**Degradation of dye Procion Red MX-5B by
electrolytic and electro-irradiated technologies using
diamond electrodes**

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Abstract

This work focuses on the treatment of synthetic wastewater polluted with dye Procion Red MX-5B by different Electrochemical Advanced Oxidation Processes (EAOP) based on diamond anodes. The influence of the current density and the supporting electrolyte has been studied on dye removal and total mineralization of the organic matter. Results show that electrolysis with diamond electrodes is a suitable technology for an efficient degradation of dye. Nonetheless, the process efficiency increases when using chloride as supporting electrolyte because of the electrochemical generation of hypochlorite in wastewater which significantly contribute to dye removal. On the contrary, the total mineralization of the organic matter is more efficient in sulfate media. In this case, large amounts of peroxodisulfate are electrogenerated, favoring the complete removal of total organic carbon (TOC). On the other hand, lower current densities (10 mA cm^{-2}) lead to a more efficient removal of both dye and TOC due to the mass transfer limitations of the technology. Finally, the coupling of UV light irradiation or ultrasound to electrolysis significantly improves the process performance, being photoelectrolysis the most efficient technology for the treatment of wastewater polluted with Procion Red MX-5B. This fact is due to the potential production of free chlorine or sulfate radicals that takes place by the activation of the electrogenerated oxidants. These species are more reactive than oxidants and, therefore, they quickly attack the organic matter present in wastewater.

Keywords: diamond, dye, electrolysis, photoelectrolysis, sonoelectrolysis.

1. Introduction.

In last decades, the increased industrial activities in different sectors such as agriculture, petroleum, textile, pharmaceutical... has caused an increase in the production of industrial wastewater (Kolpin et al., 2002). These wastewaters contain high concentration of organic pollutants which are not possible to completely degraded by traditional processes located in Wastewater Treatment Plants (WWTP). Hence, these pollutants are considered as Persistent Organic Pollutants (POPs) (Bueno et al., 2012). Textile industries are among the industrial activities that produce larger amount of wastewaters polluted with POPs. Specifically, textile effluents contain high concentration of inorganic salts and different types of reactive dyes which are used to provide color in clothes (Vandevivere et al., 1998; O'Neill et al., 1999). These compounds are characterized by a large number of carbons in their structure as aromatic rings. Likewise, dyes can also contain chlorine, sulfur or nitrogen in their molecule. This last one forms azo groups where two nitrogen atoms are linked to each other by a double bond and each one is linked to a carbon ($C-N=N-C$). For this reason, they are commonly called azo dyes and depending on the number of $N=N$ bonds, they can be classified as monoazo, diazo, triazo... Based on the above, dyes are hazardous compounds that should be removed from wastewater before discharge to WWTP (Alves de Lima et al., 2007). Therefore, it is necessary to develop clean and efficient technologies that guarantee the complete removal of these pollutants. In this context, Electrochemical Advanced Oxidation Processes (EAOPs) can be considered as a good alternative to traditional methods due to their high efficiencies in the removal of organic pollutants such as pharmaceuticals, pesticides and dyes among others (Rodrigo et al., 2014; Sirés et al., 2014). These technologies are based on the production of large amounts of hydroxyl radicals, a powerful oxidant which significantly contribute to the degradation of the organic matter. Among EAOPs, electroFenton has been successfully checked on

the removal of different pollutants (including dyes) by Brillas' and Oturan's groups (Brillas et al., 2009). During this process, it is required the addition of iron salts to promote Fenton's reaction with the electrogenerated hydrogen peroxide over the cathode surface by oxygen reduction. Likewise, in order to favor the production of large amounts of hydrogen peroxide, pH solution should be maintained around 3. Under these conditions, it has been recently reported that the organic matter of wastewater polluted with different organics such as tetracaine (Ridruejo et al., 2018), naproxen (Coria et al., 2016), fluometuron (Diaw et al., 2017) and dyes (Panizza and Cerisola, 2009b; Labiadh et al., 2016) are completely mineralized.

On the other hand, electrochemical oxidation with diamond electrodes is considered another promising EAOP for the removal of a great variety of organic pollutants (Panizza and Cerisola, 2009a). Diamond anodes present an excellent electrocatalytic properties towards the production of large amounts of hydroxyl radicals by water oxidation over its surface (Marselli et al., 2003). Likewise, this material allows to generate other powerful oxidants from the electrolysis of the ions naturally contained in wastewater which also contribute to the mineralization of the organic matter (Cañizares et al., 2009b). For this reason, it is not necessary the addition of chemicals to improve the process performance and, therefore, electrolysis with diamond anodes is particularly suitable for the treatment of wastewater polluted with POPs. Nonetheless, the main drawback of this technology is the mass transfer of the pollutant to the anode surface (Cañizares et al., 2006; Bebelis et al., 2013). In this context, the application of ultrasound to electrolysis (sonoelectrolysis) can promote the mass transfer in the system, favoring the degradation of the organics present in wastewater. In addition, ultrasound can encourage the production of free radicals from water sonolysis when working with high frequencies. These radicals also contribute to the degradation of the organic matter and,

therefore, enhance the electrochemical treatment (Adewuyi, 2005; Almazán-Sánchez et al., 2017; Cotillas et al., 2018). Likewise, the irradiation of the solution with UV light during electrolysis (photoelectrolysis) favors the potential production of free radicals from the photo-activation of the oxidants present in wastewater (Cotillas et al., 2016; Rubí-Juárez et al., 2016). Therefore, both technologies (ultrasound and UV light irradiation) enhance the removal rate of electrolysis with diamond electrodes (Martínez-Huitle et al., 2015).

With this background, the main aim of the present work is to study the removal of Procion Red MX-5B as model of dye by electrolysis, photoelectrolysis and sonoelectrolysis using diamond anodes. This compound has been selected because it is widely used to dye cotton, wool, silk polyamide fibers in textile industry. The influence of the current density ($10\text{--}100\text{ mA cm}^{-2}$) and the supporting electrolyte (Na_2SO_4 ; NaCl) has been checked because these parameters significantly affect the process efficiency (Araújo et al., 2015b).

2. Material and methods.

2.1. Chemicals.

Procion Red MX-5B ($\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_7\text{S}_2$, dye content 40%), sodium sulfate and sodium chloride (Sigma Aldrich) were analytical grade and use as received. Double deionized water (Millipore Milli-Q system, resistivity: $18.2\text{ M}\Omega\text{cm}$ at 25°C) was used to prepare all solutions.

2.2. Analytical techniques.

The concentration of Procion Red MX-5B (PR) was followed by spectrophotometry using a Cary Series UV-Vis Spectrophotometer (Agilent Technologies) at 538 nm. TOC

concentration was monitored using a ~~TOC concentration was monitored using a~~ Multi N/C 3100 Analytik Jena analyzer (concentration accuracy: $\pm 1\%$). The concentration of hypochlorite was determined by titration with 0.001 M As_2O_3 in 2 M NaOH (Wilpert, 1957; Freytag, 1959) (concentration accuracy: $\pm 3\%$). Chlorate and perchlorate were measured by ion chromatography (Metrohm 930 Compact IC Flex) coupled to a conductivity detector (concentration accuracy: $\pm 0.5\%$). A Metrosep A Supp 7 column was used and the mobile phase consisting of 85:15 v/v 3.6 mM Na_2CO_3 /acetone with a flow rate of 0.8 mL min^{-1} . Persulfate concentration was analyzed iodometrically according to Kolthoff & Carr (Kolthoff and Carr, 1953) (concentration accuracy: $\pm 3\%$) and also, spectrophotometrically according to the procedure described by Liang et al. (Liang et al., 2008) (concentration accuracy: $\pm 5\%$). pH and conductivity were measured using a multiparameter analyzer SESSION+ MM150DL (Hach).

2.3. Electrochemical cell.

Electrolyses were carried out in a single compartment electrochemical flow cell. Boron doped diamond (BDD) (WaterDiam, Switzerland) was used as anode and cathode. The electrodes were circular with a geometric area of 78 cm^2 . The main characteristics of the diamond electrode used in this work are: boron concentration of 500 mg L^{-1} , a thickness of 2.62 μm , sp^3/sp^2 ratio of 206 and p-Si as support. The electrode gap between anode and cathode was 5 mm and, the electric current was provided by a Delta Electronika ES030-10 power supply (0-30 V, 0-10 A). Photoelectrolyses were carried out by using an UVG ERG-11 lamp (Baquias Cabre i Berga, S.L.) and an Epoch 650 ultrasound (US) horn (Olympus) was used during sonoelectrolyses. Both devices were introduced in the bulk solution during the treatment. The UV lamp irradiated 4 W whereas the ultrasound horn emitted 10 MHz and a power of 200 W. Wastewater was

stored in a glass tank (1 L). Synthetic wastewater consisted of a solution containing 100 mg L⁻¹ of dye (commercial reagent) and 3,000 mg L⁻¹ of supporting electrolyte (Na₂SO₄ or NaCl). All experiments (1 L) were carried out under galvanostatic conditions and discontinuous mode. The current density applied ranged from 10 to 100 mA cm⁻² and the temperature was maintained at 25 °C.

3. Results and discussion.

Figure 1 shows changes in Procion Red MX-5B concentration during the electrolysis, photoelectrolysis and sonoelectrolysis of synthetic wastewater polluted with 100 mg L⁻¹ of dye at different current densities. Sulfate and chloride were used as supporting electrolytes.

As can be observed, the concentration of dye decreases with the applied electric charge for all the tests carried out, regardless the current density and the supporting electrolyte. However, the process efficiency is clearly influenced by these parameters. In this context, the use of low current densities (Fig. 1a) requires applied electric charges lower than 15 Ah L⁻¹ to attain a complete removal of the dye whereas values higher than 20 Ah L⁻¹ are needed for a total depletion of the pollutant at 100 mA cm⁻² (Fig. 1b). This behavior is most remarkable during the electrolysis in sulfate media and it is related to mass transfer limitations of the pollutant to the anode surface (direct electrolysis) and the production of large amounts of hydroxyl radicals from water oxidation at higher current densities (Eq. (1)). These species present a high oxidant capacity and they can attack the organic matter present in the effluent, favoring its complete degradation (indirect electrolysis). Nonetheless, these electrogenerated hydroxyl radicals can be also wasted in other secondary reactions during the treatment, decreasing the process efficiency in terms of pollutant removal at 100 mA cm⁻² (Panizza and Cerisola, 2005).

Likewise, the limiting current density (j_{lim}) for the removal of 100 mg L⁻¹ of dye is 0.0053 mA cm⁻². This parameter has been calculated by Eq. (2) where n is the number of electrons involved in the oxidation of dye, F the Faraday constant, C_0 the initial concentration of Procion Red MX-5B and k_m is the mass transfer coefficient calculated from a standard limiting current test. The value obtained is lower than the current densities employed in this work (10-100 mA cm⁻²) and, hence, it clearly indicates the existence of mass transfer limitations.

$$j_{lim} = n \cdot F \cdot k_m \cdot C_0 \quad (2)$$

Regarding the influence of the supporting electrolyte, the removal rate of Procion Red MX-5B is higher when using chloride salts. This fact is related to the potential production of hypochlorite from the electrooxidation of chloride ions which significantly contribute to the removal of the pollutant (Eqs. (3)-(5)) (Brillas and Martínez-Huitle, 2015). Likewise, sulfate can be oxidized during the treatment with BDD anodes, favoring the generation of peroxodisulfate (Eq. (6)) (Serrano et al., 2002). Both compounds are powerful oxidants which contribute to the degradation of Procion Red MX-5B. However, the potential required for the generation of active chlorine is lower than that needed for peroxodisulfate (1.36 vs. 2.01 V / SHE). For this reason, large amounts of hypochlorite can be generated in comparison with the concentration of peroxodisulfate in wastewater and, therefore, the process efficiency increases working in chloride media (Cañizares et al., 2009a).

On the other hand, the coupling of UV light or ultrasound to electrolysis improves the removal of dye in sulfate media. Specifically, the process efficiency follows the order photoelectrolysis > sonoelectrolysis > electrolysis. This fact is mainly due to the photo- and sono-activation of the electrogenerated oxidants during the treatment. In this context, peroxodisulfate can be activated promoting the generation of free sulfate radicals (Eqs. (7)-(8)) (Araújo et al., 2015a; Almazán-Sánchez et al., 2017). These species are known to be more efficient, i.e. several log units, than peroxodisulfate for the removal of pollutants (Mercado et al., 2018).

In the case of chloride media, similar behaviors are observed for all the studied technologies at different current densities. Nonetheless, the electrogenerated hypochlorite can be also activated during the process favoring the production of free chlorine radicals (Eqs. (9)-(10)), even though they do not seem to have a great influence on dye removal. These results suggest that chlorine radicals are rapidly recombined, favoring the production of chlorine gas (Eq. (11)) and, therefore, a potential generation of hypochlorite (Eqs. (4)-(5)).

Figure 2 shows the concentration of oxidants electrogenerated during the removal of Procion Red MX-5B at different current densities. It is important to highlight that the concentration of peroxodisulfate was similar with the different analytical techniques used. Once again, different behaviors can be seen depending on the current density and the electrolyte. The amount of electrogenerated oxidants is lower when working at 10

mA cm⁻², regardless the electrolyte used (Fig. 2a). This fact is related to the different mechanisms that take place during the production of oxidants by electrolysis with BDD anodes (Cañizares et al., 2007). In this context, hypochlorite and peroxodisulfate are mainly generated by the direct oxidation of chloride (Eqs. (3)-(5)) and sulfate (Eq. (6)) over the anode surface under these conditions (10 mA cm⁻²). On the other hand, large amounts of hydroxyl radicals are produced when working at 100 mA cm⁻². These species not only attack the organic matter present in the effluent but also react with the anions contained in wastewater, favoring the generation of oxidants such as, hypochlorite (Eq. (12)) and peroxodisulfate (Eq. (13)). For this reason, the concentration of electrogenerated oxidants is higher at 100 mA cm⁻² (Fig. 2b) since these species can be produced by two mechanisms simultaneously: direct and mediated electrolysis.

For each applied current, the maximum concentration of peroxodisulfate is lower than that of hypochlorite. This fact is related to the potential required for the generation of each oxidant, as previously commented. Likewise, it is well known that the life-time of peroxodisulfate in wastewater containing organics is lower due to its potential higher reactivity (Cañizares et al., 2009a). On the other hand, it is important to point out that the irradiation of UV light or ultrasound leads to a lower production of oxidants during the treatment both at 10 mA cm⁻² and 100 mA cm⁻² (Fig. 2a). In fact, the use of electroirradiated technologies favors the production of free chlorine and sulfate radicals from the activation of hypochlorite and peroxodisulfate (Eqs. (7)-(10)) and, hence, the concentration of this species (ClO⁻ and S₂O₈²⁻) is lower.

It is also important to observe that peroxodisulfate concentration reaches a steady state at the end of electrolyses, meaning that the generation and consumption rates of this

species are similar during the process. On the contrary, hypochlorite concentration shows a maximum value at about 5 Ah L⁻¹ and afterword it decreases even up to zero. This trend can be due to the reaction between the organic matter and this compound, favoring the removal of dye; or to the transformation of hypochlorite to other chlorine compounds in high oxidation state. In this context, significant amounts of chlorate and perchlorate can be generated from the electrolysis of chlorides with BDD anodes (Eqs. (14)-(16)) (Sánchez-Carretero et al., 2011).

Likewise, the presence of high concentrations of electrogenerated hydroxyl radicals can promote the production of chlorate and perchlorate in wastewater (Eqs. (17)-(19)).

Both species are toxic and harmful to human health and, therefore, their presence should be avoided in wastewater treatment. For this reason, the concentration of chlorate and perchlorate was monitored during the process. Figure 3 shows changes in the concentration of these species with the applied electric charge during the degradation of Procion Red MX-5B in chloride media by different technologies at 10 and 100 mA cm⁻².

As can be observed, at low current density (Fig. 3a), the concentration of both compounds increases with the applied electric charge, regardless the technology employed and in particular, chlorate is the predominant species in the system. This is due to the fact that the electrochemical production of perchlorate is thermodynamically

273 favored but it is kinetically limited under these conditions (Sánchez-Carretero et al.,
274 2011). On the contrary, perchlorate is the final product when working at 100 mA cm⁻²
275 (Fig. 3b). This fact is related to the large amounts of hydroxyl radicals that are generated
276 during the process at higher current densities, favoring the complete oxidation of
277 chlorides to perchlorate as final product.

278 On the other hand, it is important to highlight the influence of electroirradiated
279 technologies on chlorine speciation. As can be seen in Fig. 3, the generation of chlorate
280 and perchlorate is less favored when UV light or US are coupled to electrolysis.
281 Specifically, the concentration of these oxoanions follows the order photoelectrolysis <
282 sonoelectrolysis < electrolysis. The activation of hypochlorite to produce free chlorine
283 radicals seems to be the responsible mechanism why the generation rate of these species
284 is lower (Eqs. (9)-(10)). In this context, the promotion of hypochlorite to chlorine radical
285 competes with the electrochemical oxidation of hypochlorite to chlorate and perchlorate,
286 hindering the potential production of these harmful species during the photo- and
287 sonoelectrolysis of wastewater polluted with Procion Red MX-5B. These results are
288 highly important because reveal that the coupling of UV light or US to electrolysis with
289 BDD anodes could avoid the potential generation of large amounts of chlorine
290 compounds in high oxidation state during wastewater treatment.

291 The electrolysis of synthetic wastewater polluted with Procion Red MX-5B can lead to
292 the formation of other intermediate organic compounds (even more hazardous than the
293 dye) or to the complete mineralization of the organic matter to carbon dioxide. To check
294 the possible formation of intermediates during the process, the concentration of total
295 organic carbon (TOC) was monitored. This parameter informs about the complete
296 mineralization of the organic matter present in wastewater and, therefore, it is an indirect
297 measure of the presence of intermediates in wastewater. Figure 4 shows the evolution

of TOC with the applied electric charge during the treatment of wastewater polluted with Procion Red MX-5B at different current densities.

As can be observed, TOC concentration decreases with the applied electric charge for all the tests carried out. At low current densities (Fig. 4a), photoelectrolysis shows the lower TOC value at the end of the experiment in sulfate media and, therefore, the higher efficiency for the mineralization of the organic matter contained in wastewater. Specifically, a removal percentage of 99% is attained under these conditions. These results suggest that the generation of sulfate radicals from the photo-activation of peroxodisulfate (Eq. (7)) favors not only the removal of dye but also the oxidation of organic intermediates generated during the process. Likewise, sonoelectrolysis follows a similar trend than that observed in TOC removal during photoelectrolysis. Nonetheless, in this case, the final value registered is higher (i.e. 94% of removal percentage). This fact can be due to a lower efficiency in the production of free sulfate radicals by the application of ultrasound. Finally, single electrolysis leads to the lowest efficiency in sulfate media for TOC depletion, reaching a final removal of 83%. This clearly reveals that the coupling of UV light or ultrasound to electrolysis with BDD anodes significantly improves the process performance in terms of both dye and TOC removal. On the other hand, final TOC values are higher when working at 10 mA cm^{-2} in chloride media. Under these conditions, it is not possible to attain a complete mineralization of the organic matter with low specific charge. The trend observed indicates that there is an initial decrease followed by a plateau zone and finally, the concentration decreases again. This behavior has been reported in literature and it is related to an accumulation of organochlorinated compounds in wastewater which are more slowly degraded (Cañizares et al., 2003). TOC removal efficiency is higher during photo- and sonoelectrolysis at the beginning of the experiments. However, the final

percentage removal is similar for all the technologies studied (electrolysis: 61%; photoelectrolysis: 67%; sonoelectrolysis: 64%). These results agree the previous obtained in dye removal (Fig. 1a) where no significant influence of electroirradiated technologies was observed.

Regarding TOC removal at 100 mA cm^{-2} (Fig. 4b), it is possible to attain a complete mineralization of the organic matter during all the technologies studied in sulfate media and even, during photoelectrolysis when using chloride as supporting electrolyte. This fact is due to the higher concentration of hydroxyl radicals electrogenerated which contribute to the degradation of the organic matter present in wastewater. Likewise, as pointed out before, hydroxyl radicals favor the production of large amounts of oxidants during the electrolysis at 100 mA cm^{-2} and, hence, the concentration of free radicals also increases during photo- and sonoelectrolysis. Both species (oxidants and radicals) attack the organic matter, improving the process performance in terms of TOC removal. Photoelectrolysis is the most efficient process for the complete mineralization of the organic matter, regardless the electrolyte used. These results reveal that the activation of oxidants by UV light irradiation seems to be more efficient than by the application of ultrasound. Nonetheless, the applied electric charge required to attain a complete TOC removal is higher when working at 100 mA cm^{-2} in comparison with the results obtained at 10 mA cm^{-2} . This behavior was also observed during the removal of dye (Fig. 1). Finally, the use of chloride as supporting electrolyte leads to the lowest efficiency in TOC removal during electrolysis. Specifically, a percentage removal of 94% is attained whereas a 98% is obtained during sonoelectrolysis and a total removal is reached when coupling UV light and electrolysis. Therefore, the evolution of TOC during the degradation of dye Procion Red MX-5B in chloride media clearly suggests that the

production of other organochlorinated compounds takes place during the process, regardless the current density applied.

For comparison purposes, the results obtained in dye and TOC removal were fitted to a first order kinetics model and removal rate constants were calculated. The values are represented in Fig. 5. As can be observed, the kinetic constants for dye removal (Fig. 5a) are higher than that obtained in the mineralization of the organic matter (Fig. 5b). This is an expected result taking into account that the degradation of dye is faster than TOC depletion. During the oxidation in sulfate media, photoelectrolysis is the fastest process for the removal organic matter (dye and TOC). Furthermore, higher current densities significantly increase the values obtained for kinetic constants. Hence, the degradation of Procion Red MX-5B is faster at 100 mA cm^{-2} despite less charge is necessary for the complete removal at 10 mA cm^{-2} . This behavior has been previously reported in literature and it indicates that the process is mainly controlled by mass transfer (Panizza and Cerisola, 2009a).

In the case of chloride media, no remarkable differences are observed when working at 10 mA cm^{-2} . However, photoelectrolysis shows the highest kinetic constant for dye removal followed by sonoelectrolysis at 100 mA cm^{-2} . Opposite to that, this last one seems to be the fastest process for TOC removal under these conditions. These results reveal that electroirradiated technologies lead to a more efficient and fast degradation of organic matter than single electrolysis at higher current densities in chloride media.

Finally, the energy consumption (W , kWh m^{-3}) per unit volume has been calculated by means of the electric charge passed (Q , Ah L^{-1}) and the cell voltage (V) (Eq. (20)). In the case of irradiated technologies, the energy consumption has been calculated taking into account the light power irradiated ($w = 0.004 \text{ kW}$) and the ultrasound power ($w = 0.2 \text{ kW}$) (considering 100% efficiency of ultrasound generator and UV lamp) (Eq. (21)).

Figure 6 shows the energy consumption at different current densities for all the technologies studied.

$$W = Q \cdot V \quad (20)$$

$$W = w \cdot t / \text{volume} \quad (21)$$

Sonoelectrolysis shows the highest energy consumption for the removal of dye at 10 mA cm⁻², regardless the electrolyte used. This is an expected result taking into account that the exposure time required to attain a complete degradation of Procion Red MX-5B is also higher under these conditions. Electrolysis and photoelectrolysis shows a similar energy consumption at low current densities which suggests that the coupling of UV light to electrolysis with diamond anodes does not lead to high energy costs. This fact is due to the low power of the UV lamp (0.004 kW) in comparison with the power of ultrasound (0.2 kW). On the other hand, similar values are obtained when working at 100 mA cm⁻² for all the technologies employed which is related to a lower time required for the removal of dye. These results reveal that electroirradiated technologies are more suitable at higher current densities because of they do not entail a high energy consumption and the process efficiency is higher.

4. Conclusions.

From this work, the following conclusions can be drawn:

- Wastewater containing dye Procion Red MX-5B can be mineralized by electrolysis, photoelectrolysis and sonoelectrolysis using diamond electrodes. The use of low current densities (10 mA cm⁻²) leads to higher efficiencies due to the mass transfer limitations that take mainly place at 100 mA cm⁻². On the other hand, the process efficiency is lower when working in chloride media

because of the potential formation of organochlorinated intermediate compounds during the treatment which are slowly oxidized.

- The electrochemical generation of oxidants has a great influence in dye and TOC removal. The concentration of these species is higher when working at 100 mA cm⁻² due to the presence of large amounts of hydroxyl radicals. These radicals not only attack the organic matter but also react with the anions present in wastewater favoring the production of higher concentration of oxidants. Likewise, significant amounts of chlorine compounds in high oxidation state are produced by hydroxyl radical mediated oxidation. These compounds are harmful to human health and, therefore, their presence should be avoided. For this reason, the application of this technology in effluents containing chlorides could be limited.
- The coupling of UV light irradiation or ultrasound to electrolysis with diamond electrodes promotes the formation of free radicals (chloride and sulfate) in the bulk solution by the activation of the electrogenerated oxidants. These compounds enhance the process efficiency since they ~~are more reactive~~ react faster than oxidants with organics. In addition, the presence of free chlorine radicals seems to decrease the potential generation of chlorate and perchlorate during the treatment. These results reveal that electroirradiated technologies based on diamond electrodes not only improves the degradation processes but also could decrease the generation of toxic compounds.

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Figure captions:

Figure 1. Dye decay as function of the applied electric charge during the electrolysis (E), photoelectrolysis (PE) and sonoelectrolysis (SE) of synthetic wastewater containing 100 mg dm⁻³ of Procion Red MX-5B and 3,000 mg dm⁻³ of supporting electrolyte. Black points: E; white points: PE; grey points: SE. (■,□,▣) Na₂SO₄; (●,○,◐) NaCl; UV_{254 nm}: 4 W; US: 200 W; (a) j: 10 mA cm⁻²; (b) j: 100 mA cm⁻².

Figure 2. Influence of the current density on electrogenerated oxidants as function of the applied electric charge during the electrolysis (E), photoelectrolysis (PE) and sonoelectrolysis (SE) of synthetic wastewater containing 100 mg dm⁻³ of Procion Red MX-5B and 3,000 mg dm⁻³ of supporting electrolyte. Black points: E; white points: PE; grey points: SE. (■,□,▣) S₂O₈²⁻; (●,○,◐) ClO⁻; UV_{254 nm}: 4 W; US: 200 W; (a) j: 10 mA cm⁻²; (b) j: 100 mA cm⁻².

Figure 3. Influence of the current density on chlorine speciation as function of the applied electric charge during the electrolysis (E), photoelectrolysis (PE) and sonoelectrolysis (SE) of synthetic wastewater containing 100 mg dm⁻³ of Procion Red MX-5B and 3,000 mg dm⁻³ of NaCl. Black points: E; white points: PE; grey points: SE. (■,▣,□) ClO₃⁻; (●,●,○) ClO₄⁻; a) j: 10 mA cm⁻²; b) j: 100 mA cm⁻².

Figure 4. TOC decay as function of the applied electric charge during the electrolysis (E), photoelectrolysis (PE) and sonoelectrolysis (SE) of synthetic wastewater containing 100 mg dm⁻³ of Procion Red MX-5B and 3,000 mg dm⁻³ of supporting electrolyte. Black

567 points: E; white points: PE; grey points: SE. (■, ■, □) Na₂SO₄; (●, ●, ○) NaCl; UV_{254 nm}:
568 4 W; US: 200 W; a) j: 10 mA cm⁻²; b) j: 100 mA cm⁻².

569

570 **Figure 5.** Kinetic constants calculated for the removal of dye (a) and total organic
571 carbon (b) as function of the current density and supporting electrolyte. Black bars:
572 electrolysis; white bars: photoelectrolysis; grey bars: sonoelectrolysis.

573

574 **Figure 6.** Energy consumption for the removal of dye as function of the current density
575 and supporting electrolyte. Black bars: electrolysis; white bars: photoelectrolysis; grey
576 bars: sonoelectrolysis.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6