Improving photolytic treatments with electrochemical technology

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Graphic Abstract

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Abstract

Photochemical reaction is an Advanced Oxidation Process that have been extensively applied to wastewater treatment. New design of reactors, improvement of the hydrodynamics and light irradiation has led to good results. However, for many aromatics and recalcitrant compounds this technology is not efficient to achieve complete degradation at short time and cost-effective. In this way, couple another technology to this system could be a good alternative to improve the efficiency. Electrochemical Oxidation (EO) appears as a robust technology that uses efficient materials like conductive diamond electrodes to generate powerful oxidant species through direct or mediated oxidation. In this work, the enhanced degradation of 2,4-D an important chlorinated phenoxy herbicide by couple photochemical reactions and electrochemical oxidation was evaluated when the photoreactor acts primarily in relation to electrolytic treatment. For this, the influence of current density on the process efficiency was determined at natural pH conditions using sulphate media as electrolyte. Results show that there is a clear negative effect when EO is coupled to photolysis at low current density. However, at higher current the effect becomes positive (there is a synergism between the process). In terms of energy, electrolysis worsens the performance of photolysis when this non electrochemical process is the primary and photolysis enhances electrolysis

when this later treatment acts as the primary treatment. In this way, photoelectrochemical process can be very promising with a rather advantageous cost/benefit ratio. Regarding to intermediates, couple EO to Photochemical process improve considerably the oxidation of these compounds, once very low or zero concentration of intermediates was detected after 1 hour especially at higher current density applied. Results are explained in terms of the generation of free radicals from the photoactivation of electrogenerated oxidants near the anode and in the bulk, improving the process performance.

Keywords

Photoreactors, Photo-electrochemical, advanced electrochemical oxidation, hybrid process, herbicides

Highlights

- 2,4-D solutions can be completely depleted and mineralized through hybrid process at higher current densities.
- hybrid process not always to lead to increase in the efficient of the system. This one depends on the process that act primary.
- The 2,4-D degradation rates in the combined process are larger than the sum of photolysis and electro-oxidation processes under higher current density
- PEC treatment is a promising process for the degradation and remediation of this herbicide more than single photochemical or electrooxidation process.

Introduction

The search for cost-effective, environmentally-friendly and easy to operate wastewater treatment technologies has been the focus of the research by scientific community and many organizations around the World. Among existing process, the so-called Advanced Oxidative Process (AOP) are considered the most effective for the removal of organics and are currently gaining significant importance as pre- or post-treatment [1-4]. They are based in the generation of powerful oxidants such as hydroxyl radicals, sulfate or peroxide and ozone radicals. Once generated, radicals oxidize the substances by transforming the organic contaminants into carbon dioxide, water and inorganic anions [2, 5-9]. Among AOPs, Electrochemical Oxidation (EO) appears as a robust technology that uses efficient materials like conductive diamond electrodes to generate power oxidants species through direct or mediated oxidation[10-13]. Besides, EO process can be easily integrated with other processes, in the search of synergistic effects and cost-effective treatments [14-16]. Another AOP extensively applied to wastewater treatment is the Photolysis [17-20]. In a photochemical reaction, the energy in form of light is absorbed by molecules creating transient excited states whose new chemical specie is formed with different chemical and physical properties. The yield of this process depends on many factors, like source of irradiation (artificial-lamps or natural-sun), the light wavelength, intensity of light, number of the light sources used in the *setup*, reactor hydrodynamics regime (which must promote an uniform UV fluence within the reactor), residence time, reaction media, pH and temperature, among other. Regarding to kinds of lamps employed in AOPs, the oldest and most popular are Low Pressure Lamps also known as Germicidal Lamps [21-23]. These LPs have two important lines in the spectral radiation at 253.7 nm and 185 nm. Radiation at 254 nm is well suited for direct UV disinfection process due to many compounds absorbing this radiation disrupting its structure. On the other hand, radiation

at 185 nm is mainly applied for AOP such UV/O₃ or UV/H₂O₂ process, where direct photolysis produces highly reactive radicals ($\cdot\text{O}$ or $\cdot\text{OH}$ respectively). Besides in aqueous solution, the 185 nm radiation is absorbed almost exclusively by water, bringing about its photolysis to yield $\cdot\text{OH}$ radicals and H atoms. This kind of lamps have others advantages like strongest diversity, highly energy and cost efficient. They also offer high UVC output, excellent lifetime, good UV efficiency, temperature stability and enable operation in high ambient temperatures. This combination makes them the right choice for compact, efficient and economic disinfection and Advanced Oxidation systems [24-26]. An emerging alternative for lamps is the use of LEDs which has become attractive due to good characteristics like low power consumption, longer lifetime, small dimensions and small-angle emittance. However, the high cost and low power of UVC-LED already is an obstacles for industrial applications[27, 28].

Conventionally, two types of photochemical reactions systems have been employed: batch system and tubular reactor, which are the most commonly used nowadays because of its low cost, simple substitution of the tubes, etc [29, 30]. Although photochemical reactors are well known and already applied in wastewater treatment, this technology deserves the attention due to it still shows some important limitations as energy cost and efficiency. In this point, the use of hybrid system consisting of photochemical technology coupled to other AOP like EO process has focused the interest of recent studies [14, 31-37].

Up to now, most of the works that couple EO and light irradiation had as main goal the activation of electrogenerated species in the anode surface by photons ($h\nu$) to form species with higher oxidant power[36-38]. Then, these species could reach the bulk where they could react with organic pollutants, improving the efficiency of the electrolytic process. In previous works, it was tested that the removal of pesticide 2,4-D and dimethyl phthalate

improves significantly when single BDD-electrolysis is combined with light irradiation because of the harsher oxidation conditions which contribute to reduce the number of intermediates and promote mineralization[23, 34]. However, the combination of more than two technologies, such as photoelectrolytic process caused a clear antagonistic effect in the degradation [33, 39]. It is important to take into account that in these combined technologies, the light was used to irradiate the anode surface. Regarding to the economic cost, most of the published works not discussed this important parameter. Some of them, shown that the consumption could be very high when lamps with high power is employed. Thus, in the case of electrolysis with metal mixed oxide electrodes of dimethyl phthalate the electrical energy consumption for the complete removal of the pollutant and complete mineralization remained around 5 and 14 kW h m⁻³, but energy consumption increased up to 1434 and 3585 kW h m⁻³, respectively, in the combined photoelectrochemical process[40]. Likewise, Souza et al. using BDD electrodes observed that the energy requirement of electrolytic and photolytic technologies are similar at low current densities[23]. This means that, in this case, the photoelectrochemical process may provide an opportunity to optimize the energy supply.

With this background, the goal of this work is to understand the synergism or antagonism effect when the photoreactor acts primarily in relation to electrolytic treatment. To do this, 2,4-Dichlorophenoxyacetic acid (2,4-D), an important chlorinated phenoxy herbicide was used as model compound. This compound is highly water-soluble (i.e., 900 mg dm⁻³ at 25°C). In addition, it has high lifetime and mobility and low biodegradability. Then, is also known to persist in the soil and contaminate surface and underlying groundwater. US EPA consider it as a highly persistent chemical in aquatic and terrestrial anaerobic environments (US EPA, 2011). Besides that, the 2,4-D have been studied applying many kinds of technologies, including photochemical process and AOP,

which permits to compare with the results obtained in this work, once until now it does not been studied with hybrid process like the one proposed here.

2. Materials and Methods

2.1. Chemicals

All chemicals, including anhydrous sodium sulphate (Fluka, Spain), 2,4 dichlorophenoxyacetic acid, hydroquinone, 1,4 - benzoquinone, 4 - chlororesorcinol, 4 - chlorophenol, 2,4 – dichlorophenol (Sigma-Aldrich) were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 M Ω cm at 25 °C) was used to prepare all solutions.

2.2. Experimental apparatus

The lab-scale system consists of: i) a cylindrical shell photoreactor of borosilicate glass ($d_{\text{int}} = 3.2$ cm, length = 23cm, thickness 1mm) with inlet and outlet pipes located perpendicularly to the fluid flow and tangentially to the shell in horizontal plane and at the top in opposite sides. Inside it, there is a concentric inner quartz tube housing an UVC germicidal lamp of 11 W ($V_{\text{illuminated}} = 60$ cm³; light path-length = 245 mm $d_{\text{ext}} = 19$ mm); ii) a recirculation storage tank with 0.15 dm³ under magnetic stirring coupled to a thermostatic bath; iii) a peristaltic pump to promote the fluid recirculation through polytetrafluoroethylene (PTFE) tubing; iv) a single compartment electrochemical flow cell. Boron-doped diamond electrodes provided by Adamant Technologies (Neuchatel, Switzerland) were used as anode and as cathode. Both electrodes were rectangular (2.0 cm x 0.5 cm diameter) covering a geometric area of 1.05 cm². The thickness of the BDD coating was 2-3 μm of the thickness, the boron concentration was 500 ppm, and the

sp^3/sp^2 ratio was 176. The inter-electrode gap was about 9 mm. Prior to use in galvanostatic electrolysis assays, the electrode was polarized during 10 min in a 1 M Na_2SO_4 solution at 15 mA cm^{-2} to remove any impurities from its surface. Fig. 1 displays the structure of this system.

2.3. Experimental and Analysis procedures

0.15 dm^3 of a solution consisting of initial 2,4-D concentrations of $100\text{ }\mu\text{M}$ was used in each test as model wastewater. The initial pH was approximately 4.5 and no pH correction was performed over the tests. Continuous recirculation through reservoir, UVC photoreactor and the electrochemical cell was kept at a flow rate of $0.78\text{ dm}^3\text{ h}^{-1}$. Before the tests, this solution was homogenized by recirculation through all the system during 10 min in the darkness. During tests, the temperature maintained at $20\text{ }^\circ\text{C}$.

The glass tube was covered with aluminum foil to avoid exposure to UVC rays. A first control sample was taken and then, the UVC lamp was switched on, starting the photochemical reactions. Samples were taken at different time intervals to evaluate the oxidation process. All the samples were filtered with $0.45\text{ }\mu\text{m}$ nylon filters from Whatman before their analysis. The decay of herbicide and the evolution of their aromatic products were followed by reversed-phase chromatography. The chromatography system was an Agilent 1100 series coupled a UV detector. The analytical column Phenomenex Gemini $5\text{ }\mu\text{m}$ C18 was used. The mobile phase consisted of 70 % acetonitrile and 30 % water to 1 % phosphoric acid with a flow rate of $1\text{ cm}^3\text{ min}^{-1}$. Other conditions were UV detection wavelength of 280 nm, the temperature oven at $25\text{ }^\circ\text{C}$, and volume injection of $20\text{ }\mu\text{L}$. The 2,4-D peak area was compared to the one from a calibration curve previously obtained in the range of 1 to 100 mg dm^{-3} using imazapyr standard (Sigma-Aldrich). The Total Organic Carbon (TOC) concentration was monitored using a Multi N/C 3100

Analytik Jena analyzer. The Chemical Oxygen Demand (COD) was monitored using a HACH DR200 analyzer. Measurements of pH were carried out with an InoLab WTW pH-meter.

The photochemical space time yield (PSTY, $\text{m}^3_{\text{water}} \text{m}^{-3}_{\text{reactor}} \text{day}^{-1} \text{kW}^{-1}$) was calculated via Eq. (1) (Leblebici et al., 2015) where the space-time yield (STY, $\text{m}^3_{\text{water}} \text{m}^{-3}_{\text{reactor}} \text{day}^{-1}$) is standardized to the volume (m^3) of the wastewater processed from 20 mg L^{-1} of 2,4-D in a 1 day by the reactor when it is scaled up to 1 m^3 (VR).

$$PSTY = \frac{STY}{LP} \quad (1)$$

$$C_A = \frac{C_{A0}}{1+k\tau} \quad (2)$$

$$STY = \frac{V_R}{\tau} = \frac{1\text{m}^3}{\tau} \quad (3)$$

LP(kW) is the standardized lamp power, which would illuminate 1 m^3 of the reactor, where the lamp power (P) in k W is normalized to the volume (V, m^3) of the reaction medium in the experimental setup (Eq.(4))

$$LP = P \frac{1\text{m}^3}{V} \quad (4)$$

The faradaic and mineralization current efficiencies were calculated following Equation 5 and 6:

$$E_f (\%) = \frac{F \cdot \Sigma[\Delta n \cdot z]}{I \cdot \Delta t} \cdot 100 \quad (5)$$

$$EC = \frac{2.67[(TOC)_t - (TOC)_{t+\Delta t}]FV}{8I\Delta t} \quad (6)$$

where F is the Faraday constant ($96\,487\text{ C mol}^{-1}$), Δn is the moles of 2,4-D removed at time Δt , z is the number of electrons exchanged, I (A) is the current applied and TOC_t and $\text{TOC}_{t+\Delta t}$ correspond to the organic load (g dm^{-3}) at a certain time t and $t+\Delta t$ (s) and V (dm^3) is the volume of the electrolyzed solution.

The electric energy consumption per unit volume of electrolyzed solution (w) was calculated by Eq.2 in which U is the cell voltage (V).

$$w = \frac{UIt}{V} \quad (7)$$

3. Results and discussion

Figure 1 shows the removal of 2,4-D during the treatment of 20 mg L^{-1} by single electrochemical (absence of light) and photochemical (absence of current) technologies and by combined photoelectrochemical process. In the case of single electrochemical process, the current densities evaluated were 10 , 30 , 300 and 500 mA cm^{-2} , whereas in the case of single photochemical process an UV-lamp of 11 W and 254 nm of wavelength was used.

Regarding electrochemical tests, it can be observed that the percentage of 2,4-D removed during the reaction period tested (1 hour) increases with the applied current density, achieving degradation percentages of 14.9% , 21.3% , 27.0% and 57.0% at 10 , 30 , 300 and 500 mA cm^{-2} , respectively. These differences can be explained by the different current charges applied to the system in each test: 0.066 , 0.2 , 2 and 3.33 A h dm^{-3} , respectively. Hence, the higher the charge, the higher is the removal. Anyway, these electric charges were not high enough to promote the complete 2,4-D oxidation, and longer reaction periods are required.

Regarding photochemical system, results obtained show that this technology, using a tubular reactor with a capacity of 60 cm^3 , is capable to attain more than 40 % of removal of 2,4-D after 60 minutes of irradiation at 254 nm and 11W. This is a significant value, once the Lamp Power (LP) is just 183 KW m^{-3} , considering that the volume in the irradiated area is only 60 cm^3 . The Power Lamp by irradiated area is 5.04 KW m^{-2} for total area cylindrical (TSA) equal to 21.8 cm^2 . Espindola and coworkers (2019) showed that 1.5 dm^3 of solution containing 20 mg dm^{-3} of Oxytetracycline was degraded about 53% after 120 min of irradiation by direct photolysis with 2 UVC lamps of 4 W. Moreover, the PSTY for this results was 0.04, very similar that one for our experiments that are 0.043[27]. S. Kundu and coworkers (2005) achieved 20.3% degradation of 3 cm^3 of 2,4 -D solution containing 30 mg L^{-1} after 45 min UV light irradiation of $\sim 350 \text{ nm}$ (with five 8W UV light having a total of 600 lux intensity) using only water as solvent media on degradation (without salts)[41]. Regarding mechanisms, they have been studied by many authors, that have demonstrated by electron spin resonance and reactive oxygen species scavenging experiments the generation of various reactive oxygen species (ROS) under light irradiation, including $\cdot\text{OH}$ and singlet oxygen $^1\text{O}_2$, which can be responsible of organics photo-oxidation [42-48].

Comparing to the single electrolytic process, the combined photoelectrochemical process is so much better, attaining higher 2,4-D removal values at all current densities studied and with improvements in herbicide removal of 64.0, 57.0, 70.0 and 45.0 % at 10 mA cm^{-2} , 30, 300 and 500 mA cm^{-2} , respectively. However, at low current density (10 and 30 mA cm^{-2}) the combined process is not able to improve results of single photochemical system and current densities above 30 mA cm^{-2} are required to, accelerate the degradation and decrease the charge required (Q) for a total removal. Thus, in the photoelectrochemical system at 500 mA cm^{-2} complete herbicide removal was obtained

with only 40 minutes of treatment. This observation may be related to the massive generation of oxidant species that occurs during electrolysis with diamond electrodes and which can act in the bulk and contribute to the overall oxidation process[1, 49, 50].

Figure 1. Relative 2,4-D concentration reduction as a function time for (!) Photochemical process (PC), Electrolysis (full points) and PEO (empty points) process at different current densities: (●) 10, (▲) 30, (▼) 300 and (◆) 500 mA cm⁻². Conditions: pH natural 4.5, T 20 °C, and 0.1 M Na₂SO₄.

Fig. 2 shows the I–V curves of sulphate or perchlorate solutions in presence and absence of UV light. As can be seen in sulphate media there is a substantial increase in the current in presence of light, compared to the dark solution. On contrary, I–V curves are almost overlapped in perchlorate media. This may be related to the reactivity of both media: sulphate ions can be further oxidized to form persulfate (eq.8) whereas in perchlorate media chlorine shows oxidation state of +7 and it cannot be further oxidized. In this point, it is well-known that persulfate and other oxidants formed during electrolysis

(hydrogen peroxide (eq. 9) or ozone (eq.10)) can be activated by UVC light irradiation to sulfate radicals and to hydroxyl radicals, according to the eqs. 11-13 [30, 51-55], and this may explain the differences observed in I-V curves.

Figure 2: Linear sweep voltammogram on boron-doped diamond (BDD) anodes of electrolyte solution on sodium sulphate media, perchlorate media and a mixture of

sulphate and perchlorate media at 0.05 M and pH = 4.5 with and without light irradiation. Scan rate 20 mV s⁻¹.

Therefore, the role of the oxidant formed during electrolysis and further activated is expected to be very relevant. To clarify this point, Figure 5 shows the influence of the current density on the current efficiency of 2,4-D removal (part a) and of faradaic efficiency of mineralization (part b) calculated from TOC values in according to eqs. 5 and 6, respectively for both electrochemical and photoelectrochemical processes. As can be observed, current efficiency is strongly influenced by the current density and light irradiation. In single electrochemical process, an increase of the current density leads to more efficient degradation but at very high current densities, the current efficiency decreases. This is the typical behavior of mass transfer controlled processes previously reported in literature [10, 56, 57] . In terms of mineralization, the higher the current density, the higher is the current efficiency. Likewise, the improvement of the combined process seems to be even more relevant at high current densities.

Figure 3: Effect of current density on the current efficiency of 2,4-D removal and b) faradaic efficiency of mineralization for EO and PEO process. Electrolysis (full points) and PEO (empty points) process at different current densities: (■) 10, (●) 30, (▲) 300 and (▼) 500 mA cm⁻². Conditions: pH natural 4.5, T 20 °C, and 0.1 M Na₂SO₄.

To quantify this improvement, experimental data were fitted to a first order kinetics and the resulting kinetic constants were used to calculate the synergy effect of the combined process, according to eq. 13.

$$Sinersistic\ index\ (S) = \frac{k_{PEO}}{K_{photo} + k_{EO}} \quad (13)$$

Figure 4 shows the synergy index of the combined system and inset the kinetic constant of the single and combined processes. The values of kinetic constant of EO processes increases moderately with the current density: 2.13×10^{-3} , 2.93×10^{-3} , 6.00×10^{-3} and

$1.35 \times 10^{-2} \text{ min}^{-1}$ for 10, 30, 300 and 500 mA cm^{-2} respectively. But this improvement is quite more relevant in presence of light: 8.5×10^{-3} , 1.01×10^{-2} , 4.28×10^{-2} and $7.57 \times 10^{-2} \text{ min}^{-1}$ for 10, 30, 300 and 500 mA cm^{-2} respectively.

A synergistic indexes of 2.5 and 3 resulted for the removal of 2,4-D during photoelectrolysis at 300 and 500 mA cm^{-2} , whereas an antagonistic effect (0.6 and 0.7 of synergistic index) was obtained at the lower current densities tested. At lower current densities the oxidants necessary to be active by light are not generated. However, at higher density current the PEO process shown very satisfactory due to the higher generation of oxidants in the anode surface that are extended to the bulk and active by light, then acting in the elimination of the target compound. This reveals that photoelectrolysis is an efficient technology for degrading 2,4-D and that the photoelectrochemical reactor tested would be an excellent alternative for the removal of organochlorinated compounds since it promotes the generation of free radicals from the photoactivation of electrogenerated oxidants near the anode and in the bulk, improving the process performance. However, it is very important which of the two processes is having the primary role: photolysis enhances electrolysis when this later treatment acts as the primary treatment. However, electrolysis does not enhance but worse the performance of photolysis when this non electrochemical process is the primary (in terms of energy).

Figure 4. Synergistic effect calculated at different current densities. Inset: Kinetic constants obtained after fitting the experimental degradation results to a first-order kinetic reaction model.

Figure 5 compare the percentage of the 2,4-D degradation after 60 minutes in all the systems tested versus current density and energy consumption (estimated from equation 7). For comparison purpose, data corresponding to single photolysis has been marked. As can be observed there is a clear negative effect when UV light is coupled to EO at low current density indicating an antagonistic effect which can be associated to the destruction of the oxidant produced photochemically by interaction with the oxidants produced electrochemically or by direct reaction on the electrode surfaces. However, at higher current the effect becomes positive (there is a synergism between the process).

As said before, photolysis is more efficient than EO at 10, 30 and 300 mA cm⁻², but the energy requirements are also higher. As observed in part b of the Figure, photolysis needs too more energy (73.3 KW m⁻³) than electrolysis at 500 mA cm⁻² (58.3 KW m⁻³) to attain similar removal percentage. Thus, in terms of energy, EO at 500 mA cm⁻² is competitive in comparison to photolysis. For PCE process, the consumption raised at higher current density but the gain in removal is great. Comparing EO and PEO process, the ratio between PEC and EO removal was calculated and the values obtained were 2.8, 2.34, 3.41 and 1.83 at 10, 30, 300 and 500 mA cm⁻², respectively, which correspond to higher improvement in the removal around 70 % at 300 mA cm⁻². Regarding to cost, the ratio between PEC and EO values are 210.5, 50.86, 3.62 and 2.24 at 10, 30, 300 and 500 mA cm⁻², respectively. The lower values were obtained at higher current densities. In this way, it is possible to calculate the cost/benefit ratio for all current densities investigated. The values obtained are: 75.1, 121.0, 1.0 and 1.2 at 10, 30, 300 and 500 mA cm⁻², respectively. This means that the combined processes can be very promising with a rather advantageous cost/benefit ratio when higher current densities are applied.

Figure 5. a) 2,4-D removal percentage at the end of 1 hour of the treatments and b) electric energy consumption obtained by (■) EO, PC (■) and (●) PEO process at 0, 10, 30, 300 and 500 mA cm⁻².

It is known that most pesticides shown UV–Vis absorption bands at relatively short UV wavelengths. Direct irradiation of those may lead to the promotion of the pesticide molecules to their excited singlet states, which may then intersystem cross to produce triplet states. Such excited states can then undergo, among other processes as homolysis, heterolysis or photoionization. Consequently, photolytic degradation of 2,4-D is expected to proceed through the formation of various reaction intermediates, whose carbon atoms are eventually converted to carbon dioxide, while heteroatoms are converted to inorganic ions. To understand the possible routes through which 2,4-D is converted to reaction by-products and, eventually, to end-products samples were analyzed samples by HPLC, where peaks were followed, and the major intermediates were identified for each process evaluated. The accomplishment of the by-products during the EO, PC and PEC process is shown in the Figure 6. As can be seen five transformation products (TPs) were identified on the basis of reactions pathways proposed in the literature and previous works of our group: Hydroquinone (HDQ), benzoquinone (BZQ), 4-chlorosorcinol (4-CRS), phenol and 4-chlorophenol (4-CP). Comparing the effect of current density, it can be seen that processes are much more efficient at higher current densities once few intermediates was identified and with lower concentrations. Comparing process, higher concentrations of the by-products are retained in the end of EO treatments, mainly at lower current densities. In these cases HDQ, B compound, and BZQ are the main intermediates.

In the Photochemical process can be seen that reasonable area is kept after one hour of the treatment once as can be discussed above 2,4-D was marginally oxidized which led to a few intermediates.

Coupling EO to Photochemical process improves considerably the oxidation of these compounds, once very low or zero concentration of intermediates was detected after 1

hour especially at higher current density applied. Besides that, same intermediates were found in the both processes (single electrolysis and photo-electrolysis), indicating that the primary mechanism of 2,4-D degradation is the same. However, at the end of the irradiated treatments (PC and PEC) peaks detected differ from those obtained when only electrolysis was carried. This means that that photons ($h\nu$) attack the herbicide differently, forming compounds no identified in this case. Many works in the literature shows that 2,4-D is oxidized to 2,4-DCP, however in this work this compound didn't identified. This behavior can be explained due to the harsh conditions created in this setup and specific conditions that leads to the generation of compounds with a short carbon chain.

Figure 6. Area of the main intermediates peaks obtained after 1 hour of the treatments by HPLC-UV using a C18 column.

These results are in agreement with the results observed for the TOC theoretical mineralization as shown the Fig. 7. TOC oxidized at the end of the process was calculated based in the initial TOC 2,4-D minus the TOC sum of the all identified intermediates

detected by HPLC (because of the non-suitable detection level of the TOC available in our Lab). As can be seen a poor mineralization was observed for experiments carried at 10 and 30 mA cm⁻² at EO process. These results show that the more reaction products are formed during the electrochemical process and they are hardly oxidized. Higher rates of mineralization were attained with light irradiation wherein complete mineralization is attained at 500 mA cm⁻². The mineralization results indicate that a faster reaction occurs between the intermediates formed and photogenerated radicals in the bulk.

Figure 7. TOC removal calculated through of the difference between initial TOC and the sum of the TOC of the identified intermediates and theoretical no identified intermediates.

The Figure 8 show the mechanism of oxidation proposed by analyzing the by-products. As can be seen these products suggest that the main degradation pathway is the elimination of alkyl group bound followed two mainly routes for only electrochemical process and the second one for when light is irradiated. For both processes, the common

mechanism consists of addition of OH species and the missed of COOH group, allowing the formation of the 4-chlororesorcinol. For the first route (I-EO) it can be seen that the 4-chlororesorcinol is oxidized to 2-chlorophenol following the formation of hydroquinone that is oxidized to benzoquinone that are very reactive compound and easily oxidized to carboxylic acids. In the process with light irradiation the main difference is the quickly appearance of the phenol followed to two compounds no identified that were eliminated very fast as demonstrated by figure above.

Figure 8. Degradation route proposed for the removal of 2,4-D according to the intermediates detected in this work.

Conclusions

From this work, the following conclusions can be drawn:

- 2,4-D can only be slightly removed with photochemical technology, attaining only 40 % of removal after 1 hour of treatment. This removal can be strongly modified when coupling electrolysis, although results obtained depends importantly on the current density range applied.
- Positive synergistic indexes higher than 2.5 can be obtained for the removal of 2,4-D when coupling both technologies at high current densities. In addition, it can be observed higher rates of mineralization caused by a faster reaction in the bulk between the intermediates formed and photogenerated radicals.
- An antagonistic effect is obtained when lower current densities were applied (synergistic index below 0.7) caused by complex scavenging interactions of the radicals formed.

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