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2 **Keywords**

3 Chlorsulfuron, wastewater treatment, electrochemical oxidation, diamond anodes,  
4 pesticide

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6

## 1 **1. Introduction**

2 In recent years, one group of phytochemicals, pesticides, has been the subject of growing  
3 concern among environmental agencies and the scientific community. This concern is for  
4 their high risks to both human health and the environment, which are often associated  
5 with their limited biodegradability, high vapor pressure and lipid affinity [1-4]. Thus,  
6 many treatment technologies are being developed for both soil and water treatment to  
7 minimize the effects of their occurrence on the environment and public health. The novel  
8 soil treatments aim to constrain pollution and remove it by means of *in situ* technologies  
9 (without excavation to preserve the characteristics of the soil). In particular, one of the  
10 most desired characteristics of such a treatment is its ability to effectively transfer the  
11 pollutant from the soil to an aqueous phase, known as flushing fluid. Electrochemically  
12 based processes, such as electrokinetic soil fences and electrokinetic soil flushing, are  
13 very promising for helping solve this serious environmental problem [2, 5, 6]. They have  
14 been studied recently for the remediation of soil spiked with pesticides, and the results  
15 are, thus far, fairly positive: it was demonstrated that pesticide can be efficiently  
16 transferred from the soil to the flushing fluid, thereby transforming the soil remediation  
17 problem into an easier wastewater treatment issue.

18 Regarding the removal of pesticides from water, many Advanced Oxidation Processes  
19 (AOPs), such as ozonation, photochemical oxidation, photolysis with H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>,  
20 Fenton processes, and photocatalysis, have been proposed and tested [7-12] over the last  
21 decade. These AOPs are characterized by the generation of very reactive and oxidizing  
22 free radicals in aqueous solutions, particularly hydroxyl radicals. Most of them show great  
23 efficiency, but the results are strongly influenced by the characteristics of the pesticide,  
24 and the occurrence of refractory species is occasionally a major problem.

1 Currently, one of the most interesting AOPs is electrolysis, which has been demonstrated  
2 to be a very efficient technology for the removal of organic pollutants [9, 13-15],  
3 including pesticides. The results obtained with this technology depend strongly on not  
4 only the operating conditions but also the anode material used. Diamond coatings have  
5 demonstrated brilliant performance due to their intrinsic properties, which lead to the  
6 efficient production of hydroxyl radicals. This radical is a very powerful oxidant ( $E^0$ : 2.80  
7 V vs. SHE), and it is ultimately responsible for the formation of other oxidants, such as  
8 peroxosulfates, peroxophosphates, peroxocarbonates, ozone and hydrogen peroxide [16-  
9 18]. The hydroxyl radicals and many other mediated oxidants that are produced at high  
10 concentrations on the surface of a diamond are responsible for the severe oxidation  
11 conditions attained [15, 19, 20]. The interaction of these oxidants with pesticides is a  
12 factor of major significance, as demonstrated in previous works in which electrolysis,  
13 sono and photoelectrolysis were used to destroy pesticides [21-23]. The literature [24, 25]  
14 indicates that US irradiation can help improve the mass transfer to anodic surfaces during  
15 electrolysis and promote the decomposition of water, thereby producing hydroxyl  
16 radicals. Alternately, the use of light irradiation mainly permits the homogeneous  
17 activation of oxidants occurring in the bulk phase [26]. Likewise, recent studies have  
18 demonstrated that a combination of technologies was a very efficient process, even more  
19 so than expected, according to the addition of effects of the single processes [22, 27, 28].

20

21 There are many types of pesticides, and they exhibit very different physico-chemical  
22 properties. Sulfonylureas, which form a group of highly selective herbicides, are used  
23 worldwide for weed and grass control and in some crops. In particular, chlorsulfuron  
24 (ClSF) has great phytotoxicity, even at low concentrations. Its bio-refractory nature thus

1 necessitates the development of new treatment technologies to eliminate this type of  
2 pesticide from contaminated water and soil [29, 30].

3

4 The purpose of the present study is to evaluate the applicability of the electrochemical  
5 oxidation of chlorsulfuron with diamond anodes. The effects of the supporting electrolyte,  
6 current density and initial herbicide concentration are studied, with the intention of  
7 elucidating how the mediated electrolytic process affects chlorsulfuron oxidation.  
8 Additionally, to clarify the role of mediated oxidation, electroirradiated tests (with  
9 irradiation of UV light or ultrasounds) are carried out.

10

## 11 **2. Experimental methodology**

### 12 **2.1. Chemicals**

13 All chemicals, including anhydrous sodium sulfate, sodium chloride (Fluka, Spain), and  
14 chlorsulfuron (Sigma-Aldrich), were analytical grade and used as received. Acetonitrile  
15 HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Double deionized  
16 water (Millipore Milli-Q system, resistivity = 18.2 M $\Omega$  cm at 25 °C) was used to prepare  
17 all solutions.

### 18 **2.2. Electrochemical cell**

19 The galvanostatic electrolyses were carried out in a single-compartment  
20 electrochemical flow cell using 1 dm<sup>3</sup> of solution. The flow rate was kept constant at  
21 26.4 dm<sup>3</sup> h<sup>-1</sup>, and the temperature was maintained at 25 °C. Boron-doped Diamond  
22 Electrodes (Adamant Technologies) were used as both anode and cathode. Both  
23 electrodes were circular (100 mm in diameter), with a geometric area of 78 cm<sup>2</sup>. The

1 interelectrode gap was approximately 9 mm. The investigated variables in the  
2 electrochemical degradation of the herbicide were i) the nature of the supporting  
3 electrolyte (NaCl and Na<sub>2</sub>SO<sub>4</sub>) by keeping the ionic strength at 0.05 mol dm<sup>-3</sup>, ii) the  
4 applied current density (30 and 100 mA cm<sup>-2</sup>) and iii) the initial herbicide concentration  
5 (20, 50 and 100 mg dm<sup>-3</sup>).

6  
7 Irradiated experiments were carried out in the electrolysis setup using the same fluid-  
8 dynamic conditions. To achieve this, the setup was equipped with an ultrasound source  
9 (UP200S ultrasound horn, Hielscher Ultrasonics GmbH, equipped with a titanium glass  
10 horn measuring 40 mm in diameter and 100 mm in length) and a UV lamp (Vilber  
11 Lourmat filtered lamp, VL-215.MC, with a power of 4 W). The ultrasound generator  
12 irradiates energy into an auxiliary tank, whereas the UV lamp is located immediately in  
13 front of the electrochemical cell and irradiates directly to the anodic surface to promote  
14 the activation of the electrochemically formed oxidants (a quartz plate and a lattice  
15 cathode of stainless steel are used). A detailed description of the electrochemical cell can  
16 be found elsewhere [23].

17

### 18 **2.3. Analysis procedures**

19 The pesticide removal was monitored by chromatographic analysis and considering the  
20 total organic carbon (TOC). HPLC (Agilent 1100 series) using analytical column  
21 Phenomenex Gemini 5- $\mu$ m C18 was used for quantification. The mobile phase consisted  
22 of 40 % acetonitrile and 60 % water (0.1 % H<sub>3</sub>PO<sub>4</sub>), with a flow rate of 0.4 cm<sup>3</sup> min<sup>-1</sup>.  
23 The detection wavelength used was 225 nm, and the oven temperature was maintained at  
24 25 °C. The volume injection was set to 50  $\mu$ L. The TOC concentration was monitored  
25 using a Multi N/C 3100 Analytik Jena analyzer. Measurements of the pH were carried

1 out with an InoLab WTW pH-meter. All samples extracted from the electrolyzed solution  
2 were filtered with 0.45- $\mu\text{m}$  nylon filters before analysis.

3 Chloride anions ( $\text{Cl}^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ) were determined by ion chromatography using a  
4 Shimadzu LC-20A equipped with a Shodex IC I-524A column; mobile phase, 2.5 mM  
5 phthalic acid at pH 4.0; flow rate,  $1 \times 10^{-3} \text{ dm}^3 \text{ min}^{-1}$ . Hypochlorite ( $\text{HClO}^-$ ) was  
6 determined by titration with 0.001 M  $\text{As}_2\text{O}_3$  in 2.0 M NaOH. Peroxosulfate was  
7 quantified iodometrically according to Kolthoff & Carr (1953) [31].

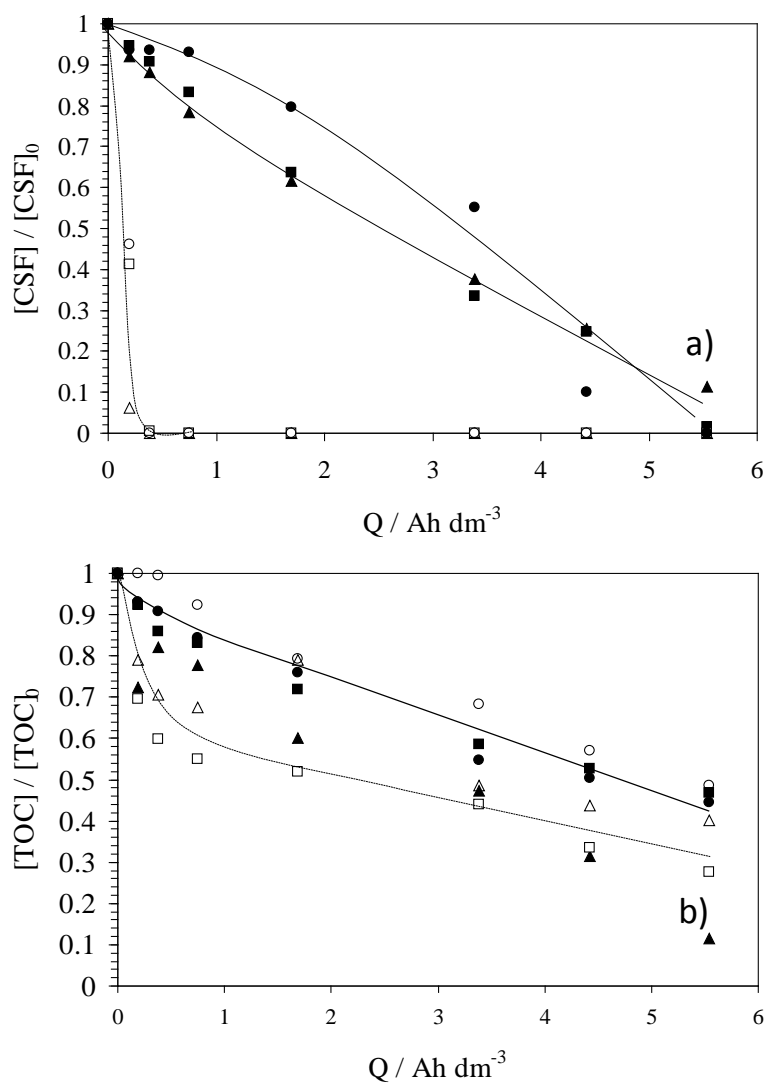
### 8 **3. Results and discussion**

#### 9 **3.1. General behavior.**

10 Figure 1 shows the progress of CISF degradation and mineralization during different  
11 electrolytic tests carried out at  $30 \text{ mA cm}^{-2}$  on synthetic wastewater polluted with CISF .  
12 As observed, CISF degradation could be attained, regardless of the initial concentration  
13 of the pollutant (at least in the range of concentrations studied). Likewise, the supporting  
14 electrolyte clearly influences the efficiency and rate of the process. The CISF degradation  
15 rate increases abruptly in the presence of chloride, but this improvement is not observed  
16 in the TOC removal rate. In fact, in a chloride medium, the specific charge required to  
17 attain the complete removal of CISF is approximately  $0.5 \text{ Ah dm}^{-3}$ , which tenfold lower  
18 than the charge required to mineralize approximately 60 % of the organic load. On the  
19 contrary, the specific charge required in a sulfate medium to attain 90 % removal of both  
20 CISF and TOC is approximately  $5.5 \text{ Ah dm}^{-3}$ . The different behavior observed provides  
21 information about the occurrence of different mechanisms of mediated oxidation that  
22 should be related to the supporting medium and can thus be related to the oxidants  
23 electrogenerated on the electrode surfaces. In light of the obtained results, it may be  
24 deduced that those oxidants formed during Conductive Diamond Electrochemical  
25 Oxidation (CDEO) in a sulfate medium are stronger and less specific, thus favoring the

1 mineralization of the organic load. On the contrary, the oxidants formed during  
 2 electrolysis in the presence of chloride seem to attack and deplete ClSF molecules very  
 3 rapidly, thus leading to the accumulation of intermediates in the reaction medium that are  
 4 slowly oxidized to carbon dioxide.

5

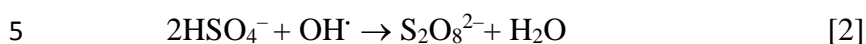
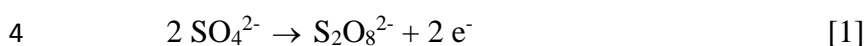


6  
 7 **Figure 1**  
 8

9 It is well known that [17, 18] peroxydisulfate is generated during the electrochemical  
 10 oxidation of wastewater with a high concentration of sulfate (Eq. 1 and 2). The latter



1 species has a high oxidizing power, and its decomposition can lead to the production of  
2 H<sub>2</sub>O<sub>2</sub> (Eq.3) and other oxidants, which can also chemically oxidize organic species  
3 contained in the wastewater.



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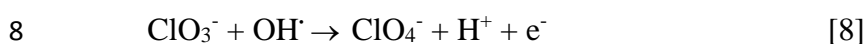
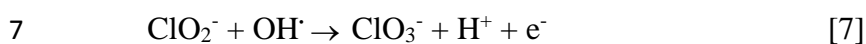
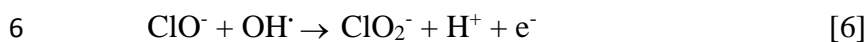
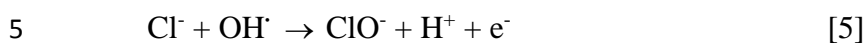
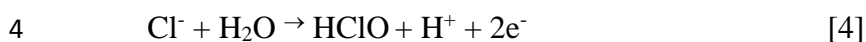
8 Figure 2a shows the concentrations of sulfate and persulfate during the electrolysis of  
9 CISF in sulfate media (at 30 mA cm<sup>-2</sup>). As observed, there are no significant variations in  
10 the sulfate concentration during the electrolysis; it just slightly decreases during the first  
11 stages of the process and then remains almost constant. This may indicate that the  
12 consumption (by oxidation to persulfate) and formation (by reduction of persulfate) rates  
13 of the sulfate ion are comparable, which may be explained by the great oxidation capacity  
14 of persulfate ions, particularly when they are activated with other oxidants present in the  
15 bulk, as reported for electrolytic processes with diamond anodes in the literature [32].  
16 Alternately, the amount of persulfate present in the solution during electrolysis is very  
17 low, and it only starts to increase at the end of the process, when the concentration of  
18 organics to be oxidized becomes low. It is important to note that these data correspond to  
19 the persulfate accumulated in the solution, that is to say, that which has not reacted  
20 previously with any other compounds present in the solution (and is thus not related to  
21 the persulfate electrogenerated).

22

23 Another important aspect to consider is the evolution of chlorine species during  
24 electrolysis (Figure 2b) in chloride media. As expected [17, 20], the oxidation of chloride  
25 results in the formation of hypochlorite, which is further oxidized to form chlorite (ClO<sub>2</sub><sup>-</sup>)

1 ), chlorate ( $\text{ClO}_3^-$ ) and even perchlorate ( $\text{ClO}_4^-$ ) via direct oxidation or, most likely, via  
2 mediation by the oxidation of hydroxyl radicals (Eqs. 4 to 8).

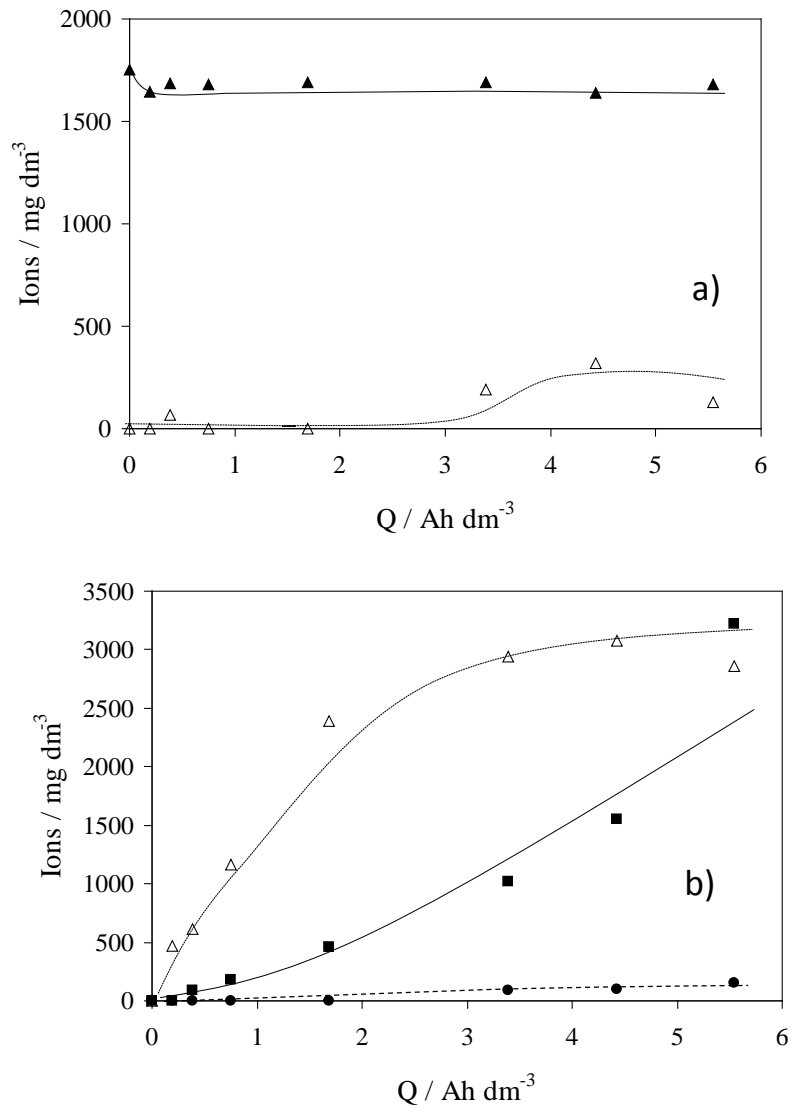
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10 These oxidants are thermodynamically stronger than hypochlorite, but they react slowly  
11 with organics at room temperature, and their contribution to organics degradation is thus  
12 expected to be negligible. This point can help explain the softer mineralization conditions  
13 observed in Figure 1b. An important point that should be mentioned is that in contrast to  
14 persulfate, the occurrence of the aforementioned chlorine species is not always considered  
15 positive from a remediation point of view, and their presence in treated wastewater is  
16 often restricted by law. In fact, the formation of organochlorinated species by the reaction  
17 of  $\text{ClO}^-$  with organics is a well-known drawback of electrolysis. Moreover, chlorate and  
18 perchlorate pose a threat to public health, and researchers are working hard to prevent  
19 their formation [33, 34].

20



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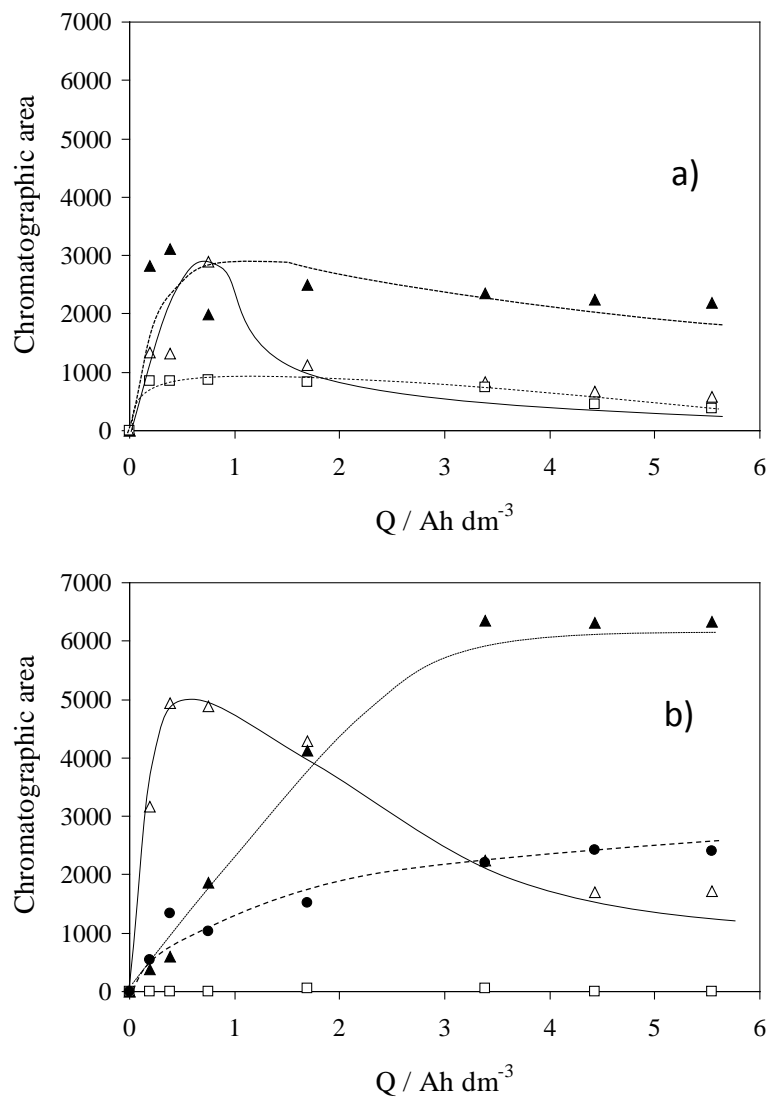
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**Figure 2.**

4 Another important point to increase the understanding of the process and clarify the role  
 5 of the supporting electrolyte in the oxidation pathway of CISF is the characterization of  
 6 the production of organic intermediates. Figure 3 shows the chromatographic area of the  
 7 main intermediates detected during the electrolysis at 30 mA cm<sup>-2</sup> of CISF solutions  
 8 containing both supporting electrolytes. As can be observed, the harsh oxidation  
 9 conditions of CDEO do not favor the production of a wide range of intermediates, and  
 10 only three compounds are formed in significant numbers in sulfate media (2-amino-4-  
 11 methoxy-6-methyl-1,3,5-Triazine, 2-chlorobenzenesulfonamida and oxalic acid), though

1 an additional fourth compound (unidentified) is formed in chloride media which may be  
2 a high MW polychlorinated derivate. In light of the monitored chromatographic area, the  
3 amount of intermediates in the reaction system is higher in chloride media, and the rapid  
4 accumulation of some of them in the first stages of the process is in agreement with the  
5 CISF degradation profile observed in Figure 1. In both cases, greater electrical charges  
6 are required to attain the complete removal of these compounds, and this is consistent  
7 with both the TOC profile and the mineralization percentages obtained. In further tests, it  
8 was verified that under those operating conditions, approximately  $25 \text{ Ah dm}^{-3}$  must be  
9 supplied to attain the complete degradation of intermediates formed and, thus, the  
10 mineralization of the organic load.



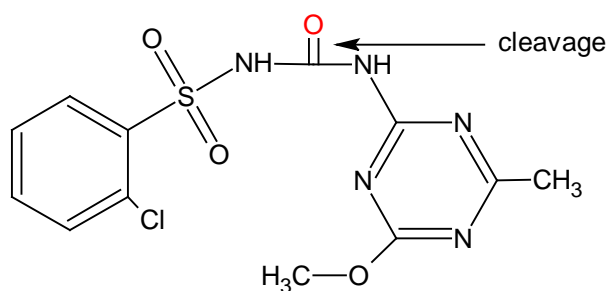
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**Figure 3.**

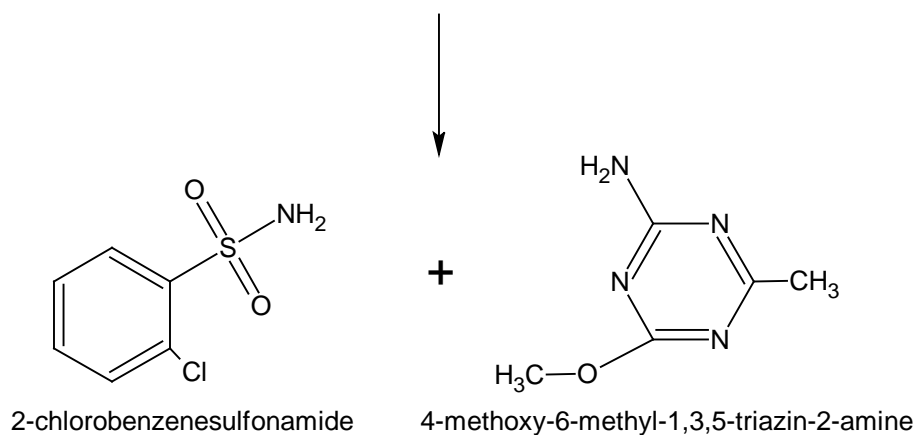
4 With this information and considering some of the mechanisms proposed in the literature  
 5 [29, 30], it can be proposed that the electrochemical oxidation of ClSF with conductive-  
 6 diamond anodes follows the mechanism shown in Figure 4. In the first step, the breakage  
 7 of the ClSF molecule takes place, which leads to the formation of 2-amino-4-methoxy-6-  
 8 methyl-1,3,5-Triazine and 2-chlorobenzenesulfonamide. Subsequently, these two  
 9 compounds seem to be rapidly oxidized to aliphatic acids. However, the presence of an  
 10 aliphatic acid, such as maleic, formic, acetic or tartaric acid, was not observed (at least in

1 a concentration over the detection limit of the HPLC technique). The mineralization of  
2 these species through carboxylic acid formation is also well known and is consistent with  
3 the relevant amount of oxalic acid found in this work. The differences in the speciation  
4 found in chloride media can be explained in terms of the very active role of hypochlorite.  
5 Its presence may promote chemical oxidation pathways with the formation of chlorinated  
6 intermediates by substitution or addition reactions of hypochlorite with the species  
7 present in the solution. Likewise, in both cases the dehalogenation of chlrosulfuron may  
8 take place in cathode surface.

9



2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]benzenesulfonamide



oxalic acid

CO<sub>2</sub>

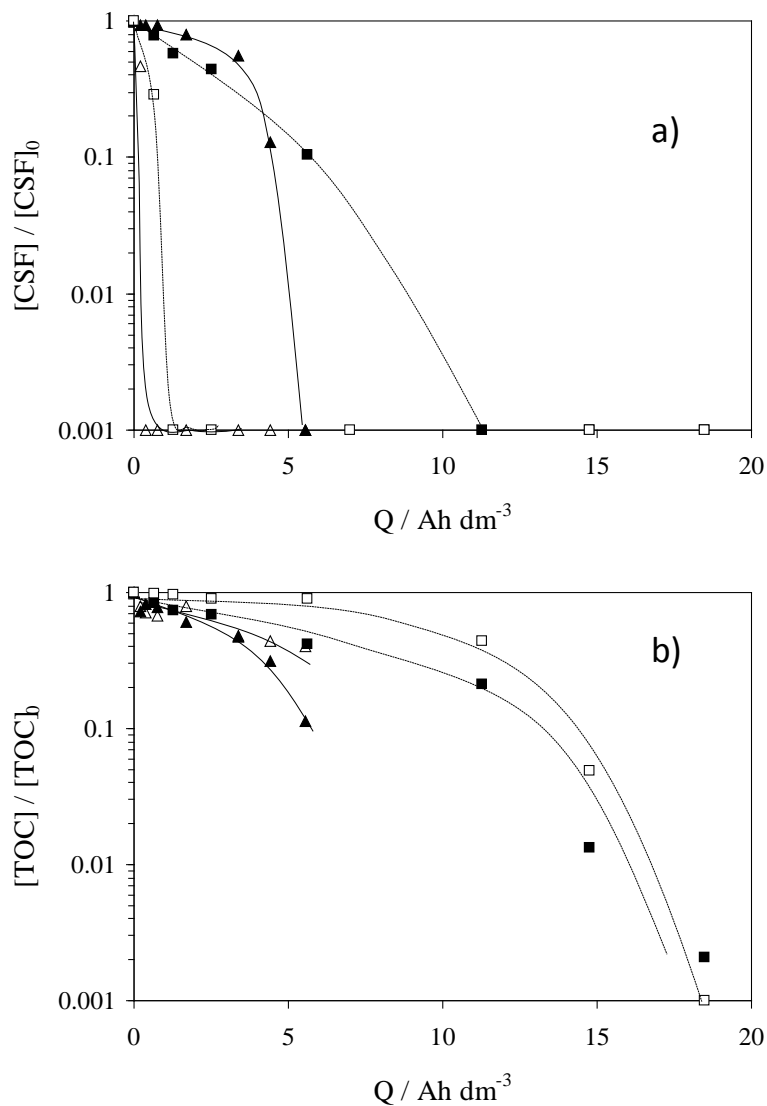
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1 **Figure 4.**

2

3 **3.2. Influence of current density.**

4 Figure 5 shows the changes in the concentration of CSIF and TOC with the applied  
5 current density (30 and 100 mA cm<sup>-2</sup>) during the electrochemical oxidation using sulfate  
6 or chloride as the supporting electrolyte. As observed, higher electrical charges are  
7 required to attain a given removal percentage when the current density increases, with  
8 these differences being more relevant in TOC depletion than in CISF degradation. For  
9 example, at an electric charge of approximately 5.5 Ah dm<sup>-3</sup>, TOC removal was 89 % at  
10 a current density of 30 mA cm<sup>-2</sup>, whereas a TOC removal of 58 % was attained at 100  
11 mA cm<sup>-2</sup>, both in sulfate media. This loss of efficiency is even higher in electrolysis in  
12 chloride media, in which, for example, the TOC depletion at 5.5 Ah dm<sup>-3</sup> decreases from  
13 60 % to 10 % when the current density increases to 100 mA cm<sup>-2</sup>. This behavior can be  
14 related both to the diffusion control of the CISF removal rate and to the promotion of a  
15 side reaction, which does not contribute to the degradation of the organic load. Thus, it is  
16 well known that when the current density increases, so too does the formation of OH·.  
17 These radicals are very reactive, and they can efficiently attack organics, though they can  
18 also promote the production of highly oxidized chlorine species (such as chlorates and  
19 perchlorates), which are kinetically slower than hypochlorite and thus give worse results.



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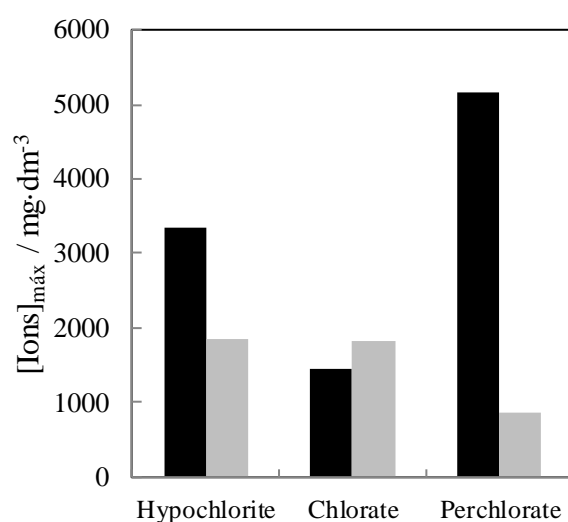
2 **Figure 5.**

3

4 Figure 6 shows the maximum concentration of ionic chlorine species detected during the  
 5 electrolysis of ClSF in chloride media at 30 and 100 mA cm<sup>-2</sup>. There is an accumulation  
 6 in the reaction system of highly oxidized chlorine species, which depends on the current  
 7 density applied (among other parameters). In this case, hypochlorite behaves as a reaction  
 8 intermediate that, depending on the operation conditions, can be further oxidized to  
 9 chlorate and perchlorate. The maximum concentration of hypochlorite was obtained at  
 10 100 mA cm<sup>-2</sup>. This is related to the fast oxidation of chloride to hypochlorite during the



1 first stages of the process (electrical charges below  $4 \text{ Ah dm}^{-3}$ ). However, this species is  
2 rapidly oxidized to form chlorate and then perchlorate, which starts to be accumulated in  
3 the reaction media when there are not enough organics in the solution to be oxidized.  
4 According to the literature [34], the efficient electrogeneration of perchlorate is favored  
5 at a current density over  $100 \text{ mA cm}^{-2}$ . However, because that perchlorate is not a good  
6 oxidant at room temperature, it is not expected to participate in the oxidation, which helps  
7 explain why the worst results were obtained for the electrolysis carried out at  $100 \text{ mA cm}^{-2}$   
8 in chloride media.



9

10 **Figure 6.**

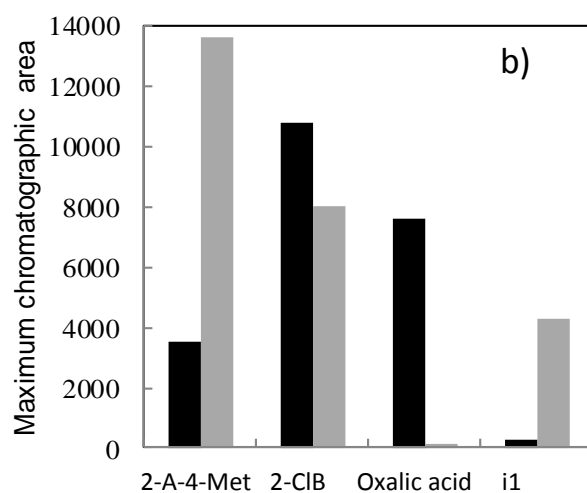
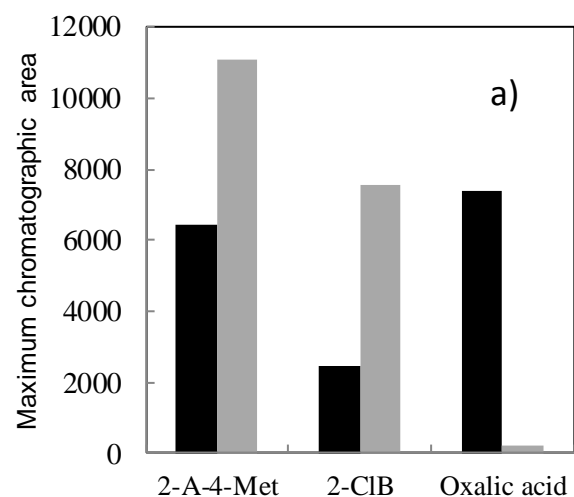
11

12 Regarding organics intermediates, it is expected that higher current densities lead to harsh  
13 oxidation conditions and that the amount of intermediates accumulated in the solution  
14 was lower. Figure 7 shows the maximum chromatographic area of organic intermediates  
15 monitored during the electrolysis of ClSF in sulfate and chloride media at current  
16 densities of  $30$  and  $100 \text{ mA cm}^{-2}$ . To obtain a better picture, this figure shows the results  
17 obtained in the electrolysis of  $100 \text{ mg dm}^{-3}$  of ClSF (at low initial concentration, the  
18 amount of intermediates accumulated is lower, which adds extra complexity to the study).

1 As observed, the number of intermediates formed at 30 and 100 mA cm<sup>-2</sup> is the same, but  
2 their relative concentrations depend on the current density. Comparing the results, the  
3 accumulation of low-oxidized intermediates is not favored at high current density with  
4 both electrolytes, but the amount of oxalic acid is higher. At this point, it must be  
5 highlighted that at high current density, the formation of both persulfate in sulfate media  
6 and highly oxidized chlorine-species (perchlorate) in a chloride medium is favored. The  
7 oxidation performed by persulfate and perchlorate is expected to be lower than that of  
8 hydroxyl radical, which can explain the accumulation of oxalic acid, which is generally  
9 more difficult to oxidize.

10

11

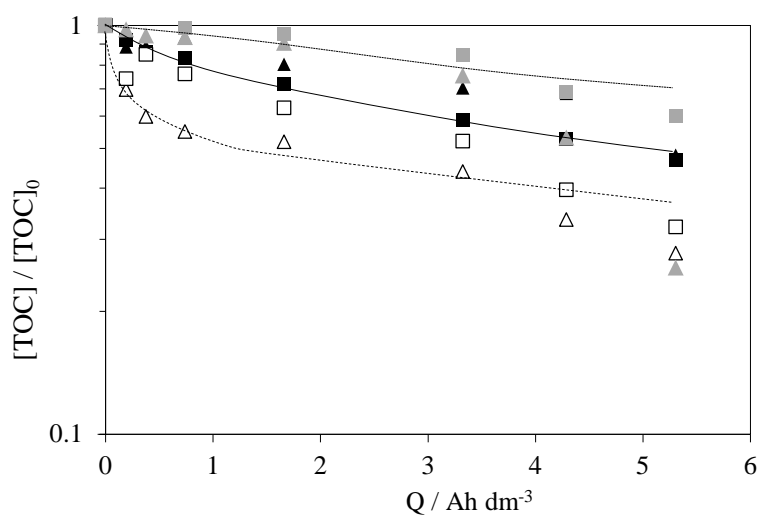


**Figure 7.**

### 3.3. Electroirradiated processes.

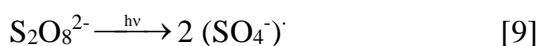
To clarify the role of mediated oxidation in the electrochemical removal of chlorsulfuron, four additional tests were carried out, in which UV light or ultrasounds were irradiated to the electrolyzed wastewater during the treatment. As reported elsewhere [22, 32], the irradiation of US and UV light can result in the transformation of molecular/ionic oxidants into radicalary species and, somehow, impacts the overall performance of the treatment. The results obtained in those tests, in terms of mineralization attained, are shown in Figure 8. It can be concluded that UV irradiation results in a less efficient process, whereas US

1 markedly improves the rate of the mineralization compared to the single electrolytic  
 2 process. This behavior is observed in both sulfate and chloride media. These results are  
 3 opposed to the very low extent of degradation achieved by single photolysis and  
 4 sonolysis, which also show a nill mineralization.



5  
6 **Figure 8.**  
7

8 UV light has the important ability to activate molecular oxidants by transforming them  
 9 into radicalary species, as shown in Eqs. 9 to 11.



13

14 When the molecular oxidant or pre-activated species is not as powerful, activation can  
 15 make a difference and significantly increase the efficiency of the process, especially when  
 16 the radicalary or activated species are strong oxidants. However, this is not the case  
 17 observed in chlorsulfuron, which leads to the conclusion that persulfate and hypochlorite

1 are more efficient oxidants for this herbicide than are the corresponding radicals. This  
2 observation was also found in a previous work of this group [29], where it was found that  
3 the mean oxidation state of carbon has a very important influence on the prediction of the  
4 UV irradiation effect on the mineralization of pollutants during electrolysis and that the  
5 combination of electrolysis and UV does not always result in a synergistic effect and is  
6 actually often antagonistic.

7

8 Regarding US irradiation, a completely different behavior was observed. US not only  
9 promotes the formation of radicals but also improves mass transfer and, hence, surface  
10 processes (both direct and those associated with anodically produced hydroxyl radicals).

11 Regarding the formation of radicals, the energy transmitted by low-frequency US (those  
12 applied in this work) is much lower and less intensive than UV irradiation; thus, this  
13 formation is limited to chlorine and sulfate radicals, but it does not entail the hydroxyl  
14 radicals produced directly from water. Nevertheless, the improvement observed clearly  
15 suggests that the enhancement in mass transport produced by this mechanical wave is  
16 very positive and that those processes taking place in the nearby surroundings/vicinity of  
17 the electrode surface (including mediated oxidation by anodically formed hydroxyl  
18 radicals) are required to explain the removal of chlorsulfuron. This observation  
19 demonstrates that the oxidation of herbicide chlorsulfuron occurs via the cocktail of  
20 oxidants produced in the electrolytic process.

21

## 22 **Conclusions**

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

- 1 – CISF can be successfully mineralized using electrolysis with conductive-diamond  
2 anodes. Salt composition and current density clearly influence the efficiency of  
3 the processes.
- 4 – Persulfate and hypochlorite are the main oxidant species responsible for CISF  
5 removal in a sulfate or chloride medium. Current density promotes the formation  
6 of chlorate and perchlorate, which are kinetically slower than hypochlorite in the  
7 oxidation of organics, thereby decreasing the process efficiency.
- 8 – The harsh oxidation conditions of the electrolysis with diamond anodes favor the  
9 rapid mineralization of CISF into carbon dioxide. Oxalic acid is the sole short-  
10 chain intermediate detected in the reaction medium.
- 11 – UV irradiation results in a less efficient process than the single-electrolytic  
12 process, whereas US greatly improves the rate of the mineralization. Thus,  
13 processes occurring near the electrode surface are required to explain the removal  
14 of CISF.

15

## 16 **Acknowledgements**

17 The authors acknowledge funding support from the EU, Spanish Government and JCCM  
18 (Junta de Comunidades de Castilla-La Mancha) through the MINECO Project CTM2013-  
19 45612-R, PEII-2014-039-P, FEDER 2007-2013 PP201010 and INNOCAMPUS.  
20 Foundation for Research Support of the State of São Paulo (FAPESP) by grant  
21 2014/02580-7 is also gratefully acknowledged.

22

1 **Figure captions**

2 **Figure 1.** Influence of the initial concentration on (a) the removal of pollutants and (b)  
3 the mineralization of the solution as a function of the applied charge (Q) during the  
4 electrochemical oxidation containing NaCl (empty points-dashed lines) and Na<sub>2</sub>SO<sub>4</sub> (full  
5 points-continuous line) as the supporting electrolyte. (▲, Δ) 20 mg dm<sup>-3</sup>, (■, □) 50 mg  
6 dm<sup>-3</sup> and (●, ○) 100 mg dm<sup>-3</sup>. Conditions: 0.05 mol dm<sup>-3</sup> of the supporting electrolyte and  
7  $j=30 \text{ mA dm}^{-3}$ .

8 **Figure 2.** Evolution of chlorine species generated during the electrochemical process. (a)  
9 (▲) sulfate and (Δ) persulfate; (b) (Δ)ClO<sup>-</sup>, (■)ClO<sub>3</sub><sup>-</sup> and (●) ClO<sub>4</sub><sup>-</sup>. Conditions: 50 mg  
10 dm<sup>-3</sup> Chlorsulfuron, 0.05 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> and NaCl and  $j=30 \text{ mA dm}^{-3}$ .

11 **Figure 3:** Evolution of the main organic intermediates during electrolysis of CISF  
12 solutions in sulfate (a) and chloride (b) media. (▲) 2-amino-4-methoxy-6-methyl-1,3,5-  
13 Triazine; (Δ) 2-chlorobenzenesulfonamida; (□) Oxalic acid, (●) unknown intermediate 1.  
14 Conditions: 50 mg dm<sup>-3</sup> Chlorsulfuron, 0.05 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> and NaCl and  $j=30 \text{ mA}$   
15  $\text{dm}^{-3}$ .

16 **Figure 4.** Mechanism for the removal of chlorsulfuron according to the intermediates  
17 detected in this work.

18 **Figure 5.** Influence of the current density on (a) the removal of pollutants and (b) the  
19 mineralization of the CISF solution (20 mg dm<sup>-3</sup>) containing NaCl (empty points) and  
20 Na<sub>2</sub>SO<sub>4</sub> (full points) as the supporting electrolyte. (▲, Δ) 30 mA cm<sup>-2</sup>; (■, □) 100 mA  
21 cm<sup>-2</sup>.

22 **Figure 6.** Maximum concentration of chloro-species chlorine accumulated in the reaction  
23 media during electrolysis of 20 mg dm<sup>-3</sup> of CLSF in chloride media. (■) 100 mA cm<sup>-2</sup> and  
24 (▲) 30 mA cm<sup>-2</sup>.

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2 **Figure 7.** Maximum chromatographic area of organic intermediates detected in the  
3 reaction media during electrolysis of  $100 \text{ mg dm}^{-3}$  CLSF in sulfate (a) and chloride (b)  
4 media. (■)  $100 \text{ mA cm}^{-2}$  and (■)  $30 \text{ mA cm}^{-2}$ .

5 **Figure 8.** Mineralization of CLSF solutions ( $50 \text{ mg dm}^{-3}$ ) containing NaCl (triangle  
6 symbols) and  $\text{Na}_2\text{SO}_4$  (square symbols) as the supporting electrolyte. (■, ▲) Electrolysis,  
7 (□, Δ) Electrolysis + US irradiation and (■, ▲) Electrolysis + UV light. Conditions:  $0.05$   
8  $\text{mol dm}^{-3}$  of supporting electrolyte and  $j=30 \text{ mA dm}^{-3}$ .

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