A comparison of the electrolysis of soil washing wastes with active and non-active electrodes.

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Abstract

A comparison between the performance of electrolysis of three different soil-washing wastes with platinum and boron doped diamond (BDD) anodes is carried out in this work. Results demonstrate that the treatment is more efficient with BDD for perchloroethylene and clopyralid but not for the case of lindane, because in this case there is a competitive oxidation between lindane and Sodium Dodecyl Sulphate used to extract this pollutant from soil. First order kinetics are observed in each compound with higher removal at the early stages and generally better results are obtained when using BDD as anode. The evolution of pH and a voltammetry study indicate a higher direct oxidation rate in the case of platinum and more importance of hydroxyl radical mediated processes with diamond anodes. Similar speciation is obtained during the electro-oxidation using BDD and platinum electrodes although the concentration of intermediates vary significantly.
Keywords
Perchloroethylene; clopyralid; lindane; soil washing; anodic oxidation

Highlights
• Important differences between electrolysis of SWF with diamond and platinum anodes
• More important direct electrolysis processes with platinum electrodes
• More important hydroxyl radical mediated processes with diamond electrodes
• Intermediates found were nearly the same, although the concentration differs importantly
1. Introduction

Occurrence of chlorinated hydrocarbons in environment is an issue of the major significance. They can be associated to industrial or agricultural activities and because of its anthropogenic nature and properties (such as high volatility and strong recalcitrance to degradation), the potentiality of damages that they can cause in the environment when they are discharged accidentally is extremely high (Huang et al., 2014; Rodrigo et al., 2014).

One of the most effective treatments for acute spills of pollutants is soil washing. It allows the fast removal of the pollutants from soil preventing their diffusion. As it is widely reported, soil washing is not a complete treatment, but it only transfers pollution from soil to a liquid (soil washing fluid) that must be further treated. As pollutants separated from soil are typically refractory to biological treatments, Electrochemical advanced oxidation processes (EAOPs) are the technologies used to remove these species from the liquid waste. Among them, anodic oxidation uses to exhibit a good performance, in particular, when considering that soil washing effluents contains naturally salts (also extracted from soil) and, hence, that they can be treated as produced, without the addition of reagents. Thus, there are many works in the literature describing successful applications of this technology (Mousset et al., 2014a; Mousset et al., 2014b, c; Huguenot et al., 2015; Trellu et al., 2016a; Trellu et al., 2016b).

When speaking about anodic oxidation, there are two different processes which are related to the anode material employed. Some types of anodes, such as platinum, lead to a soft oxidation with the production of a very large number of intermediates (including sometimes polymers) and not very high mineralization efficient. (Pulgarin et al., 1994; Subba Rao and Venkatarangaiah, 2014) In a pioneering work of Comninellis (Foti et al., 1999), these electrodes were named as active electrodes and their performance was
explained in terms of the use of the hydroxyl radicals (formed during oxidation of water) for the oxidation of the surface of the anode which, in turn, was the main responsible for the oxidation of the pollutant. Thus, the oxidation of the pollutant was a simple chemical reaction between a component of the electrode surface in a higher oxidation state and the pollutant. On the contrary, the anodic oxidation carried out by other anodes such as those based on conductive diamond coatings (so-called non-active electrodes) was much more efficient. It was explained in terms of the lack of possibilities of interactions between the surface of these electrodes and the hydroxyl radicals formed during the oxidation of the water molecule. Thus, once produced and during their very low lifetime, hydroxyl radicals cannot combine with the species contained in the surface but only with those contained in wastewater, promoting complete oxidation of the organics to CO₂ (Panizza and Cerisola, 2009). Among them, it is not only important to consider the pollutants but also ions such as sulfate, phosphate or carbonate that can be transformed into longer-lifetime oxidants, which expands the oxidation region from the very nearness of the electrode surface to the bulk (Cañizares et al., 2009). In addition, hydroxyl radical can be recombined to form hydrogen peroxide and oxygen and it can also oxidize oxygen and form ozone, resulting in the production of a very efficient oxidation cocktail, as it is pointed out by many researchers (Canizares et al., 2007; Tang et al., 2019).

In the literature, there are works focused on the comparison of the performance of active and non-active electrodes from the late nineties of the last century, which have been extensively discussed in recent reviews (Sirés et al., 2014; Martínez-Huitle et al., 2015; Martínez-Huitle and Panizza, 2018). However, most of them are related to synthetic wastewater with only one electrolyte (mainly sulfate or chloride) and they have a mechanistic interest. To the knowledge of the authors, no previous comparison has been made with the fluid obtained after washing soil directly with a suitable soil washing fluid.
In this work, the performance of the anodic oxidation of soil washing effluents polluted with perchloroethylene, clopyralid and lindane with platinum and boron doped diamond electrodes is compared. The treatment of these wastes by anodic oxidation was exhaustively studied with boron doped diamond, finding that it was an efficient treatment in which the interactions of the pollutant with the waste matrix are a point of the major significance (Cotillas et al., 2017; Muñoz-Morales et al., 2017; Muñoz-Morales et al., 2019). Opposite we did not evaluate platinum before, as the treatment expectations were much poorer according to previous works of other authors. So, the aim of this work is not to describe these treatments but to shed light on the mechanisms involved in the processes and clarify which of the two types of electrolysis exhibits better performance for this innovative advanced oxidation process.

2. Materials and methods

2.1 Chemical Products

Perchloroethylene (PCE, C\textsubscript{2}Cl\textsubscript{4}, >99%), was chosen as a volatile and non-polar pollutant, lindane (C\textsubscript{6}H\textsubscript{6}Cl\textsubscript{6}, 97%) as a model of non-volatile and non-polar species and clopyralid (99%) as a model of non-volatile and polar compound. These three chlorinated hydrocarbons were obtained from Sigma Aldrich and they were used as received. Sodium Dodecyl Sulfate (SDS, 99% by Sigma Aldrich) has been used as solubilizing agent. Hexane (C\textsubscript{6}H\textsubscript{14}, 97%) was used to solubilize PCE and Lindane during the pollution process. The hydrophobic lubricant oil Serie FORTE was obtained from Josval (Zaragoza, Spain) and it was used to mix with perchloroethylene and pollute the soil. Hexane and ethyl acetate (HPLC grade) were obtained from VWR INTERNATIONAL EUROLAB S.L (Barcelona- Spain) and they were used as extraction solvent of
perchloroethylene and lindane respectively for using Gas Chromatography with an
electron capture detector (GC-ECD). Methanol and formic acid were obtained from VWR
INTERNATIONAL EUROLAB S.L. Double deionized water (Millipore Milli-Q System,
resistivity: 18.2 MΩ cm at 25 °C) was also used.

2.2 Analytical Techniques

To determine the concentration of non-polar pesticides (perchloroethylene and lindane)
and their intermediates in liquid phase an extraction process was used before the analysis.
This process was carried out in separator flasks of 10 cm$^3$ using hexane and ethyl acetate
respectively. The ratio chlorinated organic vs solvent was 3:1 for PCE and 1:1 for lindane.
After that, all samples extracted from electrolyzed solution were filtered with 0.25 μm
nylon filters before analysis by GC ECD (Thermo Fisher Scientific) using analytical
column using a TG-5MS capillary column (30 m × 0.25 mm 0.25 mm), 63 Ni micro-
electron capture detector, a split/splitless injector and ChromCard Software. Under these
conditions the limit of detection was 0.25 mg dm$^{-3}$ for PCE and 0.1 mg dm$^{-3}$ for lindane.
The flow rate of gas He was 1.0 cm$^3$ min$^{-1}$. The temperature of the oven was programmed
as follows: 50 °C for 1 minute, ramp at 10 °C min$^{-1}$ to reach 260 °C followed by 2 minutes
hold. The temperature of the injector was 260 °C. The concentration of the clopyralid and
intermediates were quantified by HPLC (Agilent 1200 series) using a ZORBAX Eclipse
Plus5 C18 analytical column with a limit of detection of 0.5 mg dm$^{-3}$. The mobile phase
consisted of 30% methanol / 70% water with 0.1% of formic acid (flow rate: 0.8 mL min$^{-1}$
). The detection wavelength of Diode Array Detector (DAD) was 280 nm, the
temperature was maintained 25 °C and the injection volume was 20 μL. The concentration
of carboxylic acids was quantified by HPLC (Agilent 1100 series) filtering with 0.22 μm
Nylon Supelco filters before analysis using a Hi-Flex H, 300x7.7mm analytical column.
The mobile phase consisted of H$_2$SO$_4$ solution (5mM) (flow rate: 0.5 mL min$^{-1}$). The detection wavelength of DAD was 210 nm, the temperature was maintained 35 ºC and the injection volume was 100 μL. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytic Jena analyzer. Measurements of pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+. The colorimetric method used to determine the concentration of the SDS surfactant has been described elsewhere (Jurado et al., 2006). Finally, the anions present in the wastewater were characterized using an Ion Chromatograph with a Shimadzu LC-20A system.

2.3. Voltammetry experiments

Voltammetric measurements were carried out in an Autolab potentiostat/galvanostat controlled with the Nova 2.0. Software. All the electrochemical experiments were conducted at room temperature in a three-electrode single-compartment glass cell, using a 3 cm$^2$ working electrode of p-Si/BDD (doped with 500 ppm B; 250 of sp$^3$/sp$^2$ ratio) obtained from Adamant Technologies (Switzerland) or platinum (99.9% purity). An Ag/AgCl (3.0 M KCl) were used as reference electrode. Voltammetry experiments were performed in unstirred solutions (150 cm$^3$). BDD and platinum were anodically polarized during 5 min with a 1 M H$_2$SO$_4$ solution at 0.1 A prior to each experiment.

2.4. Preparation of polluted soil and soil-washing fluid

The soil used in this study was obtained from a quarry located in Toledo (Spain). This soil is characterized by its inertness, low hydraulic conductivity ($10^{-8}$ cm s$^{-1}$) and lack of organic content. Procedure for soil contamination and soil washing is extensively describe in previous works of our group (Cotillas et al., 2017; Muñoz-Morales et al., 2017)
2.5. Experimental set-up

Surfactant-Aided Soil Washing (SASW) effluents were treated by anodic using a bench-scale stirred electrochemical setup. P-Si Boron doped diamond (500 ppm of boron concentration and 250 of sp³/sp² ratio) or platinum electrodes (99.9% purity Metrohm) were used as anodes and graphite as cathode. The surface of the electrodes were 3 cm². The electrical current was applied using a Delta Electronika ES030 (0–30 V, 0–10 A) and the electrolysis were carried out galvanostatically at 300 A m⁻². Prior to use in galvanostatic electrolysis assays, the electrode was polarized for 10 min in a 0.035 M Na₂SO₄ solution at 150 A m⁻² to remove any impurities from its surface. Temperature was kept constant (25 ºC) using a thermo-regulated water bath.

3. Results and Discussion

The first stage in the treatment of the soils studied in this work consists of the extraction of pollutants using a soil washing fluid (SWF). This operation has been extensively described in previous papers of our group. Thus, as already explained in those previous works (Saez et al., 2010; dos Santos et al., 2016; Muñoz-Morales et al., 2017; Vieira dos Santos et al., 2017), this is a critical stage in the overall remediation process and reaching high efficiencies depends on:

1) the application of intense mixing conditions during the soil washing process and,
2) the use of a suitable concentration of surfactant reagent which helps to drag the pollutant from soil, in the case of pollutants with low solubility in water.

**Fig. 1** shows the extraction efficiency of three chlorinated hydrocarbons tested and confirms this information by showing that clopyralid can be completely exhausted from soil without the need of surfactant by using ratios SWF soil⁻¹ of only 2.5 L kg⁻¹, while the
concentration of surfactant (SDS) added influences on different ways with the other two pollutants studied, which have a much lower solubility in water.

![Fig. 1](image)

(a) Extraction efficiency of chlorinated hydrocarbons in the liquid wastes and (b) volume of soil washing fluid recovered after the soil washing process using different ratios surfactant soil with similar mixing conditions. Perchloroethylene (black bars); lindane (white bars) and clopyralid (grey bars).

In the case of PCE, the higher the dose applied, the higher is the extraction efficiency attained, reaching the almost complete exhaustion with a dose of 0.1 g SDS g$^{-1}$ soil. Opposite, in the case of lindane, a more complex relationship is observed, although the efficiency is lower, mainly because of the higher solubility of PCE in water. The surfactant promotes the extraction of lindane, but it remains mainly in the interphase with the micelles formed by soil and surfactant. Thus, the clarified phase does not show a direct relationship with the dose of SDS and, in fact, higher dose seems lower lindane contained in the upper phase, because it is concentrated in the interphase, which was kept with the soil. This behavior is caused by the complex interaction of the surfactant with the pollutant and soil. However, considering the further electrolysis process, upper phase is the most useful to study the differences of depletion of lindane with BDD and Pt anodes and it was the phase used for later stages of this work. At this point, it is worth to consider...
the SWF retained in the soil after the treatment depends on the amount of surfactant dosed and, in this case, there is a direct relationship between the water that can be retained, and the amount of surfactant added. For an efficient treatment, the lower the amount of SWF retained the better is the performance of the overall process.

After the extraction, the soil washing fluid becomes a highly polluted waste (soil washing wastes, SWW) with a high concentration of ions extracted from soil and a conductivity that is always over 1 mS cm⁻¹, high enough to undergo electrolysis at a suitable cell voltage without the necessity of adding salts. By applying electrolysis with diamond and platinum electrodes, the expected first-order decays already discussed in the literature were obtained. However, here we are focusing on the comparison of the performance among different pollutants and electrodes. Thus, Fig. 2a, compares the removal of pollutants (mg) and the electrical efficiencies (mmol Ah⁻¹) reached for an arbitrarily selected applied electric charge passed of 1.05 Ah and Fig. 2b for a larger applied charge of 3.30 Ah. It was chosen these 2 values to compare the efficiencies of the process with the applied electric charge.

**Fig. 2.** Total removal of pollutants from the SWW after applying an arbitrarily electric charge of (a) 1.05 Ah and (b) 3.30 Ah. Platinum anodes (black bars), BDD anodes (white bars). J= 300 A m⁻²; V= 150 cm³.
As seen, in all cases the efficiency in the removal of the pollutant decreases during operation. That is, it is more efficient the degradation in the first moments of the electrolysis, and this behavior can be explained in terms of the well-known first order kinetic undergone by the pollutants during electrolysis (Aquino et al., 2014; Sopaj et al., 2015), which reflects on a linear dependence on the concentration. In addition, there are important differences between the removals of the different pollutants. Clopyralid is slightly more oxidizable by BDD than by Pt, although both electrolysis lead to similar values. On the contrary, large discrepancies occur when emulsified wastes are treated. PCE is very efficiently degraded with diamond electrodes and this is not the case for platinum. Contradictory, lindane exhibits exactly the opposite behavior, although in this case the degradation of SDS can help to explain this unexpected behavior. Thus, oxidation of SDS (data not shown) is more important with BDD (13.15 mmol Ah\(^{-1}\)) than with platinum (1.16 mmol Ah\(^{-1}\)) and this difference helps to explain the lower removal obtained in the case of the electrolysis of lindane. SDS is a very complex linear molecule whose concentration in the SWF is 3-logs over the concentration of lindane. It is known to be easily oxidized by BDD anodes, leading to the formation of sulfates and persulfates which mainly increase the conductivity of the SWF. In the case of the oxidation of PCE, its influence is much lower, and this can be explained considering that SDS is also combined with the oil extracted during the soil washing and this helps to explain a more important decrease in the removal of PCE, which behaves as a very easily oxidizable molecule.

Results obtained in the treatment of soil washing wastes obtained with a SWF soil\(^{-1}\) ratio of 2.5 L kg\(^{-1}\) are reproduced when higher amounts of soil washing fluid are added during the extraction and this can be seen in Fig. 3, in which the kinetic constants obtained after the fitting of experimental results to first order kinetics are obtained. Fig. SM-1 shows the
decay trend from which kinetic constants have been estimated. Except for the case of lindane (which is explained because of the concurrent oxidation of SDS), electrolysis with platinum is always much less efficient than with BDD anodes and kinetic constants reflect the differences in the oxidation capacity of the different pollutants. Again, results obtained with PCE washing fluids demonstrate to be the most easily oxidizable wastes by diamond and it exhibits a very poor efficiency for Pt. The fitting of electrolytic results to first order kinetic indicates that it is important to obtain wastes as much concentrated as possible. For this reason, concentration techniques such as those recently proposed in works of our group for these pollutants can be of extreme significance for the development of successful treatments (Muñoz et al., 2017; Raschitor et al., 2017; Llanos et al., 2018).

![Fig. 3. Kinetic constants obtained by fitting the experimental decay of organochloride compounds to first order kinetics during 8 hours of treatment of SWW using (a) platinum and (b) BDD anodes. Perchloroethylene (white bars); lindane (grey bars) and clopyralid (black bars).](image)

A very important point when comparing the anodic oxidation of pollutants with different electrodes is the production of oxidants. In this work, they are measured in a globalized...
way by considering the concentration of oxidants capable to oxidize $I^-$ to $I_2$. This means that we are considering all stable oxidants in this measurement but not others, like the hydroxyl radical, whose action is almost instantaneous. As seen in Fig. SM-2, there are not very important differences in the concentration of stable oxidants formed in the electrolyte during the electrolysis and, in fact, they seem to be higher in the case of using platinum than when using BDD, which initially is an unexpected outcome because the formation of persulfates is only efficient with the BDD anode and because the oxidation with diamond was found to be more efficient (even in the case of lindane in which higher concentration of SDS is oxidized). However, this result can be easily explained in terms of the chemistry of chlorine in the system. Platinum anodes can transform the chloride contained in the SWF (and that obtained by the dehalogenation of the chlorinated hydrocarbons) into chlorine and hypochlorite, while in the electrolysis with the diamond anode the oxidation does not stop at this point and hypochlorite is transformed into chlorates and perchlorates. Because of the very low kinetic rate of the oxidation carried out by these two oxoanions, they should result in a negative impact in terms of the oxidation of $I^-$ to $I_2$ as it can be observed in the Fig. SM-2. Thus, after passing 1.05 Ah, the concentrations of perchlorate obtained in the diamond electrolysis were 96.6, 28.5 and 9.0 mg dm$^{-3}$ Cl-ClO$_4^-$, respectively for clopyralid, lindane and perchloroethylene. These values are important, taking into account that the initial concentration of chloride was close to 160 mg L$^{-1}$ and the variability among the different tests demonstrates the complexity of the processes happening in the cell with many competing reactions. With platinum anode, perchlorate was only detected in the electrolysis of the SWF obtained with clopyralid and the concentration was less than four times lower than in the case of using diamond. However, this difference does not reflect on a major point with respect to the oxidative capacity of both electrodes as observed in the figures.
The other important parameter compared in Fig. SM-3 is the pH. Initial pH was 6.5 in the SWF with lindane and PCE and 7.1 in the case of the SWF with clopyralid. In comparing the values reached after passing an arbitrary current charge, it can be noticed a very important difference: in the case of diamond anodes it decreases very significantly, while in the case of the platinum electrolysis it does not undergo such a severe change, in fact, it increases during the electrolysis.

Initially this may inform about different mechanisms in the oxidation of the pollutants. The change in the pH is observed from the first moments, indicating that it should not be related to the oxidation of organics to carboxylic acid but to other simpler processes. In order to know more about this change, a voltammetric study was carried out where the response of both electrodes were compared for the three polluted SWF (obtained by washing soil with and without the pollutant). Results shown in Fig. 4, are surprising. The higher intensities obtained for the platinum electrolysis indicate that there is a higher direct oxidation rate on the surface of these electrodes as compared with changes observed on the diamond electrode. Initially, it can be thought of the simple effect of the lower resistance of the platinum electrode as compared to the BDD. However, it is not only the lower electric conductivity of the platinum but also the oxidation process occurring on the surface as the shape of the voltammograms is not linear but exponential. In addition, in comparing the responses for the platinum, it can be observed that there are no differences between the electrolysis of the SWF with PCE or lindane. This may suggest that, in this case, the oxidation of SDS on the surface of the electrode is more important than the oxidation of the pollutant (which in fact is negligible in terms of direct oxidation according to the voltammetry because both curves are fully overlapped). Initially, this can be predictable because the pollutant is expected to be present as micelles. On the other
hand, this response can also be due to the oxidation of chloride and/or any other inorganic
compound. In the case of clopyralid (Fig. 4c), in which there is no SDS in the SWF, the
presence of the organic pollutant leads to a very significant increase in the intensities
recorded confirming that there is a direct oxidation pathway for these species. In addition,
the base curve (obtain with SWF without clopyralid) also match with the base curve of
the lindane and PCE experiments, indicating (because with clopyralid there is no SDS)
that it should due to the oxidation of chloride or any other organic compound but not of
the surfactant.

Fig. 4. Voltammetries of the SWF with lindane (a), perchloroethylene (b) and clopyralid
c using boron doped diamond (black line) or platinum (discontinuous line) as working
electrodes. Grey line: soil washing waste without pollutant.

The lower voltammetric response of the electrolysis with BDD indicates a lower direct
electrochemical reactivity, which is not seen in the bulk results and should be more related
to the production of hydroxyl radicals. In fact, the intensities recorded at very high
overpotentials are considerably much slower. This may indicate a higher extension in the
oxidation of water, which is also consistent with the higher decrease in the pH value (Eq.
1) explaining the changes observed in the pH when using both electrodes.

\[
\text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD} \cdot \text{OH} + \text{H}^+ + \text{e}^- \quad (1)
\]
BDD($\cdot$OH) + R $\rightarrow$ BDD + CO$_2$ + H$_2$O  \hspace{1cm} (2)

In addition, there is an important difference between the presence of lindane and PCE in the SWF, with an important increase in the intensities obtained, which clearly indicates that these species are also undergoing a direct oxidation on the surface of the electrode. This is not as clear as in the case of the clopyralid in which the difference is extremely low and which indicates that these species should be primarily removed by mediated oxidation processes.

However, these differences are not observed in terms of speciation. In the case of lindane, by GC-MS, it was confirmed almost the same intermediates in the electrolysis (Table SM-1), which fits well to the oxidation mechanisms proposed in the literature (Nitoi et al., 2013; Dominguez et al., 2018) and shown in Fig. 5. Additionally, it can be observed similar speciation obtained with both electrodes. However, during the electrolysis with BDD anodes the maximum concentration of intermediates is higher than during the electrolysis with platinum.
Fig. 5. Mechanisms of the electrochemical oxidation of lindane contained in the SWW using platinum and BDD anodes.

In the case of perchloroethylene, again nearly the same intermediates are found in the electrolysis with diamond and platinum. They are summarized in Table SM-2 and they follow the oxidation mechanisms suggested in bibliography (Miao et al., 2015; Karimaei et al., 2017), which is shown in Fig. 6. In this case, there are acids that are detected using BDD and other using platinum, however dechlorinated compounds are mainly detected in platinum anodes. These results are in concomitance with the experiments that showed higher efficiency in the removal of PCE with BDD anodes because the higher mineralization degree and less intermediates obtained.
Fig. 6. Mechanisms for the electrochemical oxidation of perchloroethylene contained in the SWW using platinum and BDD anodes.

In the case of the clopyralid no GC-MS but HPLC was used to characterize intermediates because of the high solubility in water of this pollutant that makes difficult the extraction of clopyralid with organics solvents to analyze by gas chromatography (Ahmad et al., 2003). Results of Table SM-3 again pointed out that the oxidation route fits well with those proposed in the literature (Carvalho de Almeida et al., 2019) (Fig. 7). Again, intermediates detected during the electrolysis of SWF of clopyralid are nearly the same with platinum and BDD anodes that it fits well with results of depletion efficiency and kinetic studies with just slightly better results using diamond than platinum electrodes.

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- + \text{ClO}_3^- + \text{ClO}_4^-
\]
Fig. 7. Mechanisms of the electrolysis of clopyralid (Carvalho de Almeida et al., 2019) contained in the SWW using platinum and BDD anodes.

Hence, despite the very important differences observed in the rates of removal of the three chlorinated organics and in the voltammetries, the oxidation mechanisms should be nearly the same, at least in terms of the intermediates formed although the concentration of intermediates differs significantly indicating the different oxidizability in both cases. All these results confirm that electrolysis can be a good technology to remove chlorinated hydrocarbons and that although platinum has a greater electrochemical reactivity, the choice of diamond as anode material has important advantages because of the much higher efficiency.
Conclusions

From this work, the following conclusions can be drawn:

- Polar organochlorinated compounds are easily extracted in the SWF with low ratio SWF soil$^{-1}$ and without surfactant, however doses of surfactants as 0.1 g SDS g$^{-1}$ soil are needed to obtain over 60% of extraction efficiency of non-polar compounds.

- First order kinetics are observed in each compound with higher removal at the early stages and generally better results are obtained using BDD as anode than platinum.

- Higher oxidants are produced with platinum because BDD anodes promotes very oxidized species with less oxidant capacity, however it does not reflect on a major point with respect to the overall oxidative capacity.

- The evolution of pH and a voltammetry study indicate that higher oxidation rate in the surface is observed with platinum anodes and a direct oxidation pathway is promoted for other additional compounds (as surfactant or chlorine ions).

- Similar intermediates species are obtained during the electrooxidation using BDD and platinum electrodes from the main mechanisms as dechlorination and ring-opening which are detected with GC-MS and HPLC.

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