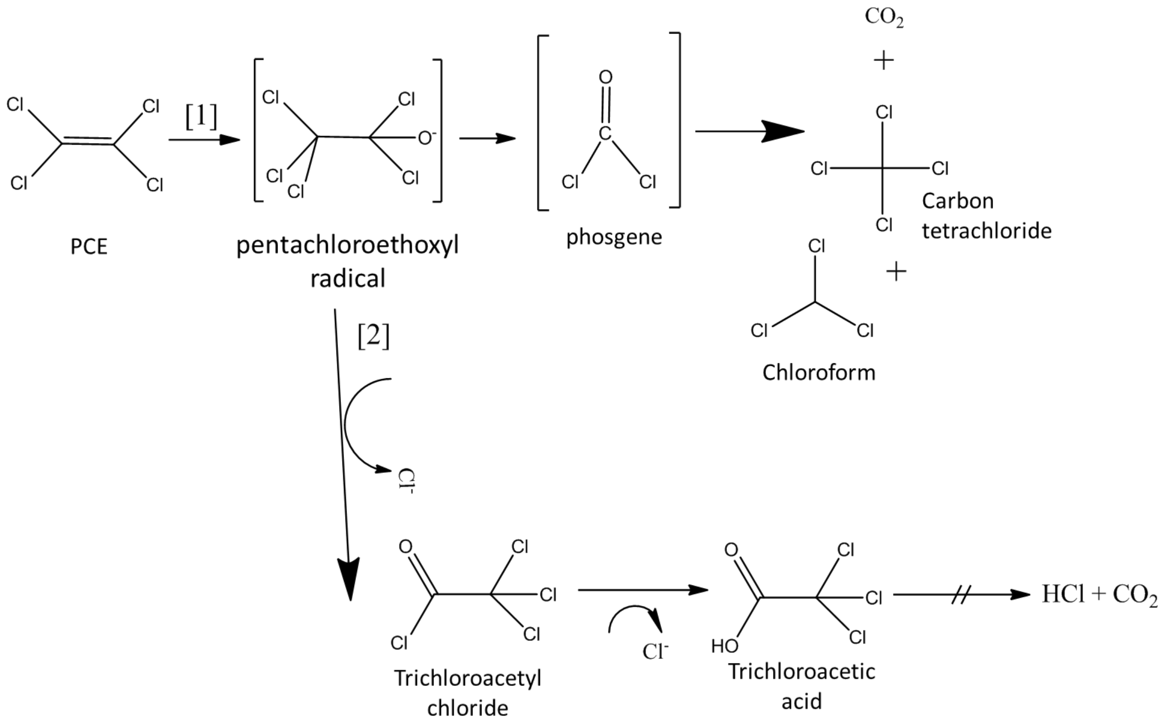

Figure 8. Proposed mechanism of reaction pathway for C_2Cl_4 degradation to different products considering the different adsorption processes evaluated.

Thus, according to the results shown, phosgene is produced always in ABS processes because of the wet hydrolysis of PCE (Meyer et al., 2001). Low current densities only attain a limited decomposition of this phosgene. Unexpected behavior occurs with UV irradiation which does not seem to favor the decomposition of this intermediate maybe because light does not promote the absorption process of PCE, so the high production of chlorine radicals are not effective to remove chlorine intermediates and just a trace amount of carbon dioxide was detected, showing an antagonist effect when an electrolysis at high current density and UV irradiation were combined. Anyhow, in the electrolysis, the ratio TCA/CCl_4 seems to be increased by working at these lower current densities which can be an interesting point for future work as TCA is a less hazardous and easier to degrade intermediate, with higher solubility and lower vapor pressure than parent PCE and the by-product CCl_4. Opposite to what stated in other works, mineralization of PCE is not favored and very low amounts of carbon dioxide are detected, being more important when high current densities are applied.

Conclusions

From this work, the following conclusions can be drawn:

- The absorption in a packed column is a viable method to remove PCE from gaseous streams. However, considerable concentration of phosgene is formed during the process due to the promotion of wet hydrolysis of perchloroethylene.
- Electro-absorption using a non-divided BDD electrolytic cell is capable to promote hard oxidation conditions leading to different reaction pathways. Lower current densities favors the phosgene formation while higher current densities promote the generation of CCl_4 (mainly in gas phase) and TCA as main reaction by-products in the liquid phase. Mineralization obtained is very low and treatment costs increased seriously with the total power applied.
- UV irradiation does not have a positive impact on the treatment, leading to a less efficient decomposition of phosgene, which was explained in terms of the transformation of the oxidant electrogenerated into radicals.
- Efforts have been done in order to better understand the possible pathway route of PCE degradation and their influence on the speciation. Conversion of PCE into phosgene is a non-electrochemical process which is promoted by wet conditions. Phosgene is transformed into CCl_4, and TCA during electrolysis, being this later by-product promoted at low current densities.
- Results were not as expected during the planning of the experimental work in terms of treatment of PCE but it is important to take in mind that PCE decomposition occurs in wet conditions, regardless of the applied technology,

and this work is a first approach to try to solve the treatment problems associated in a realistic way. Despite results are not positive from the viewpoint of the treatment technology, it is important to state that the treatment of this gaseous streams is more difficult than expected and it is a challenging aspect worth to be faced by other researchers.

Acknowledgements

Financial support from the Spanish Agencia Estatal de Investigación through project PID2019-107271RB-I00 (AEI/FEDER, UE) and Spanish Government (Grant Nº FPU16/0067) are gratefully acknowledged. Martin Muñoz-Morales acknowledges the FPU grant no.016/0067. Fernanda L. Souza is gratefully acknowledged to Coordenação de Aperfeiçoamento de Pessoal de nível Superior (CAPES) process 88881.171154/2018-01 for the scholarship awarded. Castañeda-Juárez acknowledges the scholarship granted by CONACyT.

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