Is it really important the addition of salts for the electrolysis of soil washing effluents?

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Abstract

The addition of salts is a common practice in the studies reported in literature for the electrochemical degradation of many types of organics contained in wastewater. Often, this addition is explained in terms of the high concentration of salts that some industrial effluents may contain. However, even in studies focused on the treatment of real wastewater, the addition of extra amount of salts is a common practice. As a consequence, after the electrochemical treatment, the effluent is polluted with salts which become non-hazardous but persistent inorganic pollution. In this work, it is compared the electrolysis of a model pollutant, the pesticide clopyralid, in a realistic matrix obtained by soil washing of spiked soil and in two synthetic electrolyte matrixes with typical concentrations of the two salts more frequently used in electrochemical oxidation of water and wastewater (sodium chloride and sulfate). Results point out that it is possible to attain the complete removal of pesticide and organic intermediates when applying current densities within the range 10-100 mA cm⁻² with BDD anodes in the realistic effluent and that no important differences arise with the addition of extra electrolyte salts. Obviously, the type of electrolyte influences the production of different oxidant species which, in turn, contributes to the degradation of the clopyralid pesticide in a different way and with

different energy efficiency. However, for soil washing effluents, it is not necessary to add large amounts of salts for pesticide removal and the electrolysis of the raw soil washing waste, with a conductivity of only 1 mS cm⁻¹, was found to attain even a better performance than those of two synthetic wastewaters in which the concentration of salts was over 3,000 mg dm⁻³.

Keywords: electrolysis, pesticide, clopyralid, diamond.

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Highlights

- Clopyralid can be removed from soil washing effluents by electrolysis with diamond anodes.
- A higher salt concentration does not necessarily mean better performance of electrolysis.
- Energy cost increases dramatically with operation current density.
- Better efficiencies reached with low concentration of various oxidants than with large concentrations of a single oxidant

1. Introduction.

In recent years, Conductive-Diamond Electrochemical Oxidation (CDEO) has become an excellent alternative to conventional wastewater treatments [1, 2]. It has been evaluated in the treatment of wastewater polluted with several compounds, for which conventional processes are unable to attain a complete mineralization of the organic matter [3-7]. Specifically, this technology has been proven efficient in the removal of different organics such as pharmaceuticals [8-10], pesticides [11, 12] and hormones [13]. In addition, it has been tested as a proper technology for disinfection [5, 14, 15] and also for the synthesis of novel oxidants [16-19].

CDEO presents many advantages over conventional wastewater treatments, being the most important that it is environmentally-friendly (because the electron in the main reagent used and it is not required the addition of chemicals during this process), and that it operates at mild conditions (room temperature and atmospheric pressure) [4, 20, 21].

Most of the research works carried out about wastewater treatment with diamond anodes are focused on the removal of pollutants from synthetic wastewater [11]. The final aim is to check if target pollutants can be mineralized or at least degraded to a point for which their reduced hazardousness allows to combine the electrolysis with a cheaper treatment, such as the bio-oxidation. During these studies, very high concentrations of salts are added as supporting electrolyte in order to increase the ionic conductivity [22, 23] and hence, to decrease the resulting cell voltage at which the electrolyses are carried out. Often, this addition is explained in terms of the high concentration of salts that some industrial effluents may contain. However, even in studies focused on the treatment of real wastewater, the addition of extra amount of salts is a common practice [24]. As a result, the physical-chemical properties of the resulting wastewater are typically very different in comparison with those of actual effluents and, therefore, conclusions cannot

always be extrapolated to real examples, increasing the difficulty of the later scale-up procedures needed for the application of the technology at the full-scale. Another advantage looked for with the addition of salts to synthetic or real effluents is the promotion of mediated electrolysis mechanisms that enhance the efficiency of the overall process. It is well-known the formation of oxidants like peroxosalts, ozone and hydrogen peroxide on the surface of the diamond electrodes during electrolysis [25, 26] and, currently, combination of CDEO with ultrasound or UV light irradiation is a topic of the major interest, because these technologies can help to transform these oxidants into very powerful radicals, which enhance hugely the mineralization of the pollutants contained in the bulk [5, 27].

However, despite the good features attained with the addition of salts to wastewater, there are many important drawbacks. The most important is that salts become in fact a new pollutant, typically with a lower hazardousness than the organic pollutant contained in the raw wastewater, but with a larger persistence, because most of them remained in the effluent after the treatment. At this point, it is important to remind that there are no treatments to decrease their concentration but just treatments like electrodialysis that allows to split up the effluent into a salty and non-salty streams. In addition, the improvement in the efficiency obtained with the extra salts addition turns into a problem when oxidation products formed becomes more hazardous than the raw pollutants contained in wastewater. This is a typical and well-known outcome when chloride salts are added to wastewater, which was a common practice in most of the research papers focused on electrolysis during the eighties and nineties of the last century and that now, fortunately, it is less frequently found, because of the great alarm caused by organochlorinated species [28, 29]. Hence, it is not clear at all the benefit to the

environment of this salt addition and electrochemical technology has to determine ways to avoid or at least minimize this practice.

With this background, the main aim of the present work is to evaluate if the conclusions drawn in electrochemical treatment of these synthetic salty media is really representative of the conclusions that can be found in the treatment of a more realistic matrix. To do this, the electrolysis of a soil washing effluent (SWE) polluted with pesticide clopyralid ($\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$) is compared to the electrolyses of synthetic wastewater made with the same concentration of clopyralid and with the two more commonly studied electrolytes in the literature: sodium chloride (synthetic wastewater 1) and sodium sulfate (synthetic wastewater 2). Hence, one of the matrixes tested corresponds to a formulation based on the real characteristics of the water supply of our region (area of La Mancha, Spain), with a conductivity of $1,030 \mu\text{S cm}^{-1}$. The other two correspond to synthetic solutions of the herbicide containing only one salt (chloride or sulfate), in a much higher concentration ($3,000 \text{ mg dm}^{-3}$), within the same range of the use in most of the studies found in the literature about electrolysis of wastewater and hence with an ionic conductivity more than 4 times higher. On the other hand, because electrolysis with diamond may have two rather different behaviors depending on the conditions applied [30], in this work the comparison was carried out at two extreme current density conditions: 10 and 100 mA cm^{-2} . In the first, the oxidation is expected to be softer than in the second and, hence, the contribution of oxidants electrogenerated on the anode (including hydroxyl radicals) is expected to be less relevant than in the second, where the typical harsh oxidation conditions applied in electrolysis with diamond anodes are tested.

2. Experimental.

2.1. Chemicals.

Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid), sodium sulfate, sodium chloride, sodium nitrate, magnesium sulfate, potassium iodide and calcium carbonate (Sigma-Aldrich, Spain) were analytical grade and used as received. Methanol HPLC grade and formic acid (Sigma-Aldrich, Spain) were used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity: 18.2MΩcm at 25°C) was used to prepare all solutions.

2.2. Analytical techniques.

The concentration of pesticide was followed by reversed-phase chromatography and measurement of Total Organic Carbon (TOC). The chromatography system was an Agilent 1200 series coupled a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used. The mobile phase consisted of 30 % methanol/70% water with 0.1 % of formic acid (flow rate: 0.8 cm³ min⁻¹). The DAD detection wavelength was 280 nm, the temperature was maintained 25°C and the injection volume was 20 µL. The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. The concentration of oxidants was measured iodometrically by titration with thiosulphate in acidic media. This method quantifies all oxidants capable to oxidize iodide (I⁻) to iodate (IO₃⁻) [31].

Organic by-products generated during the degradation of clopyralid were extracted with ethyl acetate (ratio pollutant/solvent: 0.6 w/w) and then, both phases were stirred using a vortex mixer during 5 minutes. Next, samples were centrifuged during 15 minutes at 4,000 rpm. The organic phase was analyzed by GC-MS using a Thermo Scientific DSQ

II Series Single Quadrupole GC-MS with a NIST05-MS library. The column was a polar TR-WAXMS (30 m x 0.25 mm x 0.25 µm). The temperature ramp was 70°C for 1 min, 30°C min⁻¹ up to 300 °C and hold time 5 minutes. The inlet, source and transfer line temperatures were 250, 200 and 300°C, respectively.

The current efficiency (η) was calculated with equation (1) where C_j is the concentration of clopyralid (in mg dm⁻³), V is the volume of the electrolyte (dm³), n is the number of electrons (mmol e⁻ / mmol clopyralid), F is the Faraday constant (96,487 C mol⁻¹), I is the current intensity (A), t is the operation time in seconds (s) and M is the molecular weight of clopyralid (192 mg mmol⁻¹).

$$\eta = \frac{C_j \cdot V \cdot n \cdot F}{I \cdot t \cdot M} \cdot 100 \quad (1)$$

2.3. Electrochemical cell.

Electrolyses were carried out in a single compartment electrochemical flow cell (50 dm³ h⁻¹). Boron doped diamond (BDD) (WaterDiam, Switzerland) was used as anode and cathode. The electrodes were circular with a geometric area of 78 cm², boron concentration of 500 mg dm⁻³, a thickness of 2.72 µm, sp³/sp² ratio of 220 and p-Si as support. The electrode gap between anode and cathode was 3 mm. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A). The current density applied was in the range 10-100 mA cm⁻². The temperature was maintained at 25°C using a thermostated bath.

Synthetic wastewaters 1 and 2 (SWW1 and SWW2) consisted of a solution (1 dm³) containing 100 mg dm⁻³ of pesticide and 3,000 mg dm⁻³ of supporting electrolyte (NaCl, Na₂SO₄). Soil washing effluent (SWE) was prepared according to literature [32] and the composition is shown in Table 1.

Table 1. Ionic composition of the synthetic groundwater

Ion	Concentration (mg dm ⁻³ / mmol dm ⁻³)
Cl ⁻	79.9 / 2.3
NO ₃ ⁻	94.9 / 1.5
SO ₄ ²⁻	259.8 / 2.7
CO ₃ ²⁻	174.8 / 2.9
I ⁻	19.5 / 0.2
Na ⁺	87.1 / 3.8
K ⁺	6.0 / 0.2
Mg ²⁺	65.8 / 2.7
Ca ²⁺	116.5 / 2.9

3. Results and discussion.

Figure 1 shows changes in pesticide concentration during the galvanostatic electrolysis of different effluents polluted with 100 mg dm⁻³ of clopyralid at two different current densities: 10 and 100 mA cm⁻². To study the influence of the nature of supporting electrolyte, electrolyses in chloride (SWW1) and sulfate (SWW2) media were evaluated and results were compared to those obtained during the electrolysis of a soil washing effluent.

Figure 1. Evolution of clopyralid concentration as function of the applied electric charge during the electrolysis of different effluents containing 100 mg dm⁻³ of pesticide. (a) 10 mA cm⁻²; (b) 100 mA cm⁻²; (▲) SWW1; (■) SWW2; (●) SWE.

As it can be observed, the concentration of clopyralid decreases with the applied electric charge, reaching a total removal of the pesticide for applied electric charges above 15 and 30 Ah dm⁻³ in the electrolyses carried out at 10 and 100 mA cm⁻², respectively. The application of higher values of current density leads to a lower efficiency due to (1) a

higher generation of hydroxyl radicals which are wasted in side reactions (like oxygen evolution) that do not contribute to clopyralid degradation and (2) to the diffusion control of the clopyralid elimination rate [33].

Additionally, it can be observed that regardless of the current density applied, clopyralid is more efficiently removed in SWE than in SWW1 and SWW2 (pure chloride or sulfate media). This is an unexpected behavior taking into account that the ionic strength is lower when using SWE (SWW1: 0.051; SWW2: 0.063; SWE: 0.026). However, the lower ionic strength the higher production of hydroxyl radicals. Therefore, the differences observed in three media is related to the role of oxidants formed electrochemically in each case [22, 25]. In this point, it must be pointed out that the SWE is a complex ionic matrix that contains sulfate, chloride and carbonates ions among other ionic species, and thus it is expected the contribution of different types of oxidant in the clopyralid degradation.

The use of chloride (SWW1) and sulfate (SWW2) as supporting electrolyte is expected to lead to the formation of hypochlorite and peroxodisulfate, respectively, by direct and $\cdot\text{OH}$ -mediated electrooxidation on the BDD anode (Eqs. 2-8) [31].

In the case of chloride (SWW1), higher oxidation-state oxoanions are also expected and, in fact measured during the tests, including chlorates and perchlorates (Eqs. 9-11) [28, 31].

Taking into account the very high concentration of salts, in this work, it was expected the production of important concentrations of oxidants in the treatment of the synthetic wastewater solutions that contained chloride and sulfate (SWW1 and SWW2) [12]. On the other hand, soil washing effluent contains only low concentrations of sulfate, chloride, nitrate and carbonate, which are expected to be also oxidized during the electrolysis, favoring the production of a mixture of oxidants in the effluent although, initially, they are expected in much lower concentrations. Figure 2 shows the total concentration of electrogenerated oxidants during the electrolyses.

As can be observed, the concentration of oxidants increases with the applied electric charge for all the experiments carried out. The production of these species in SWW2 is lower in comparison with the results obtained in other effluents at 10 mA cm^{-2} (Figure 2a). This fact is directly related to the lower efficiency obtained in the removal of clopyralid in SWW2 under these conditions (Figure 1a) and can be explained in terms of the higher overpotential required for the generation of peroxodisulfate (the main oxidant during the electrolysis of wastewater containing sulfate solutions) as compared to the cell potential required for the other anions present in the effluents [19]. Thus, the production of peroxodisulfate is known to be more efficient when working at higher current densities (Figure 2b) [19, 34]. Under these conditions, significant concentrations of hydroxyl

237 radicals are produced [31], which react with sulfates and, therefore, the potential
 238 generation of peroxodisulfate is favored as it can be seen in Figure 2b (Eqs. 7-8).
 239 Alternatively, the low concentration of peroxodisulfate may indicate a higher reactivity
 240 of the produced oxidant. In fact, this fits well with the higher mineralization rate observed
 241 in this media (shown in Figure 4).

242

Figure 2. Evolution of oxidants as function of the applied electric charge during the electrolysis of effluents containing 100 mg dm^{-3} of pesticide. (a) 10 mA cm^{-2} ; (b) 100 mA cm^{-2} ; (▲) SWW1; (■) SWW2; (●) SWE.

The final concentration of oxidant species is higher during the process with SWE in comparing the results obtained in others media at 100 mA cm^{-2} (Figure 2b). Likewise, the trend observed in the oxidants concentration during the treatment of SWW1 at low current densities (Figure 2a) (an initial increase followed by a significant decrease) suggests that its final value will be also higher at higher electric charges for the effluent SWE. This behavior reveals that the presence of small amounts of different ions in the effluent is enough to produce significant concentrations of oxidants, improving the efficiencies obtained with a pure electrolyte in high concentration during the electrochemical oxidation with BDD anodes. Nonetheless, it is important to remark that the oxidant concentrations in chloride media (SWW1) are higher than those obtained in SWE. This fact is related to the soft operation conditions required for hypochlorite generation [35]. Even so, this species can react with the organic matter present in the effluent, favoring the production of undesirable organochlorinated compounds [36]. This can be clearly seen in Figure 1a where the concentration of clopyralid is not completely removed in SWW1. Likewise, the concentration of oxidants in SWW1 during the electrolysis at 100 mA cm^{-2} reaches zero values at applied electric charges near to 100 Ah dm^{-3} . This behavior is due to the evolution of hypochlorite to other chlorinated compounds in high oxidation state such as chlorate and perchlorate [35]. These species are very harmful and their presence in water should be avoided.

Figure 3 shows the evolution of inorganic chlorine compounds during the electrolysis of clopyralid in SWW1.

Figure 3. Evolution of chlorine compounds during the electrolysis of 100 mg dm⁻³ of clopyralid in SWW1. (■) hypochlorite; (▲) chlorate; (●) perchlorate. Filled symbols: 10 mA cm⁻²; empty symbols: 100 mA cm⁻².

As can be observed, hypochlorite and chlorate follow a typical intermediate trend, regardless the current density applied. This decrease is mainly related to the evolution of these species to perchlorate, the final specie of the oxidation of chloride. Nonetheless, hypochlorite can react with the organic matter present in the effluent, favoring the formation of organochlorinated compounds.

The concentration of chlorine compounds in high oxidation state is clearly influenced by the current density. In this context, the use of high values (100 mA cm⁻²) leads to the total conversion of chlorine to perchlorate. In this point, it is important to point out that perchlorate does not oxidize the organic matter [37, 38], and thus a lower clopyralid removal efficiency is observed.

The rapid degradation of clopyralid may be related to its rapid partial oxidation or to its efficient mineralization to carbon dioxide. To check this, both the organic matter

284 concentration and the presence of reaction intermediates were monitored. Figure 4 shows
285 the evolution of TOC removal during the electrolysis of different effluents polluted with
286 clopyralid at different current densities.

287 As it can be observed, the complete mineralization of the organic matter present in the
288 effluents is attained in most of cases. However, different behaviors can be seen depending
289 on the type of effluent used and the current density applied. In the electrolyses at 10 mA
290 cm^{-2} , the mineralization process is more efficient in SWW2 during the first stages of the
291 treatment in spite of the lower efficiency observed in the degradation of clopyralid (Figure
292 1a). This may indicate that once clopyralid molecule is attacked by peroxodisulfate it is
293 rapidly degraded to carbon dioxide (almost direct mineralization).

Figure 4. Evolution of TOC removal as function of the applied electric charge during the electrolysis of different effluents containing 100 mg dm⁻³ of pesticide. (a) 10 mA cm⁻²; (b) 100 mA cm⁻²; (▲) SWW1; (■) SWW2; (●) SWE.

On contrary, SWW1 is less efficient to attain a complete mineralization of the organic matter at low current densities. This fact suggests the generation of other organochlorinated compounds during the process [39]. Nonetheless, the final mineralization attained in this effluent was around 90 %. On the other hand, the use of

SWE leads to an efficient complete mineralization when working at 10 mA cm^{-2} . In this case, electric charge required for mineralization is equal to that required for clopyralid degradation (Figure 1a), indicating that in presence of small concentrations of different ions the use of BDD anodes minimizes the formation of intermediate compounds during the electrochemical oxidation of clopyralid at least at 10 mA cm^{-2} of current density.

Regarding the evolution of TOC at higher current densities, it can be observed that SWW2 and SWE lead to a complete mineralization of the organic matter at applied electric charges lower than 50 Ah dm^{-3} . This behavior verifies the higher production of oxidants during the process in presence of large amounts of sulfate ions by the action of hydroxyl radicals (Eqs. 3-4). Likewise, this species contributes to the potential formation of higher concentration of different oxidants in SWE which favor the mineralization process.

In the case of electrolysis of SWW1 at 100 mA cm^{-2} , the mineralization process is less efficient and higher electric charges must be applied to reach around 97 % of mineralization. In this case, TOC profile shows a strange trend with a plateau zone at charges around 30 Ah dm^{-3} . This behavior has been previously reported in literature for the electrooxidation of chlorinated compounds [39] and it may be related to the accumulation in the reaction system of organochlorinated compounds which are slowly oxidized. At this point, it is also important to remark that it can take place a competitive oxidation between the organic matter and the evolution of chlorine to other compounds in high oxidation state in this media (chlorate and perchlorate), and therefore, the mineralization process became less efficient.

For comparison purposes, Table 2 summarizes the integral current efficiency (Eq. 1) calculated for the removal of a 90 % of TOC by CDEO using different electrolytes and current densities.

327

Table 2. Integral current efficiency calculated for the removal of TOC.

	j (mA cm ⁻²)	η (%)
SWW1	10	6.23
	100	1.06
SWW2	10	5.08
	100	2.01
SWE	10	7.05
	100	4.06

328

329 As it can be seen, the treatment of SWE leads to an efficient removal of pesticide,
 330 regardless the current density applied. At 10 mA cm⁻², SWW2 shows the lower integral
 331 efficiency for the removal of clopyralid. This can be related to a lower production of
 332 oxidants under these conditions. On the other hand, SWW2 is more efficiently degraded
 333 than SWW1 when working at 100 mA cm⁻². This fact suggests that there is a higher
 334 production of organic intermediate compounds during the process when the effluent
 335 contains large amounts of chlorides [40].

336 In comparing the results obtained with both current densities, the integral efficiency is
 337 higher when working at low values (10 mA cm⁻²). This agrees with other works found in
 338 the literature based on electrolysis with diamond anodes and is related to the occurrence
 339 of competitive reactions during electrolysis at 100 mA cm⁻² [25]. Likewise, the integral
 340 current efficiency clearly indicates that the most efficiency degraded is SWE.

Taking into account the results obtained for the removal of clopyralid in terms of pollutant and TOC removal, Figure 5 shows the total chromatographic area of the organic intermediate compounds found, in order to shed light on the elimination of the pesticide in different media.

Figure 5. Total intermediates found as function of the applied electric charge during the electrolysis of different effluents containing 100 mg dm^{-3} of pesticide. Filled symbols: 10 mA cm^{-2} ; empty symbols: 100 mA cm^{-2} ; ($\blacktriangle$) SWW1; ($\blacksquare$) SWW2; ($\bullet$) SWE.

As it can be observed, the chromatographic area increases during the first stages of the process and after a maximum it decreases, regardless the current density applied. This fact indicates that the removal of clopyralid by CDEO leads to the formation of other organic compounds before its total mineralization. At low current densities, the area of the intermediates decreases up to zero values in SWE at applied electric charges lower than 10 Ah dm^{-3} . A similar trend was observed during the process in SWW2 but, in this case, the area does not decrease until zero values. These results are in agreement with

those shown in figures 1 and 4. Nonetheless, the area during the treatment in SWE is higher which suggests that the structure of intermediates is more complex in this media. Likewise, this can be related to a higher concentration of the organics or a higher number of different organic compounds in the effluent. At this point, it is important to highlight that the presence of different ions in SWE can favor the generation of a wide variety of intermediate compounds during the electrolysis of clopyralid. Therefore, the higher area observed can be mainly due to the formation of different organics.

Regarding the formation of intermediate compounds in SWW1, the area is higher than that observed in other effluents. Likewise, there is no a total decrease until reach zero values with the applied electric charge when working at 10 mA cm^{-2} . Once again, this result is in agreement with the evolution of total organic carbon in SWW1, where it is not possible to attain a complete mineralization of the organic matter (Figure 4).

Once the evolution of intermediate organic compounds has been described, a GC-MS analysis was carried out in order to identify the main organics produced during the electrolysis of clopyralid with diamond anodes. The results are summarized in Table 3. As it can be observed, the main intermediates found during the electrolysis of clopyralid are 2,5-dichloropyridine, pyridine and acetic acid. This means that the oxidation pathway does not differ significantly regardless of the matrix electrolyzed (SWE, SWW1 or SWW2).

Table 3. Intermediates detected during the electrolysis of different effluents polluted with 100 mg dm^{-3} of clopyralid using diamond anodes at 10 mA cm^{-2} .

Compound	Molecular structure	M _w (g mol ⁻¹)	Retention time (min)	Main fragmentation ions (<i>m/z</i>)	Presence in SWW1	Presence in SWW2	Presence in SWE
Clopyralid		191	7.14	76, 112, 147	Yes	Yes	Yes
2,5-dichloropyridine		147	5.31	50, 149	Yes	No	Yes
Pyridine		79	5.67	52, 79	Yes	Yes	Yes
Acetic acid		60	4.37	43, 60	No	Yes	Yes
Urea		60	4.45	17, 61	No	No	Yes
Methyl formate		60	4.43	31, 44	No	Yes	Yes

379

380 Finally, Figure 6 shows the cell voltage and the electric consumption (W) monitored
381 during the electrolyses carried out in this work. As it can be observed, the cell voltage
382 remains practically constant during the process, regardless the electrolyte used (Figure
383 6a). However, its value is higher when using SWE. This fact is due to lower conductivity
384 of this effluent (1,030 $\mu\text{S cm}^{-1}$) as compared to the values obtained from 3,000 mg dm^{-3}
385 of a pure salt (SWW1: 5,520 $\mu\text{S cm}^{-1}$; SWW2: 4,220 $\mu\text{S cm}^{-1}$). In this context, a lower
386 conductivity increases the resistance in the electrochemical systems and, according to
387 Ohm's Law, the cell voltage increases when working at constant current intensity. Even
388 so, it can be seen that the differences of cell voltage between SWWs and SWE are not
389 very high.

390 Cell voltage is directly related to the energy consumption of the electrochemical
391 oxidation, although in this later parameter, the removal efficiency (in terms of electric
392 charge used in the removal of clopyralid) is also important. As shown in Figure 6b, the
393 removal efficiency increases exponentially with the mineralization percentage, following
394 the same trend regardless the electrolyte used and showing very low differences when
395 using the same current density. This means that the higher cell voltage measured in the

electrolysis of the SWE is partially compensated by the higher efficiency of the oxidants cocktail formed. Results shown in this Figure, also point out the importance of the operation current density in the energy cost of the electrochemical processes. As it can be observed, to obtain the same degree of removal, energy requirement is multiplied by a factor of more than 10, which means that this type of processes should be operated at low current densities in order to prevent very high operation costs.

Figure 6. Cell voltage (a) and energy consumption (b) as function of mineralization percentage during the electrolysis of different effluents containing 100 mg dm⁻³ of pesticide. Filled symbols: 10 mA cm⁻²; empty symbols: 100 mA cm⁻²; (▲) SWW1; (■) SWW2; (●) SWE.

4. Conclusions.

From this work the following conclusions can be drawn:

- Clopyralid can be removed from wastewater by conductive diamond electrochemical oxidation. During the process, large amounts of oxidants (mainly persulfate and hypochlorite) are produced which favor not only the pollutant removal but also the complete mineralization of the organic matter.
- The process efficiency is clearly influenced by the current density applied and the supporting electrolyte used. Low current densities (10 mA cm⁻²) during the treatment of soil washing effluents increase the process performance in both pollutant and TOC removal. This reveals that the use of large amounts of pure electrolytes (3,000 mg dm⁻³) does not improve the degradation efficiencies and, therefore, a mixture of oxidants electrogenerated during electrolysis of SWE significantly favors the total removal of organic matter.
- Chlorine compounds in high oxidation state are potentially generated during the electrolysis in synthetic wastewater containing large amounts of chloride ions. Hypochlorite and chlorate follows an intermediate compound trend whereas perchlorate gradually increases with the applied electric charge. In fact, at 100 mA cm⁻², the conversion of chloride to perchlorate reaches to 100 %.

- The oxidation pathway does not differ significantly, regardless of the matrix electrolyzed (SWE, SWW1 or SWW2) and the same organic intermediates are found in the electrolyses of the three wastes.
- Low energy consumption is required to attain a complete mineralization of the organic matter during the treatment of SWE in spite of the cell voltage is quite higher.

Acknowledgements

Financial support from the Spanish Ministry of Economy, Industry and Competitiveness and European Union through projects CTM2013-45612-R and CTM2016-76197-R and FEDER 2007-2013 PP201010 (AEI/FEDER, UE) is gratefully acknowledged. CYTEMA E2TP program of University of Castilla-La Mancha is also acknowledged for the grant to Dr. Salvador Cotillas.

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